A STUDY OF SOME TRANSITION
METAL COMPLEXES WITH
PENTAMETHYLENETETRAZOLE

Thesis for the Degree of M. S.
MICHIGAN STATE UNIVERSITY
Frank Michael D'Itri
1966

ABSTRACT

A STUDY OF SOME TRANSITION

METAL COMPLEXES WITH PENTAMETHYLENETETRAZOLE

by Frank M. D'Itri

Complex compounds of pentamethylenetetrazole (metrazole, hereafter abbreviated as PMT) have been prepared with manganese(II), iron(II), iron(III), cobalt(II), nickel(II), copper(II), and zinc(II) perchlorates by the following two techniques.

1. The hydrated metal perchlorates were dissolved in 2,2'-dimethoxypropane. The water of hydration was removed by the reaction with the solvent. The excess PMT was added and the respective complexes precipitated out as microcrystalline powders.

2. Hydrated copper(II) perchlorate was dissolved in anhydrous acetic acid, and a calculated amount of acetic anhydride was added to react with the water of hydration. Anhydrous salt $Cu(ClO_4)_2 \cdot xHOAc$ precipitated out. The crystals were filtered, dissolved in hot HOAc and an excess of PMT was added. The $Cu(PMT)_4(ClO)_2$ complex precipitated out.

The above techniques had to be used since it is virtually impossible to remove the water of hydration from transition metal perchlorates (except $AgClO_4$). The usual dehydration procedures lead to decomposition (sometimes explosive!) of the

salt. The data indicate that the complexes with iron(II) and iron(III) perchlorates contain 3-5% impurities and that, in all probability, they are a mixture of the respective iron(II) and iron(III) complexes. Using the same method of preparation, $Cu(PMT)_2ClO_4$ and $Cu(PMT)_4(ClO_4)_2$ complexes were also isolated. All of these complexes are quite stable below 100° and, except for $Cu(PMT)_2ClO_4$, they are soluble in water and polar non-aqueous solvents but insoluble in non-polar solvents. Karl Fischer titrations and elemental analyses indicate that the complexes are anhydrous. The reflectance spectra of all of the complexes were obtained. It is interesting to note that the spectra of the cobalt(II) and nickel(II) complexes corresponded to the respective ions in an octahedral configuration. On the other hand, the X-ray powder diffraction measurements on these complexes indicate that all complexes containing six PMT molecules per metal ion are isomorphous. These data combined with the reflectance spectra data seem to indicate that in the $Cu(PMT)_6(ClO_4)_2$ complex, six PMT molecules are coordinated to the copper(II) ion. Six coordinate copper(II) is rather unusual since all attempts to prepare corresponding solid copper pyridine complexes (in this laboratory as well as in others) have been unsuccessful so far.

Magnetic susceptibility studies on the hexakis(PMT)-transition metal perchlorate complexes were interpreted on the basis of octahedral coordination, and the complexes are of the high spin type.

Frank M. D'Itri

The electron spin resonance spectra of $Mn(PMT)_6(ClO_4)_2$, $Cu(PMT)_6(ClO_4)_2$ and $Cu(PMT)_4(ClO_4)_2$ were obtained. For $Mn(PMT)_6(ClO_4)_2$ complex dispersed in $Zn(PMT)_6(ClO_4)_2$ the data indicate that the metal-ligand bonds are highly ionic (91%) and that there is a large distortion from octahedral symmetry. The measurements on $Cu(PMT)_6(ClO_4)_2$ show that the copper symmetry is tetragonal.

Nuclear magnetic resonance studies of the complexes revealed that only the diamagnetic $Zn(PMT)_6(ClO_4)_2$ and $Cu(PMT)_2ClO_4$ yielded the predicted spectra. The remainder of the complexes, being paramagnetic complexes, yielded no spectra within the sweep width limits of the Varian A60 NMR Spectrometer. It is believed that the absorbances were shifted beyond the range of the instrument.

Infrared spectra of these complexes dispersed in Nujol were obtained in the 5000-670 cm^{-1} region. The spectra were essentially those of the ligand with very little perturbation. The infrared spectra also indicated that the complexes are ionic since there is only a large single broad band at approximately 1080 cm^{-1} for the perchlorate ion. The far infrared measurements, however, show two distinct types of spectra. Those of the hexakis and tetrakis(PMT) transition metal complexes show two new bands located in the 277-288 cm^{-1} and 236-198 cm^{-1}

regions. These bands have been very tentatively assigned to the asymmetric stretch of the metal-nitrogen bond and the metal-ligand bending mode, respectively. There is a trend for the bands in the 320-180 cm^{-1} region to increase in frequency with a decrease in ionic radius (increase in polarizing ability) of the central metal ion. The spectrum of the bis(PMT)copper(I) perchlorate, on the other hand, has a band at 281 cm^{-1} and what appear to be weak bands at 255 and 198 cm^{-1}. The 281 and 255 cm^{-1} bands could be assigned to the PMT with no bands present for the metal-nitrogen asymmetric stretch or metal-ligand bending mode. An alternative assignment for the 281 cm^{-1} would be the metal-nitrogen asymmetric stretch while the 198 cm^{-1} band could correspond to the metal-ligand bonding mode.

A STUDY OF SOME
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By

Frank Michael D'Itri

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

Department of Chemistry

1966

ACKNOWLEDGEMENT

The author wishes to express his sincere appreciation to Professor Alexander I. Popov for his guidance, assistance, and encouragement during the course of this investigation.

Special thanks goes to my wife, Patricia Ann, for her patience and understanding.

Financial assistance from the Mental Health Institute of Public Health Service is gratefully acknowledged.

The author also wishes to express thanks to Professor Luigi Sacconi, University of Florence, Italy, for the reflectance spectra and some of the X-ray diffraction patterns, Professor Alexander Tulinsky for assistance with the X-ray powder diffraction pattern interpretation, Dr. Henry A. Kuska for the electron spin resonance and its interpretation, Joseph A. Caruso for the reproduction of most of the figures, the Dow Chemical Company for the thermogravimetric analysis and generous supplies of chemicals and Professor Carl H. Brubaker, Jr., Joseph T. Lundquist and John H. Bloor for their many helpful discussions during the course of this investigation.

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I. HISTORICAL

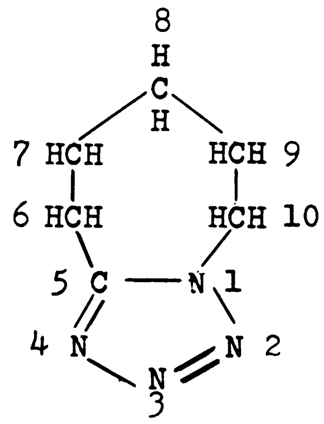
General

Tetrazoles are five membered, heterocyclic ring compounds which contain one carbon and four nitrogen atoms linked by three single and two double bonds. The tetrazole ring is numbered so the nitrogen single bonded to the carbon is the one position. The remaining three nitrogens are then numbered consecutively two through four with the carbon at the five position. The parent compound may exist in tautomeric forms I and II (1,2).

I　　　　II

It has been found that 97% of an equilibrium mixture of I and II exist in the form I (3).

The tetrazole ring is unusual among cyclic systems in that it offers only two points of substitution--in position 1 or 2 and in position 5. Pentamethylenetetrazole III represents a special group of substituted tetrazole derivatives in which the pentamethylene chain forms part of a seven membered ring fused to the tetrazole ring.



III

Pentamethylene tetrazole was first prepared by Schmidt (4) in 1925. His synthesis is described in detail elsewhere (5). Schmidt also reported the preparation of one of the first metal-PMT complexes--a precipitate which formed when an aqueous solution of mercury (II) chloride was added to a solution of PMT in water.

Chemical investigations of tetrazoles have shown that they are nucleophilic reagents and that their nucleophilic character varies with the nature of the groups substituted on the ring. In this respect, substituted tetrazoles present an especially interesting problem both for the pharmacologist and the chemist. As drugs they possess a wide spectrum of neurotropic activities from strong convulsants (such as PMT) to depressants (e.g. 1-methyl-5-aminophenyltetrazole).

In a series of papers (6-10) Gross and Featherstone have described in detail the pharmacological properties of a wide variety of tetrazole compounds. They attempted to correlate pharmacological action with structure change of the tetrazole molecule. In a later study (11) they attempted to correlate the absorption spectra of a series of substituted tetrazoles with the pharmacological action of the compounds.

Analytical Studies on PMT

Most of the tetrazole research has been in the area of synthesis and the determination of the pharmacological properties of these neurotropic drugs. Little work, however, has been done with respect to the physicochemical and especially the donor properties of tetrazoles. Most of the studies have been concerned with the identification, separation, and determination of PMT (12-30).

At present, the most widely used analytical procedure for the quantitative determination of PMT seems to be a precipitation of its more or less insoluble complexes with various inorganic salts. Zwikker (14) prepared addition compounds of PMT with tetrahydrogenhexacyanoferrate(II), trihydrogenhexacyanoferrate(III) and some salts of cadmium(II), mercury(II), zinc(II), and copper(I). A copper(I)-PMT-complex having the approximate composition PMT·2 CuCl was precipitated from a hydrochloric acid solution of copper(I) chloride. This compound served as the basis for the first analytical procedure for the determination of PMT. He also found that PMT could be extracted quantitatively from a saturated aqueous ammonium sulfate solution into carbon tetrachloride.

Paulsen (31) modified the copper(I) chloride-PMT complex method by dissolving the precipitate in a hydrogen peroxide solution and measuring the amount of copper complexometrically. Horseley (21) regarded this gravimetric method as being rather cumbersome and claimed that the procedure was simplified by precipitating PMT as the mercury(II) chloride complex. Dister (32) compiled a detailed report on the physical and chemical properties of PMT and repeated some of this work. However, much of the work reported was qualitative.

Lindgren et al. (33), proposed a determination based on the precipitation of the PMT in a 3:2 isopropanol-water mixture with excess cadmium chloride. The cadmium in the precipitate was then titrated complexiometrically. In his precipitation and extraction studies of PMT, Golton (5) concluded that neither of these above methods yields satisfactory results.

Kolusheve and Nino'o (34) precipitated a double salt of PMT having the formula $(PMT)_4 \cdot 3\ CdCl_2$ from a hydrochloric acid solution. The precipitate was removed by filtration and the excess cadmium ion titrated complexiometrically, but the method was not quantitative. Troop (35) determined PMT by precipitating it in an aqueous solution as the silver-PMT-phosphotungstate salt, $Ag_3(PMT)_4PW_{12}O_{40} \cdot 4\ H_2O$ (solubility in water is $8.3 \pm 0.6 \times 10^{-6}$ moles per liter), using an excess of silver nitrate. After the precipitation was complete, the excess silver ion was titrated potentiometrically with a standard hydrochloric acid solution. The author claimed an accuracy of ten parts per thousand.

Acid-Base Studies

Olivera-Mandala (1,36) was one of the first investigators to study acidic and basic dissociation constants of tetrazole derivatives. The acidic dissociation constants were obtained by means of conductivity measurements while hydrolysis constants of 1-substituted tetrazole hydrochlorides were determined from the influence of these substances on the rate of hydrolysis of methyl acetate. Tetrazole and 5-substituted tetrazoles generally behave as acidic substances and show a range of acid strengths. In aqueous solution tetrazole has a pKa of 4.93 (1,37) while the pKa of 5-phenyltetrazole is 4.5 (38,39). Both can be titrated with strong base using phenolphthalein as the indicator. It is probable that all 5-substituted tetrazoles are acids having pKa values of 7 or less. The 5-substituted tetrazoles can also act as bases due to the presence of three other nitrogen atoms. Their basic strength, as calculated from the hydrolysis constants of the respective hydrochlorides, appears to be of the same order of magnitude as that of aniline (40). Herbst and Mihina (41) determined the pKa values for 5-phenyl and 5-tolyltetrazole potentiometrically using a water-methanol mixture of varying composition. They noted that these compounds were stronger acids than the benzoic acid or the respective toluic acids. Unfortunately these relative values may be in doubt since no account was made for the changing liquid junction potential when the solvent composition was changed. Herbst and Wilson (38) found that the apparent acidic dissociation constants of the 5-

alkyltetrazoles were about 10 to 20 percent of those for the corresponding carboxylic acids. Herbst and Garbrecht (42) prepared 5-acetylaminotetrazole which can be titrated as a weak monoprotic acid. They speculated that the compound could quite possibly behave as a diprotic acid in a nonaqueous media. Maher and Yohe (43) titrated 5-acetylaminotetrazole potentiometrically using ethylenediamine as the solvent and sodium aminoethoxide as the titrant. They were able to determine the two endpoints with the second hydrogen having about the same acid strength as phenol in the same solvent.

Tetrazoles substituted in the one position do not behave as acids. Stolle _et al_. (44) reported that they removed the 5-carbon hydrogen from 1-phenyltetrazole with methyl magnesium iodide in ether to form 1-phenyltetrazolemagnesium iodide. However, in this laboratory their results could not be duplicated (45). Recently, Garber (46) has successfully removed the 5-carbon hydrogen using n-butyl lithium in anhydrous tetrahydrofuran.

Pentamethylenetetrazole, substituted PMT, and 1-5 dialkyl tetrazoles have surprisingly weak basic properties in aqueous solutions. The first hint of the basic character of these compounds came from the distribution studies performed by Dister (32) in which he noted that the distribution coefficient (organic)/(aqueous) was larger for basic media. This would indicate that PMT can behave as a weak base. Popov and Holm (47) ti

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titrated PMT potentiometrically in glacial acetic acid with perchloric acid in the same solvent and found that PMT does possess weak basic properties in acetic acid. A more detailed treatment of the proton affinity of PMT, substituted PMT, and 1-5 dialkyl tetrazoles by Popov and Marshall (48,49) was carried out in anhydrous formic acid to enhance the basic character of these weak bases. They were able to determine potentiometrically the pKa values of these tetrazoles in this solvent.

Dipole Moment Studies

Jensen and Friediger (50) determined the dipole moment of tetrazole, 5-aminotetrazole, and 1-methyltetrazole in dioxane (D) or benzene (B). The respective measured dipole moments were 5.11(D), 5.71(D) and 5.38(B) debyes. These fairly large moments were attributed to the contribution of various charge separated structures which are characteristic for the tetrazole ring system. Kaufman, Ernsberger and McEwan (51) determined the dipole moments of twelve substituted tetrazoles and also attributed the origin of the respective dipole moments to the resonance contribution of a number of charge separated structures. The experimental dipole moments of 1 and 2 ethyl tetrazole are 5.46 and 2.65 debyes respectively, which implies that the tetrazole tautomer represented by structure I, (page 1) having a dipole moment of 5.11 debyes, predominates. These authors also established that such measurements are not suitable for recognizing meso-ionic compounds *i.e.* compounds which exhibit aromatic characteristics and can be represented only as resonance hybrids of a large number of contributing ionic forms. Lounsbury (3) undertook a theoretical examination of the dipole moments of tetrazoles. His results show that the largest contributors to the difference in the dipole moments of 1 and 2 substituted tetrazoles lies in the difference in the vectorial summation of the lone pair moments and the sigma moments. In order to obtain the observed apparent dipole moment of 5.11 debyes for tetrazole from a mixture of I and II (see page 1), 97% of an equilibrium mixture of 1-5, and 2-5 tetrazole must exist as the 1-5 tautomer. This conclusion also agrees with the results of an NMR study (2) of the chemical shifts of the carbon bound proton on the tetrazole ring in tetrazole and 1 alkyl substituted tetrazoles.

Kaufman and Woodman (52) determined the dipole moments of various chloro-, bromo-, and nitrophenyl tetrazoles to investigate the geometry of the tetrazole ring. Popov and Holm (53) measured the dipole moments of PMT, 8-sec-butyl PMT, 8-t-butyl PMT and 1-cyclohexyl-5-methyltetrazole in benzene solution obtaining the values 6.74, 6.18, 6.20, and 6.00 debyes for the respective compounds.

Coordination Compounds

Since tetrazole and 5-substituted tetrazoles are acid, many of the corresponding metal salts have been easily prepared in aqueous solution. Thiele and Ingle (54,55) neutralized a dilute aqueous solution of tetrazole with sodium hydroxide and precipitated very slightly soluble crystals of sodium tetrazolate monohydrate. The water of cyrstallization could not be removed even at reduced pressures. When barium hydroxide was used to neutralize the dilute tetrazole solution, barium tetrazolate trihydrate crystals were isolated after the excess barium ion was precipitated with carbon dioxide. Bladin (56) prepared the first silver salt of tetrazole and 5-substituted tetrazoles by adding hot silver nitrate solution to an aqueous solution of the respective tetrazole. This reaction has since been used as an identification and purification method. The copper(II) salt of tetrazole was prepared in a similar manner. Strain (57) reacted tetrazole with gaseous ammonia to produce ammonium tetrazolate and prepared calcium tetrazolate by allowing tetrazole to react with metallic calcium in liquid ammonia. These early workers considered the metal tetrazolates to be simple salts. However, recent studies have shown that some of them are actually coordination compounds (47,58 and 59). Herbst and Garbrecht (42) prepared the silver salts of 5-substituted tetrazoles by adding equimolar amounts of silver ion to solutions of the tetrazolate ion. Such complexes have been used to characterize 5-substituted tetrazoles (41). Olivera-Mandala and Alagna (60) presumably prepared one of the first true coordination complexes involving a tetrazole derivative. Upon the addition of platinum(IV) chloride to an alcoholic hydrogen chloride mixture containing 1-ethyl tetrazole, a canary yellow precipitate characterized as bis-(1-ethyltetrazole)-tetrachloroplatinate(IV) was isolated.

In order to study the electron donor properties of PMT complexes, Popov, Bisi, and Craft (61) determined spectrophotometrically the formation constants of the 1:1 PMT complexes: iodine monochloride, iodine monobromide, and iodine in carbon tetrachloride solution. Only the PMT-ICl complex could be obtained as a solid crystalline form which could be purified by recrystallization from chloroform. Popov, Wehman and Vaughn (62) extended this work by the spectrophotometric investigation of the complexes of iodine monochloride with 7-methyl, 8-sec-butyl and 8-t-butyl PMT. Repeated attempts were made to isolate the respective solid iodine monochloride complexes of the above PMT derivatives, however, only oily residues which decomposed on standing were obtained. The formation constants of the three complexes were determined, and in all cases the complexes are slightly stronger than the corresponding complex for the unsubstituted PMT. Person, Humphrey, Deskin and Popov (63), in their infrared spectra study of iodine monochloride charge transfer complexes, found that the spectrum of the I-Cl fundamental stretching vibration was very sensitive to the strength of the interaction between the halogen and the donor molecule with which it is complexed. On this basis the PMT molecule was concluded to be a moderately strong donor. Rheinboldt and

Stelliner (64), Dister (32) and Zwikker (14) have reported the preparation of PMT-Silver complexes; however, the stabilities of complexes in water were never determined. Popov and Holm (47) prepared silver complexes in acetonitrile, having the general formula, $(Tz)_2AgNO_3$, with PMT, substituted PMTs and 1-cyclohexyl-5-methyl tetrazole. The stabilities of these complexes were determined potentiometrically in acetonitrile, and the approximate formation constants were of the order of 10^2. Only the $(PMT)_2AgNO_3$ complex was obtained in the crystalline form by the slow evaporation of an aqueous solution of the complex. This demonstrates that loss of the ring hydrogens is not necessary for coordination to occur. The coordination could occur either through the electrons of the tetrazole ring or through one of the nitrogen atoms of the ring. At the present time, however, no clear cut evidence is available to unambiguously distinguish between the two possibilities.

Brubaker (59) prepared and characterized two crystalline forms of bis-(5-aminotetrazolato)-copper(II). The method of continuous variation clearly indicated that a 1:2 metal to tetrazole complex was formed in solution. The hypsochromic shift and accompanying hyperchromic effect suggest coordination rather than simple salt formation. Further studies showed that similar behavior is observed using tetrazole, 5-phenyltetrazole and 1-ethyltetrazole. Brubaker found that there is very little interaction between the copper(II) ion and 1-5 dimethyltetrazole.

This fact, together with the relatively low formation constant values for $(PMT)_2AgNO_3$ ($\sim 10^2$) (47), indicates that a replacable ring hydrogen is required to form this type of complex.

Brubaker and Daugherty (65) found that nickel(II) forms only impure and poorly characterized complexes when its salts react with various 5-substituted tetrazoles. Copper(II) complexes (66) with 5-substituted tetrazoles are obtained in good purity simply by mixing aqueous solutions of the reactants.

Brubaker and Gilbert (67) prepared complexes of various 1-substituted tetrazoles with cobalt(II), nickel(II), platinum(II) and zinc(II) chlorides. The solid complexes, with the exception of the zinc complex, are insoluble in common solvents. They decompose upon heating without melting which suggests the possibility of polymeric structures.

Brubaker (66) suggests the following three possible methods of coordination between metal ions and tetrazoles:

1. One of the nitrogens of the tetrazole ring acts as a Lewis base and donates its pair of electrons to the central metal ion.
2. The central metal ion may coordinate to the π electron system of the tetrazolate anion.
3. Since the tetrazolate anion seems to satisfy two coordination sites on the copper ion, coordination could occur by the formation of bonds to two different nitrogen atoms of the tetrazole ring.

Jonassen *et al*. (68) prepared microcrystalline complexes of iron(II) conforming to the general formula Fe(tetrazolato)$_2 \cdot 2\ H_2O$. They used the anions of 5-chlorotetrazole, 5-trifluoromethyltetrazole and 5-nitrotetrazole. Using infrared and Mössbauer studies, they proposed the formation of an analog to ferrocene when the tetrazole has strongly electronegative groups on the carbon. Jonassen, Harris and Archer (69) obtained reflectance spectra of divalent metal ions in 5-trifluoromethyltetrazole complexes. Based on the correlation of these reflectance spectra with previously obtained magnetic susceptibility and visible solution spectral data, they re-evaluated the proposed structure of the Fe(tetrazolato)$_2 \cdot 2H_2O$ complexes. The new experimental evidence indicated that the structure of the iron(II) and respective copper(II), cobalt(II), and nickel(II) 5-trifluoromethyltetrazole complexes are octahedral or distorted octahedral σ-bonded complexes involving coordination by tetrazolyl anion and water. Jonassen, Terry and Harris (70) showed the 5-trifluoromethyltetrazolyl anion to be a weakly coordinating ligand in aqueous solution. The transition metal ions used in their investigation were cobalt(II), nickel(II) and copper(II), which again shows that the tetrazolyl ion can participate in coordination with some transition metal ions.

II. EXPERIMENTAL

REAGENTS

Pentamethylenetetrazole (PMT)

All PMT used in this investigation was obtained from the Knoll Pharmaceutical Corporation under the registered name "Metrazol." The PMT was purified by recrystallization from anhydrous ether. The crystals obtained were washed with small volumes of chilled ether. Residual ether was removed under vacuum and the crystals were stored in an evacuated desiccator over phosphorus pentoxide. The melting point of the crystals was 60.5-61°C. The literature value is 61°C (61).

Nitromethane

Nitromethane was first passed through a cationic ion exchange unit prepared in the following manner: Seventy-five grams of Amberlite IR-120 resin (hydrogen form) were slurried with anhydrous methanol. The methanol was decanted and discarded. This process was repeated several times and then the resin was transferred to a column 2 cm. in diameter and 25 cm. in length. Then the resin in the column was washed first with one liter of anhydrous methanol at a rate of 1-2 ml. per minute, and then with two 300 ml. portions of nitromethane. The eluate was discarded. The crude nitromethane was then passed through the column at a rate of 2-5 ml. per minute. (71). A vapor phase chromatogram of the purified material gave a single sharp peak using a Beckman GC-2 chromatograph equipped with a silicone 30 column (current 200 ma, attenuation 10, temperature 70°C). The water content, which was determined by a Karl Fischer titration, corresponded approximately to a 10^{-3} M solution.

2,2-Dimethoxypropane (98%)

This reagent was of technical grade and used without further purification. It was obtained from the Dow Chemical Co.

Barium Oxide

This chemical was obtained from Barium and Chemicals, Inc. and was the 1/4" x 1/8" screened mesh variety.

Analytical Methods

Copper Determination

The following two methods were used:

Iodometric Pentamethylenetetrazole reacts with iodine and, therefore, interferes in the iodometric determination of the copper in the copper-PMT complexes. The interference was removed by the following method. The complex was dissolved in 12 M nitric acid and the solution was boiled gently for ten minutes to decompose the PMT. Then, 10 ml. of 12 M sulfuric acid was added and the solution evaporated to dryness overnight on an 80°C hot plate. The residue was redissolved in 100 ml. of distilled water, neutralized to pH 7 with sodium hydroxide, and then acidified with acetic acid to the approximate pH of 4. After the addition of potassium iodide, the liberated iodine was titrated with standard thiosulfate solution (72).

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Complexometric An aqueous solution of the respective copper complex was made basic to a pH of 8-9 with ammonia. Murexide (ammonium purpurate) indicator was added and the solution was titrated with 0.01 M EDTA[a] until the color changed from yellow to violet (73).

Nickel Determination

An aqueous solution containing the complex was neutralized to pH 7 with sodium hydroxide, then murexide indicator and 10 ml. of 1 M ammonium chloride was added. The solution was titrated with 0.01 M EDTA. Just prior to the end point, 10 ml. of concentrated ammonia was added and the titration continued to the end point when the color changed from yellow to bluish violet (73).

Cobalt Determination

An aqueous solution containing the complex was made slightly acidic (pH 6). Murexide indicator was added and the pH of the solution adjusted with ammonia until the color of the indicator changed from orange to yellow. The solution was then titrated with 0.01 M EDTA to a sharp color change from yellow to violet (73).

Zinc Determination

An aqueous solution containing the complex was neutralized to pH 7 with sodium hydroxide. Then, 2 ml. of pH 10 buffer, and Eriochrome Black T(1-[1-Hydroxy-2-naphthylazo]-6-nitro-2-

[a]EDTA = Ethylenediamine tetraacetic acid.

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naphthol-4-sulfonic acid sodium salt indicator) was added. The solution was then titrated with 0.01 M EDTA until the color changed from red to blue (73).

Iron Determination

Several attempts were made to determine the iron content of the iron complexes but they were unsuccessful. The carbon, nitrogen, hydrogen, and perchlorate analyses, however, are good indications of the stoichiometry of these complexes.

Manganese Determination

An aqueous solution containing the complex was made weakly acid to pH 5. Ascorbic acid (0.5 grams) was added and the mixture was warmed over a Meeker burner. After five minutes the solution was neutralized with sodium hydroxide and 5 ml. of 0.1 M zinc sulfate, 2 ml. of pH 10 buffer and several drops of Eriochrome black T were added. The solution was then titrated with 0.01 M EDTA to the red-blue color change (73).

Carbon, Hydrogen, and Nitrogen Analyses

The Spang Microanalytical Laboratory, Ann Arbor, Michigan, determined the carbon, hydrogen and nitrogen percentages in the transition metal complexes of PMT.

Perchlorate Determination

The complex was first dissolved in 75 ml. of 0.5 M sodium chloride solution (which makes the precipitate more granular), and

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and then heated to boiling. The precipitation was carried out in a hot solution by adding an excess of 0.1 M tetraphenylarsonium(III) chloride. The precipitate was allowed to digest for 6 hours at room temperature, then filtered, washed several times with ice water, dried at 110°C, and weighed as tetraphenylarsonium(III) perchlorate (74).

Water Determination

The water content of the transition metal complexes of PMT was determined by Karl Fischer titration. The complexes were dissolved in purified nitromethane or acetone and the water reacted with the Karl Fischer reagent (75).

Instrumentation

The following instruments were employed in making the appropriate measurements.

Cary Model 14 recording spectrophotometer was used to obtain near infrared, visible, and ultraviolet absorption spectra.

Beckman IR5A infrared spectrophotometer was used to obtain infrared absorption spectra utilizing KBr pellets and nujol or fluorlube mulls.

An Alpha Scientific Laboratories AL 7500 M Electromagnet and Al 7500 PS Power Supply equipped with a Mettler single pan balance was used for the magnetic susceptibility measurements.

A Varian A60 nuclear magnetic resonance spectrometer was used to obtain the NMR spectra.

A Varian model V-4500 spectrometer having a 100 Kc field modulator was used to obtain the ESR Spectra. The magnetic field was measured with a proton nuclear magnetic resonance gaussmeter.

Beckman GC-2 Gas Chromatograph was used to check the purity of the nitromethane.

Fisher-Johns Melting Point Apparatus was used to obtain all melting points.

A North American Philips Company, type 12045, X-ray generator equipped with a North American Philips Company, type 52056, camera was used to obtain the X-ray powder diffraction photographs.

A Perkin-Elmer Model 301 Far-Infrared Double-Beam Spectrophotometer which utilizes various choppers, mirrors and filters was used to obtain the far-infrared spectra of the respective complexes.

Beckman DU Spectrophotometer equipped with a reflectance attachment was used to record the reflectance spectra. These spectra were obtained by Professor Luigi Sacconi, Institute of Inorganic Chemistry, University of Florence, Italy.

Experimental Procedures

Temperature Control

Unless otherwise stated, no temperature control was employed during any of the measurements. All standard solutions were prepared at room temperature of approximately 25°C.

Fisher-Johns Melting Point Apparatus Calibration

The Fisher-Johns melting point apparatus was calibrated using appropriate Arthur H. Thomas Company (Philadelphia, Pa.) micro-melting point standards.

Thermometer Stem Correction

The following formula was used to correct all melting points obtained during this study (76).

$$K = (0.000154)(t-t') N$$

where:

- K = correction in degrees added to temperature read
- t = temperature read
- t' = average temperature of the exposed column of mercury
- N = the length, measured in degrees, of the thread of mercury exposed between the electrical heating block and the point t.

Preparation of Solutions

All solutions of PMT in nitromethane were prepared from weighed amounts of PMT. Solutions of copper(II) perchlorate hexahydrate were prepared from weighed amounts of this compound. The copper in a 10 ml. aliquot was then extracted into water and the copper titer determined iodometrically (77).

Selection of a Copper(II) Salt for the Spectrophotometric Study of the Donor Properties of PMT

Solubility of Various Copper Salts in Purified Nitromethane

In order to find a copper salt which would be the best source of copper(II) ions in nitromethane for the spectrophotometric studies of the donor properties of PMT, the following compounds were investigated:

(1) Anhydrous copper(II) chloride -- $CuCl_2$

(2) Anhydrous copper(II) bromide -- $CuBr_2$

(3) Anhydrous copper(II) sulfate -- $CuSO_4$

(4) Copper(II) acetate monohydrate -- $Cu(C_2H_3O_2)_2 \cdot H_2O$

(5) Copper(II) nitrate trihydrate -- $Cu(NO_3)_2 \cdot H_2O$

(6) Copper(II) perchlorate hexahydrate -- $Cu(ClO_4)_2 \cdot 6H_2O$

(7) Copper(II) p-toluenesulfonate -- $Cu(C_7H_7SO_3)_2$

All of the above copper salts with the exception of copper(II) p-toluene sulfonate are commercially available. Copper(II) p-toluene sulfonate was prepared by adding dry copper(II) carbonate directly to a saturated aqueous solution of p-toluene sulfonic acid until the pH was about 3.5. The filtered solution was then evaporated on a steam bath. The product was recrystallized twice from hot water at 110°C for four hours (78).

<u>Analysis</u>: Calculated: Cu, 15.91%; C, 41.46%; H, 3.45%; S, 15.78%. Found: Cu, 15.80%; C, 40.37%; H, 3.66%; S, 14.41%.

The anhydrous copper(II) sulfate and copper(II) p-toluene sulfonate were insoluble in nitromethane and therefore could not be used in this study.

Copper(II) chloride, bromide, sulfate and acetate were eliminated because of the combination of low solubility

($\sim 1 \times 10^{-3}$ moles per liter) and relatively low molar absorptivities (~ 20). Furlani, Sgamellotte and Guillo (78) reported that copper(II) paratoluene sulfonate was soluble to the extent of 2.0×10^{-2} $\underline{M}$ in acetonitrile at room temperature. However, in this laboratory it was found to be practically insoluble in nitromethane ($\sim 2.5 \times 10^{-4}$ moles per liter). The spectrum of a saturated solution of this compound in nitromethane showed no appreciable absorption in near infrared or visible region, and there was no change on addition of PMT. Therefore it was not studied further.

Copper(II) nitrate trihydrate and copper(II) perchlorate hexahydrate dissolve relatively well in nitromethane having approximate solubilities of 3.5×10^{-3} and 5.3×10^{-2} moles per liter respectively. Both of these copper salts have molar absorptivities of approximately 20, an absorption maximum at about 780 mμ; and each gave a hypsochromic shift with accompanying hyperchromic effect upon addition of PMT. Copper(II) perchlorate hexahydrate was ultimately selected for this study primarily because of its high solubility as compared with the other copper salts.

Attempted Preparation of Anhydrous Copper(II) Perchlorate

In order to investigate the extent of complexing ability of PMT towards copper(II) ions, anhydrous copper(II) perchlorate was used because a hydrated salt would introduce water into the system.

Since water is a fairly strong electron donor, it would effectively compete with PMT (a weak donor) for the coordination sites of the copper ion.

The following methods were used in an attempt to prepare anhydrous copper(II) perchlorate, starting with copper(II) perchlorate hexahydrate.

1. Copper(II) perchlorate hexahydrate was dried in a vacuum oven at 75°C and 5 mm pressure for forty-eight hours, as described by Larson and Iwamoto (79). Analysis of the products showed a copper content varying between 17.20 and 19.00 percent. Thus, only the adsorbed water and, at most, two of the six waters of hydration were removed.

2. Copper(II) perchlorate hexahydrate was recrystallized from hot nitromethane. The product has a copper content of approximately 19 percent. Again only the adsorbed moisture was removed.

3. Recrystallization of copper(II) perchlorate hexahydrate from hot 72% perchloric acid was attempted. This method once again only removed the adsorbed moisture since the copper content was found to be, as before, approximately 19 percent.

4. Copper(II) perchlorate hexahydrate was dissolved in 72% perchloric acid and the excess acid fumed off at 200°C under nitrogen atmosphere. The resulting azure blue powdery material was analyzed for its copper content by iodometric titration while the perchlorate content was determined by gravimetric

analysis using tetraphenylarsonium(III) chloride as the precipitating agent. The analyzed copper content was 24.23% which was within one percent of the theoretical calculated value for anhydrous copper perchlorate. The percentage of perchlorate found was 61.78% or about fifteen percent lower than the theoretically calculated value. Only about 90% of this azure substance dissolved in water or nitromethane. If the respective solutions were made slightly acidic, the insoluble material dissolved completely. It seems, therefore, that the product was indeed anhydrous copper(II) perchlorate contaminated with a basic copper oxide. Attempts to identify the insoluble material by X-ray powder diffraction methods were not successful.

Preparation of Coordination Compounds of Pentamethylenetetrazole

Since standard drying techniques mentioned above do not remove the water of hydration from transition metal perchlorates, Erley (80) suggested the use of 2,2-dimethoxypropane (hereafter referred to as DMP) as a dehydrating agent. One mole of DMP reacts endothermically and rapidly with one mole of water of hydration to form two moles of methanol and one mole of acetone.

$$CH_3C(OCH_3)_2CH_3 + H_2O \longrightarrow CH_3\overset{O}{\overset{\|}{C}}-CH_3 + 2CH_3OH$$

Erley indicated that approximately 96% of the water reacts at 30°C when mixed with DMP in a 1 to 1 mole ratio.

<u>Bis(pentamethylenetetrazole)copper(I) Perchlorate</u>

This complex was prepared by two different methods:

(1) <u>Reaction in DMP</u>

A solution containing 3.71 grams (0.01 moles) of copper(II) perchlorate hexahydrate in 65 ml. of DMP was prepared with the use of a magnetic stirrer; the mixture was stirred long enough to disperse the copper(II) perchlorate hexahydrate which has limited solubility in DMP. As the mixture was stirred, the color of the copper(II) perchlorate mixture changed from blue to light green. To the mixture was added 3.45 grams (0.025 moles) of dry PMT. A blue oily substance formed immediately. The stirring was continued for approximately three hours during which the oily substance slowly solidified to a white solid. The precipitate was filtered and washed several times with chilled acetone and dried at 110°C. The solid was slightly soluble in acetone and nitromethane but insoluble in most other solvents. It could not be purified by recrystallization. The compound is stable at room temperature and begins to decompose at 226°C. A positive test for copper(I) was obtained when 2,2'-biquinoline was added to a *t*-butyl alcohol solution containing the complex (81). The solid was identified as a copper(I) complex with the composition $Cu(PMT)_2ClO_4$ which was obtained in 48.7% yield.

Analysis: Calculated: Cu, 14.46%; C, 32.80%; H, 4.56%; N, 25.51%. Found: Cu, 14.53%; C, 32.41%; H, 5.05%; N, 25.12%.

(2) Reaction in Nitromethane

To 200 ml. of nitromethane, 3.71 grams (0.01 moles) of vacuum dried copper(II) perchlorate hexahydrate were added. After the dissolution of the salt, 3.45 grams (0.025 moles) of PMT were added. The solution was evaporated on a steam bath until only a viscous blue syrup remained. Upon addition of 200 ml. of boiling water, a white, fluffy precipitate was formed which was washed several times with chilled acetone. The product was obtained in a 79% yield. A positive test for copper(I) was obtained upon the addition of 2,2'-biquinoline to a *t*-butyl alcohol solution containing the complex. This white compound (decomposition point 226°C) is slightly soluble in nitromethane and acetone but insoluble in most other solvents; it could not be purified by recrystallization.

Analysis: Calculated: Cu, 14.46%; C, 32.80%; H, 4.56%; N, 25.51%. Found: Cu, 14.46%; C, 31.42%; H, 4.55%; N, 25.11%.

These two complexes are presumed to be the same as shown by the respective elemental analysis and physical properties (Table I).

Tetrakis(pentamethylenetetrazole)copper(II) Perchlorate

This complex was prepared by three independent methods:

(1) Reaction in DMP

A 3.71 gram sample (0.01 moles) of copper(II) perchlorate hexahydrate was added to 25 ml. of DMP. The mixture was stirred with a magnetic stirrer for about five minutes during which the color of the solution changed from blue to light green. To the solution being stirred, 5.52 grams (0.04 moles) of dry PMT was added. The color of the solution immediately turned blue. After approximately five minutes, a blue precipitate was formed. This was filtered, washed several times with chilled ether, and dried at 110°C. The product was obtained in 96% yield. The melting point of the complex was spread over a range of 141-145°C.

Analysis: Calculated: Cu, 7.80%; C, 35.39%; H, 4.95%; N, 27.52%. Found: Cu, 7.60%; C, 35.46%; H, 5.14%; N, 26.73%.

(2) Reaction in Anhydrous Acetic Acid

To 200 ml. of acetic acid was added 7.44 grams (0.02 moles) of vacuum dried copper(II) perchlorate hexahydrate. After the copper perchlorate was completely dissolved, a stoichiometric amount of acetic anhydride (11.33 ml. or 0.12 moles) required to react with the hydrated water of the copper(II) perchlorate was added; and $Cu(ClO_4)_2 \cdot xHOAc$ precipitated as light blue crystals in four to six hours. These crystals were filtered and redissolved in hot acetic acid. An eight molar excess of dry PMT (22.08 grams) was added to the hot solution which turned deep blue, indicating complexation. Large, deep blue crystals precipitated in four to six hours. The product (13.0 grams) was obtained in a 43.2% yield. The crystals were purified by recrystallization from acetic acid and dried at 110°C. These crystals melt sharply at 154°C.

<u>Analysis</u>: Calculated: Cu, 7.80%; C, 35.39%; H, 4.95%; N, 27.52%; Cl, 8.71%; ClO_4^-, 24.52%. Found: Cu, 7.71%; C, 35.37%; H, 5.06%; N, 27.39%; Cl, 8.85%; ClO_4^-, 24.16%.

(3) <u>Reaction in Nitromethane</u>

To 200 ml. of nitromethane was added 3.71 grams (0.01 moles) of vacuum dried copper(II) perchlorate hexahydrate. After the copper perchlorate had completely dissolved, 11.04 grams of dry PMT were added to the solution which turned a deeper blue indicating complexation. The solution was allowed to evaporate slowly at room temperature and after the volume was reduced to about 25 ml., royal-blue crystals were formed. The product was obtained in a 52% yield. The crystals were purified by recrystallization from nitromethane and dried at 110°C. These crystals melted over a range of 141-145°C.

Analysis: Calculated: Cu, 7.80%; ClO_4^-, 24.52%. Found: Cu, 7.73%; ClO_4^-, 24.64%.

Hexakis-(Pentamethylenetetrazole)-Copper(II) Perchlorate

A solution was prepared containing 3.72 grams (0.01 moles) of vacuum dried copper(II) perchlorate hexahydrate in 50 ml. of DMP. The mixture was stirred long enough (five to ten minutes) to disperse the copper(II) perchlorate which has a limited solubility in DMP. As the mixture was stirred, the color of the copper(II) perchlorate in solution changed from blue to light green indicating that dehydration was taking place (82,83). An eight mole excess of dry PMT (11.04 grams) was then added to the solution. A light blue precipitate formed after about five minutes. It was filtered, washed several times with chilled ethyl ether, and then dried at room temperature under vacuum. The product was obtained in 96% yield. The melting point of the complex was 117.5°C.

Analysis: Calculated: Cu, 5.80%; C, 39.65%; H, 5.55%; N, 30.83%; ClO_4^-, 18.20%. Found: Cu, 5.71%; C, 39.62%; H, 5.63%; N, 31.10%; ClO_4^-, 18.75%.

Preparation of Hexakis-(Pentamethylenetetrazole)-Copper(II) Perchlorate Crystals

The complex was recrystallized from carbon tetrachloride in the following manner: To 80 ml. of carbon tetrachloride, in a tall narrow beaker, about 10 ml. of a 0.05 *M* chloroform solution of the complex was carefully introduced as a layer on top of the carbon tetrachloride. The beaker was then tightly covered to prevent evaporation of the solvent. The carbon tetrachloride diffused through the solution thereby lowering the solubility of the complex. The complex crystallized out of solution overnight as the blue tetrakis(PMT)copper(II) perchlorate. The melting point of this complex (153°C) compares favorably with the tetrakis(PMT)copper(II) perchlorate prepared in acetic acid (154°C). Infrared spectra and X-ray powder diffraction likewise indicate that the compounds are identical as shown in Figure 1 and Tables X and XII. When the solution is allowed to evaporate very slowly over a period of two weeks, some of the tetrakis(PMT)copper(II) perchlorate is slowly converted to light blue hexakis(PMT)copper(II) perchlorate. These crystals have the same color, melting point, infrared spectrum and X-ray powder diffraction pattern as the hexakis(PMT)copper(II) perchlorate complex prepared by the DMP method (Figure 2 and Tables I, VII).

Hexakis(pentamethylenetetrazole)nickel(II) Perchlorate

This complex was prepared exactly like the corresponding hexakis(PMT)copper(II) perchlorate. A light blue product was obtained in 95% yield. The decomposition of the complex began at approximately 237°C.

TABLE I

The Physical Properties and Transition Metal Analysis Data of the Transition Metal Complexes of Pentamethylenetetrazole

Complex	Color	Melting Point °C	Percent Metal Calculated	Percent Metal Found	Note
$Cu(PMT)_2ClO_4$	white	226d	14.46	14.53	a
$Cu(PMT)_2ClO_4$	white	226d	14.46	14.46	b
$Cu(PMT)_4(ClO_4)_2$	blue	141-145	7.80	7.60	c
$Cu(PMT)_4(ClO_4)_2$	blue	154	7.80	7.71	d
$Cu(PMT)_4(ClO_4)_2$	blue	141-145	7.80	7.73	e
$Cu(PMT)_6(ClO_4)_2$	lt. blue	117.5	5.80	5.71	f
$Cu(PMT)_6(ClO_4)_2$	lt. blue	118.0	5.80	5.75	g
$Ni(PMT)_6(ClO_4)_2$	lt. blue	237d	5.40	5.46	f
$Ni(PMT)_6(ClO_4)_2$	lt. blue	235d	5.40	5.43	h
$Mn(PMT)_6(ClO_4)_2$	white	195-212	5.08	5.30	f
$Co(PMT)_6(ClO_4)_2$	rose	195-205	5.43	5.61	f
$Zn(PMT)_6(ClO_4)_2$	white	148-150	5.98	5.98	f
$Fe(PMT)_6(ClO_4)_2$	lt.brown	194d	-----	-----	f
$Fe(PMT)_6(ClO_4)_3$	lt.brown	196d	-----	-----	f

a. This complex was prepared in DMP (see p. 25).
b. This complex was prepared in nitromethane (see p. 26).
c. This complex was prepared in DMP (see p. 27).
d. This complex was precipitated from acetic acid (see p. 27).
e. This complex was prepared in nitromethane (see p. 28).
f. This complex was prepared in DMP (see p. 29).
g. This complex was recrystallized from $CHCl_3$-CCl_4 mixture (see p. 29).
h. This complex was precipitated from water (see p. 34).

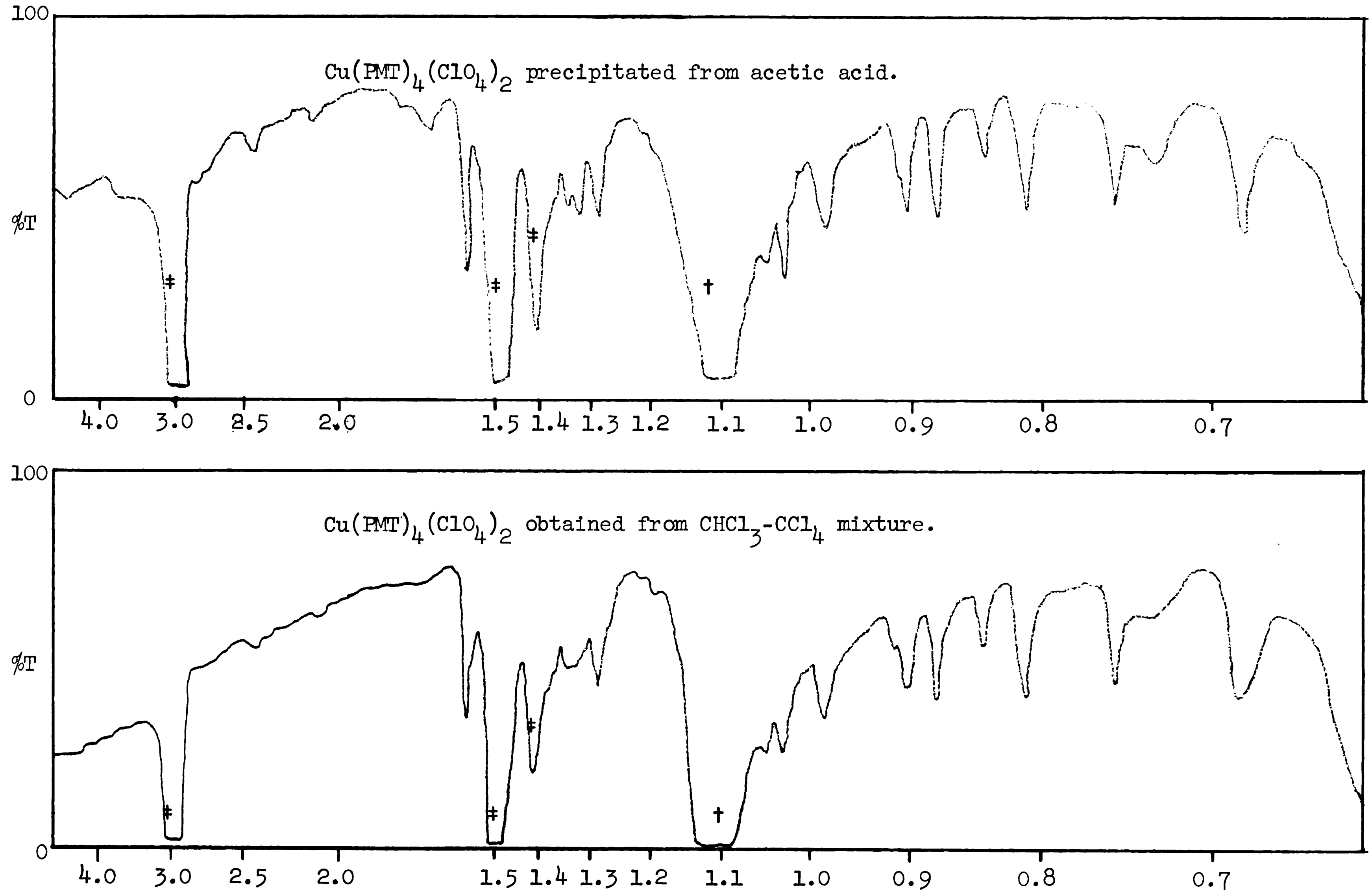

Figure 1. Infrared Absorption Spectra (in $cm^{-1} \times 10^{-3}$). Nujol mull.

‡ - Nujol bands   † - Perchlorate band

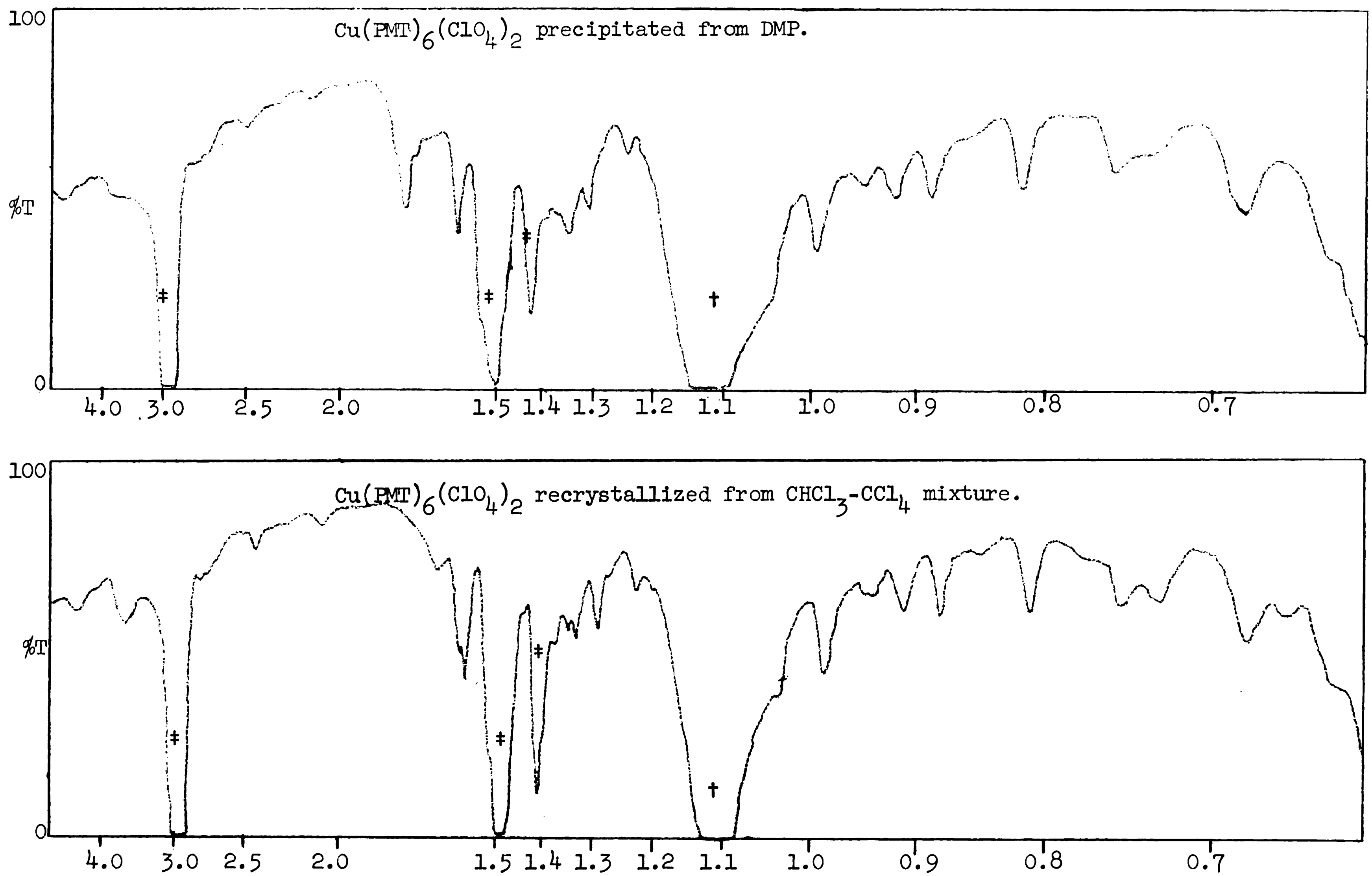

Figure 2. Infrared Absorption Spectra (in $cm^{-1} \times 10^{-3}$). Nujol mull.

‡ - Nujol bands † - Perchlorate band

Analysis: Calculated: Ni, 5.40%; C, 39.79%; H, 5.57%; N, 30.94%; ClO_4^-, 18.28%. Found: Ni, 5.46%; C, 39.42%; H, 5.70%; N, 30.75%; ClO_4^-, 18.52%.

Hexakis(PMT)nickel(II) perchlorate was also prepared by adding a twenty molar excess of PMT to an aqueous solution of nickel(II) perchlorate. The complex slowly crystallized out of solution over a period of five to ten days. The light blue product (decomposition point 235°C) was identical in all respects to that obtained by the DMP method. The infrared spectra match rather well as shown in Figure 3 as do their respective spectra (Figure 11).

Analysis: Calculated: Ni, 5.40%; C, 39.79%; H, 5.57%; N, 30.94%; ClO_4^-, 18.28%. Found: Ni, 5.43%; C, 39.67%; H, 5.56%; N, 31.09%; ClO_4^-, 18.36%.

Hexakis(pentamethylenetetrazole)manganese(II) Perchlorate

This complex was prepared exactly like the corresponding hexakis(PMT)copper(II) perchlorate. A white product was obtained in 94.5% yield. The complex melted over a range of 195-212°C.

Analysis: Calculated: Mn, 5.08%; C, 39.97%; H, 5.59%; N, 31.07%; ClO_4^-, 18.34%. Found: Mn, 5.30%; C, 39.11%; H, 5.54%; N, 31.05%; ClO_4^-, 19.74%.

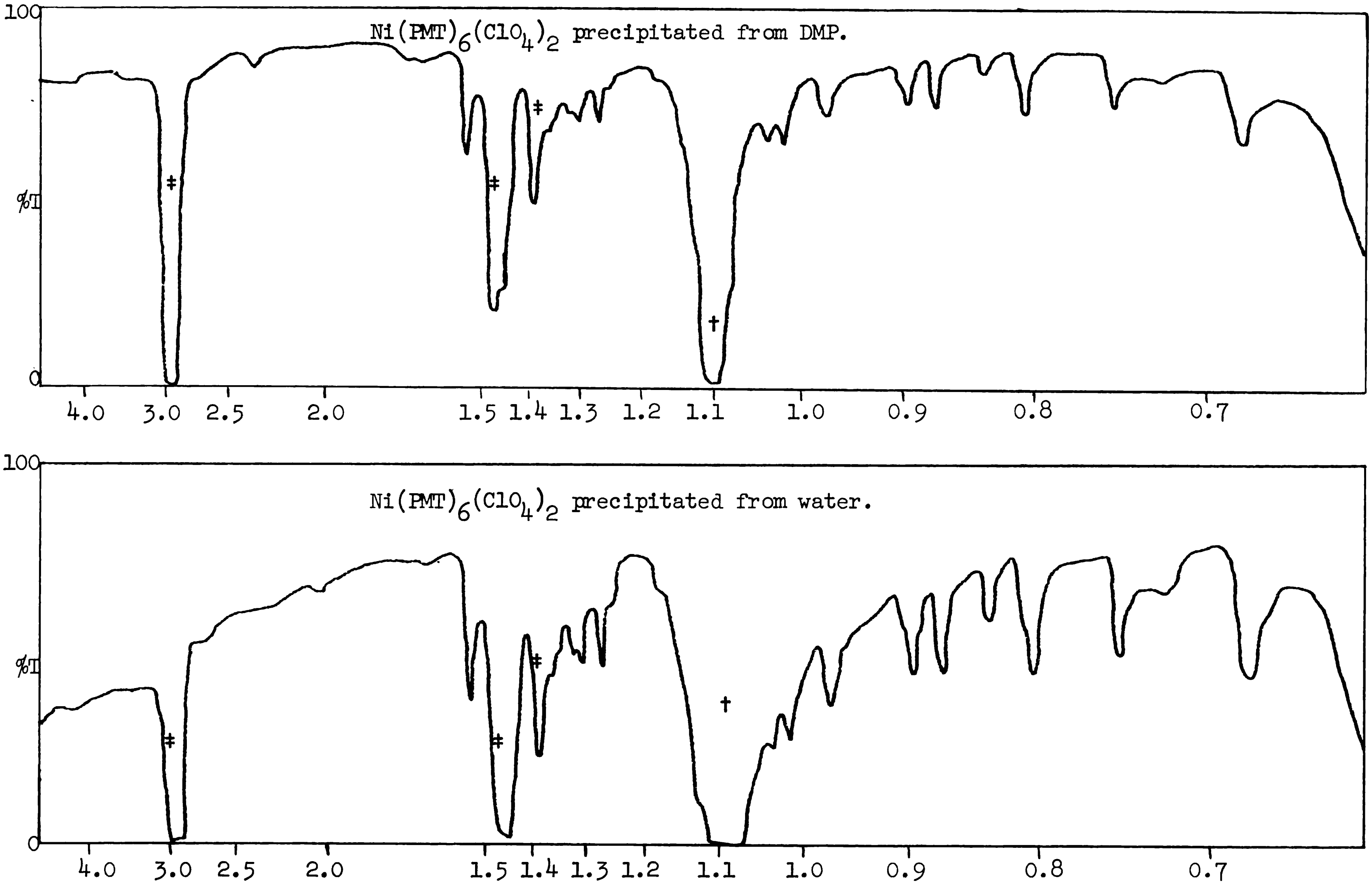

Figure 3. Infrared Absorption Spectra (in $cm^{-1} \times 10^{-3}$). Nujol mull.

‡ - Nujol bands † - Perchlorate band

Hexakis(pentamethylenetetrazole)cobalt(II) Perchlorate

This complex was prepared exactly like the corresponding hexakis(PMT)copper(II) perchlorate. A rose colored product was obtained in 94.5% yield. The melting point of the complex was 195-205°C.

Analysis: Calculated: Co, 5.43%; C, 39.82%; H, 5.57%; N, 30.96%; ClO_4^-, 18.28%. Found: Co, 5.61%; C, 38.74%; H, 5.41%; N, 29.59%; ClO_4^-, 19.24%.

Hexakis(pentamethylenetetrazole)zinc(II) Perchlorate

This complex was prepared exactly like the corresponding hexakis(PMT)copper(II) perchlorate. A white product was obtained in 97.2% yield. The melting point of the complex was 148-150°C.

Analysis: Calculated: Zn, 5.98%; C, 39.58%; H, 5.49%; N, 30.77%; ClO_4^-, 18.16%. Found: Zn, 5.98%; C, 38.83%; H, 5.39%; N, 30.64%; ClO_4^-, 18.98%.

Hexakis(pentamethylenetetrazole)iron(II) Perchlorate

This complex was prepared exactly like the corresponding hexakis(PMT)copper(II) perchlorate. The light brown product was obtained in 86.3% yield. The decomposition point of this complex was 194°C.

Analysis: Calculated: C, 39.93%; H, 5.54%; N, 31.05%; ClO_4^-, 18.33%. Found: C, 39.11%; H, 5.60%; N, 30.30%; ClO_4^-, 19.84%.

Hexakis(pentamethylenetetrazole)iron(III) Perchlorate

This complex was prepared exactly in the same manner as hexakis(PMT)copper(II) perchlorate except the precipitation of the complex occurred only after the reactants had stirred for three to four hours. A light brown product was obtained in 74% yield. The decomposition point of the complex was 196°C.

Analysis: Calculated: C, 39.93%; H, 5.54%; N, 31.05%; ClO_4^-, 25.21%. Found: C, 39.21%; H, 5.53%; N, 31.08%; ClO_4^-, 22.61%.

The primary experimental difficulty encountered in all the preparations of pure hexakis(PMT) transition metal complexes was that in most cases no satisfactory purification method such as recrystallization could be devised.

All of the hexacoordinated PMT transition metal complexes described, except that of copper(II), can be prepared by the method described for hexakis(PMT)copper(II) perchlorate (see p. 29) using a 4:1 ratio of PMT to transition metal perchlorate. This is shown by the X-ray diffraction analysis (Tables VI and VIII), infrared spectra (Figures 19-25), and their physical properties.

The Attempted Preparation of the Chromium(III) and Vanadyl Pentamethylenetetrazole Complexes

Preparation of the chromium(III) and vanadyl complexes was attempted using the procedure outlined above for hexakis(PMT)-copper(II) perchlorate. The respective PMT complexes, however, could not be isolated.

Karl Fischer Analysis of the Transition Metal Complexes of Pentamethylenetetrazole

The Karl Fischer analysis of the respective complexes was performed as previously described (see p. 18). The data show that the complexes contain less than 0.20% water and are essentially anhydrous; the small amount of water found is probably adsorbed by the complex.

Karl Fischer analysis was not obtained for hexakis(pentamethylenetetrazole)copper(II), iron(II) and iron(III) perchlorate or tetrakis(pentamethylenetetrazole)copper(II) perchlorate due to the premature liberation of iodine. However, these complexes are essentially anhydrous as shown by their elemental analyses. The titration of bis(pentamethylenetetrazole)copper(I) perchlorate was not carried out since the complex is insoluble in most organic solvents.

Spectrophotometric Studies of Copper(II) Complexes in Pentamethylenetetrazole

Beer's Law Study

Solutions of copper(II) perchlorate hexahydrate in nitromethane were shown to obey Beer's law at 790 mμ in the concentration range $2.8 \times 10^{-4} - 2.8 \times 10^{-3}$ M.

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Mole Ratio and Continuous Variation Studies of Copper-PMT Complexes in Purified Nitromethane

A mole ratio study of the PMT-copper(II) perchlorate system at 700 mμ is shown in Figure 4. It can be seen that the absorbance increases with increasing PMT/Cu^{2+} ratio but even at a ratio of 60:1 the limiting absorbance has not been reached. The data are insufficient for any conclusions about the nature of the colored species and it is planned to continue this work.

The method of continuous variation (84) was investigated using 0.025 and 0.05 M solutions (Figures 5,6); maxima were obtained at a ligand mole fraction of approximately 0.8. The measurements were carried out, at four different wavelengths, and a shift of the maxima to lower values of mole fraction of the ligand is noted as the wavelength is decreased.

A continuous variation study of the copper(II)-PMT complex in water was carried out but no complex formation was indicated. There was no increase or shift of the aquated copper(II) ion absorption peak which indicates that under our experimental conditions, water can successfully compete with PMT for the coordination position around the copper ion.

Spectrophotometric Study of the Copper(II) Perchlorate-Pentamethylenetetrazole System in Nitromethane

Copper(II) Perchlorate-Hexahydrate

As increasing amounts of PMT are added to a 0.01 M copper(II)

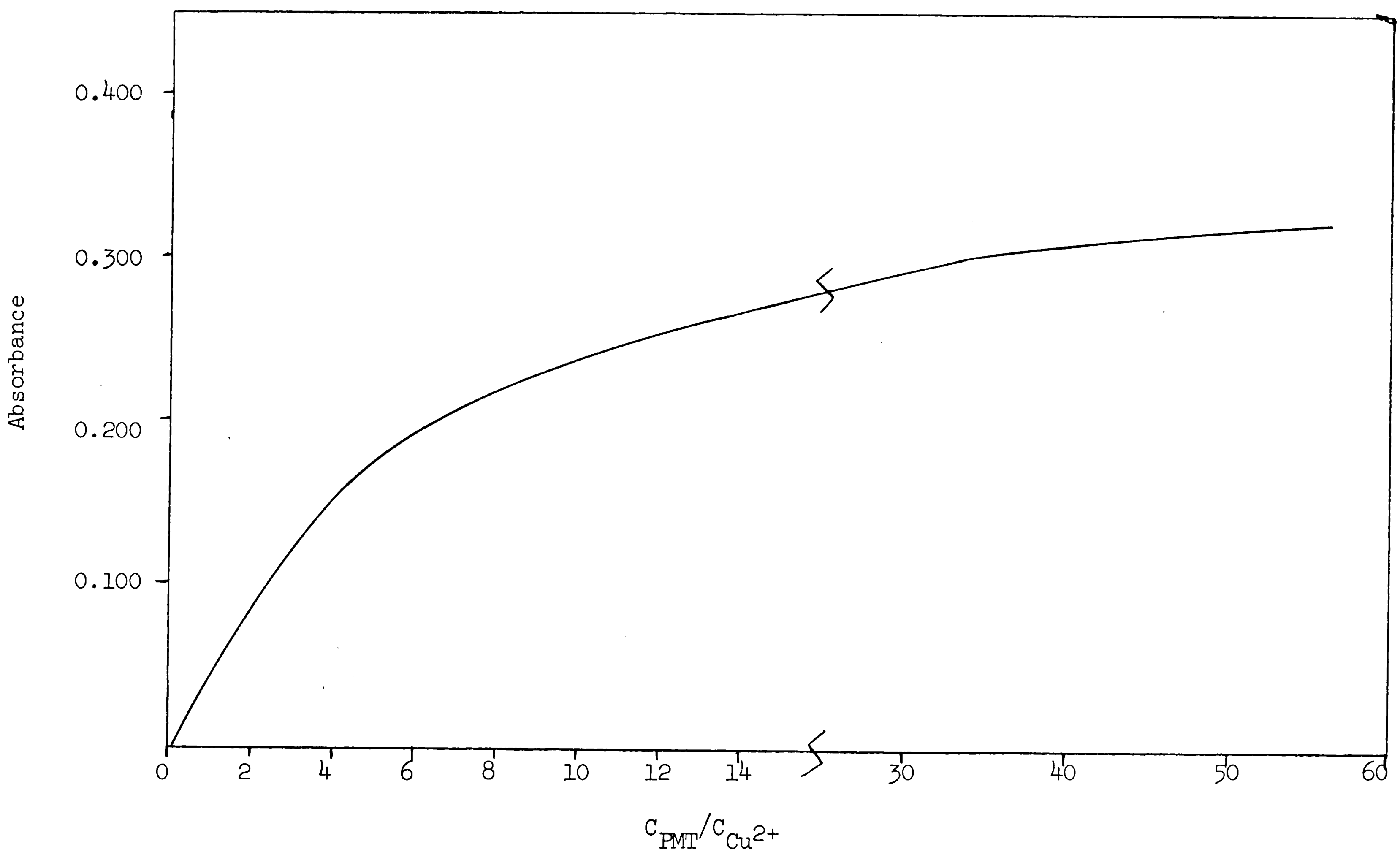

Figure 4. Molar ratio study in nitromethane of 5 x 10^{-2} $\underline{M}$ $Cu(ClO_4)_2 \cdot 6\ H_2O$ with PMT in nitromethane at 700 mμ.

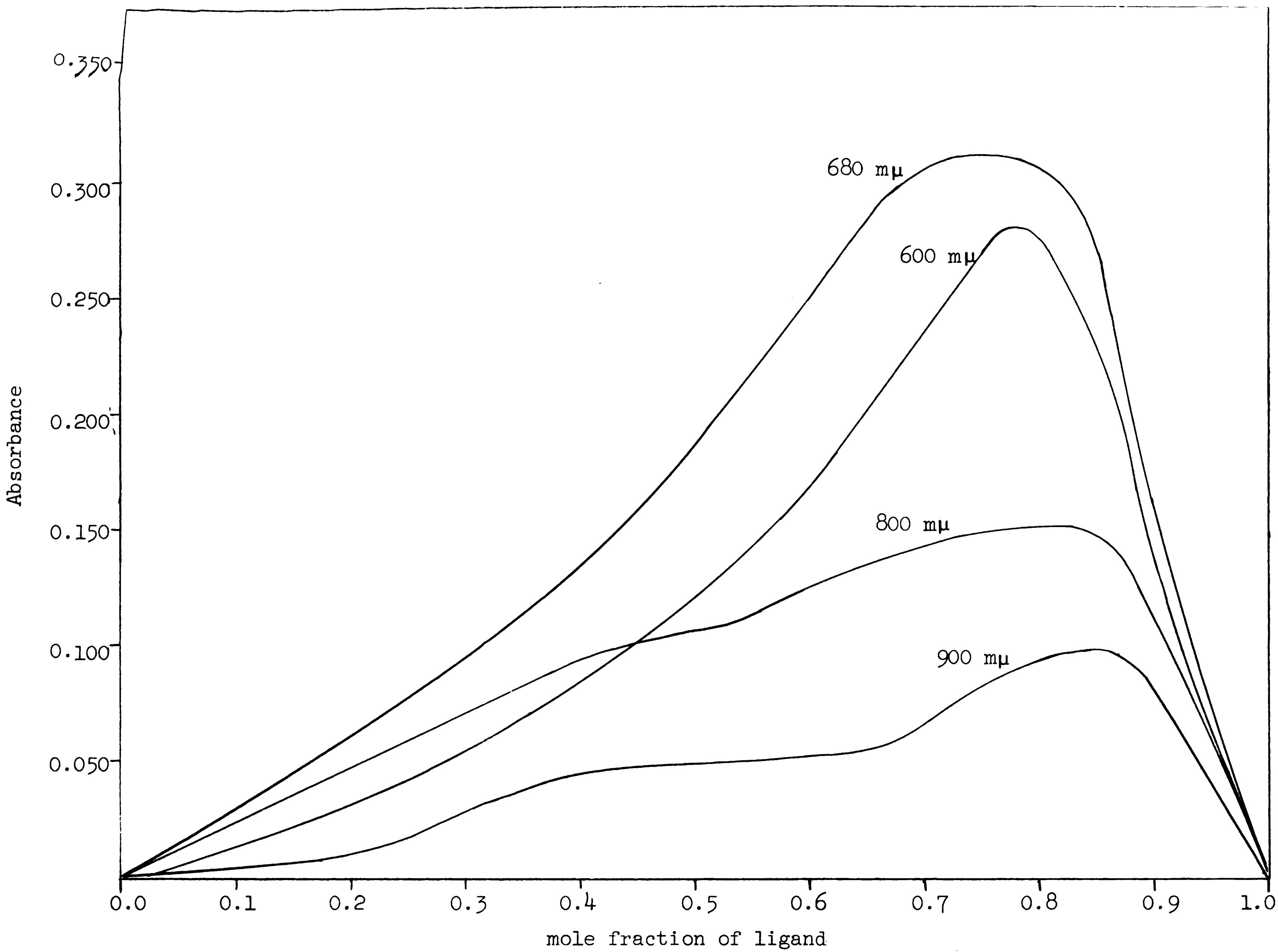

Figure 5. A continuous variation study at various wavelengths of the $Cu(ClO_4)_2 \cdot 6\ H_2O$-PMT system in nitromethane having a total analytical concentration of 2.5×10^{-2} M.

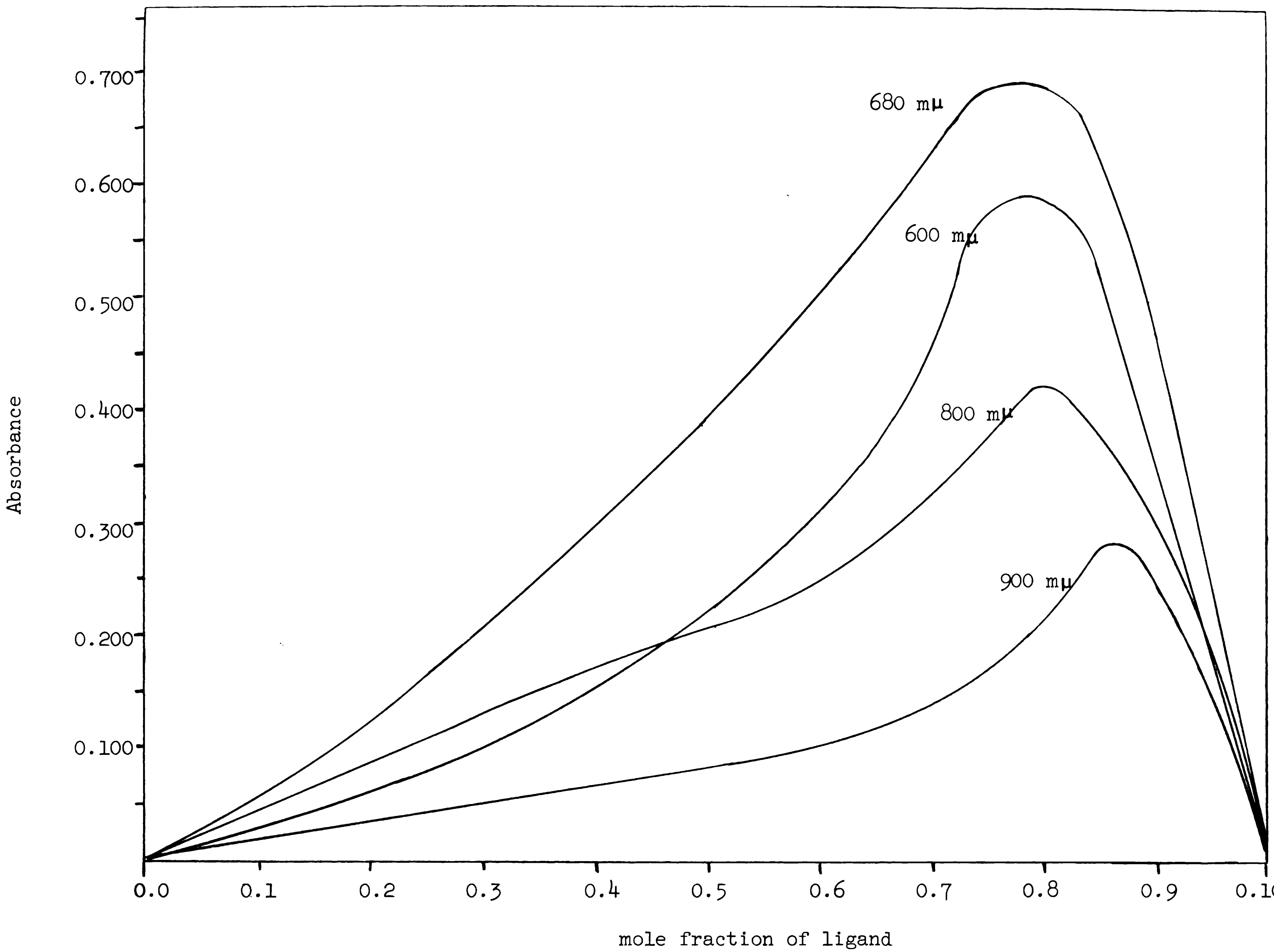

Figure 6. A continuous variation study at various wavelengths of the $Cu(ClO_4)_2 \cdot 6\ H_2O$-PMT system in nitromethane having a total analytical concentration of 5.0×10^{-2} M.

perchlorate hexahydrate solution in nitromethane a hypsochromic shift with an accompanying hyperchromic effect was noted. The solvated copper ion absorption band shifted progressively from 770 mμ (molar absorptivity 15) down to 670 mμ at a 4:1 PMT to Cu^{2+} ratio (apparent molar absorptivity 82.5). As the PMT to copper ratio was increased further, the peak started to shift in the opposite direction. The maximum displacement was obtained at PMT/Cu^{2+} ratio 40:1 at which point the absorbance maximum was 705 mμ with an apparent molar absorptivity of 113 (Figure 7). As additional PMT was added,the maximum did not shift but the absorbance increased. Although the limiting absorbance was not reached, it appeared that the absorbance tends toward a limiting value. This behavior will be reinvestigated.

The Hexakis(pentamethylenetetrazole)copper(II) Perchlorate

The apparent molar absorptivity of a 0.01 M hexakis(PMT)-copper(II) perchlorate in nitromethane was 102.3 at 680 mμ (Figure 8). When additional PMT was added, a bathochromic shift to 705 mμ with an accompanying hyperchromic effect was noted, similar to the behavior described above.

The Tetrakis(pentamethylenetetrazole)copper(II) Perchlorate

A 0.01 M solution of tetrakis(PMT)copper(II) perchlorate in nitromethane had an absorbance maximum at 670 mμ with an apparent molar absorptivity of 80.2. Upon addition of excess PMT, the peak shifted to a limiting value of 705 mμ (apparent molar absorptivity 119) at a 20 mole excess of PMT (Figure 9).

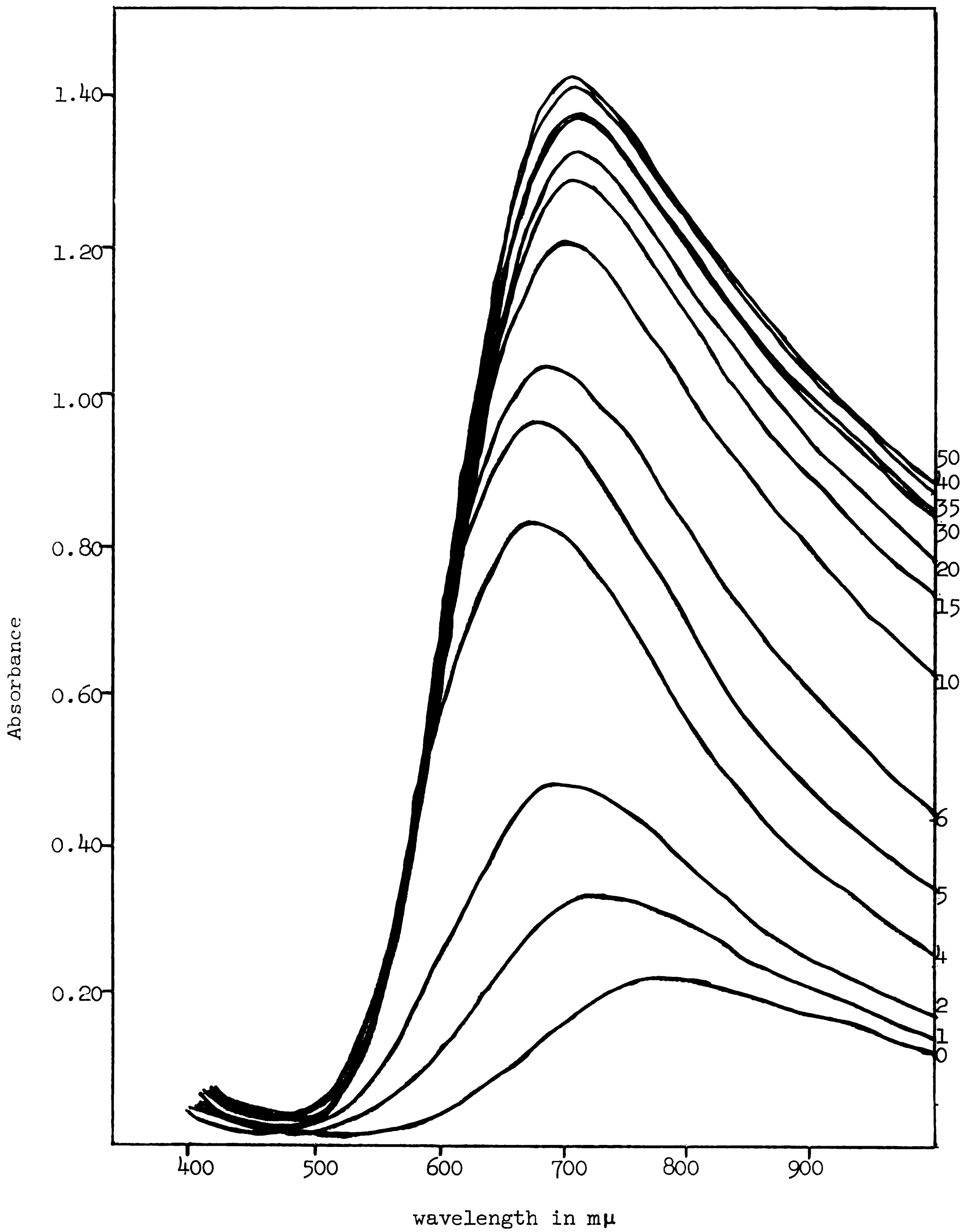

Figure 7. A spectrophotometric study of 1.0×10^{-2} $\underline{M}$ $Cu(ClO_4)_2 \cdot 6\ H_2O$ in nitromethane upon addition of PMT. The respective PMT/Cu^{2+} ratio is indicated on each curve.

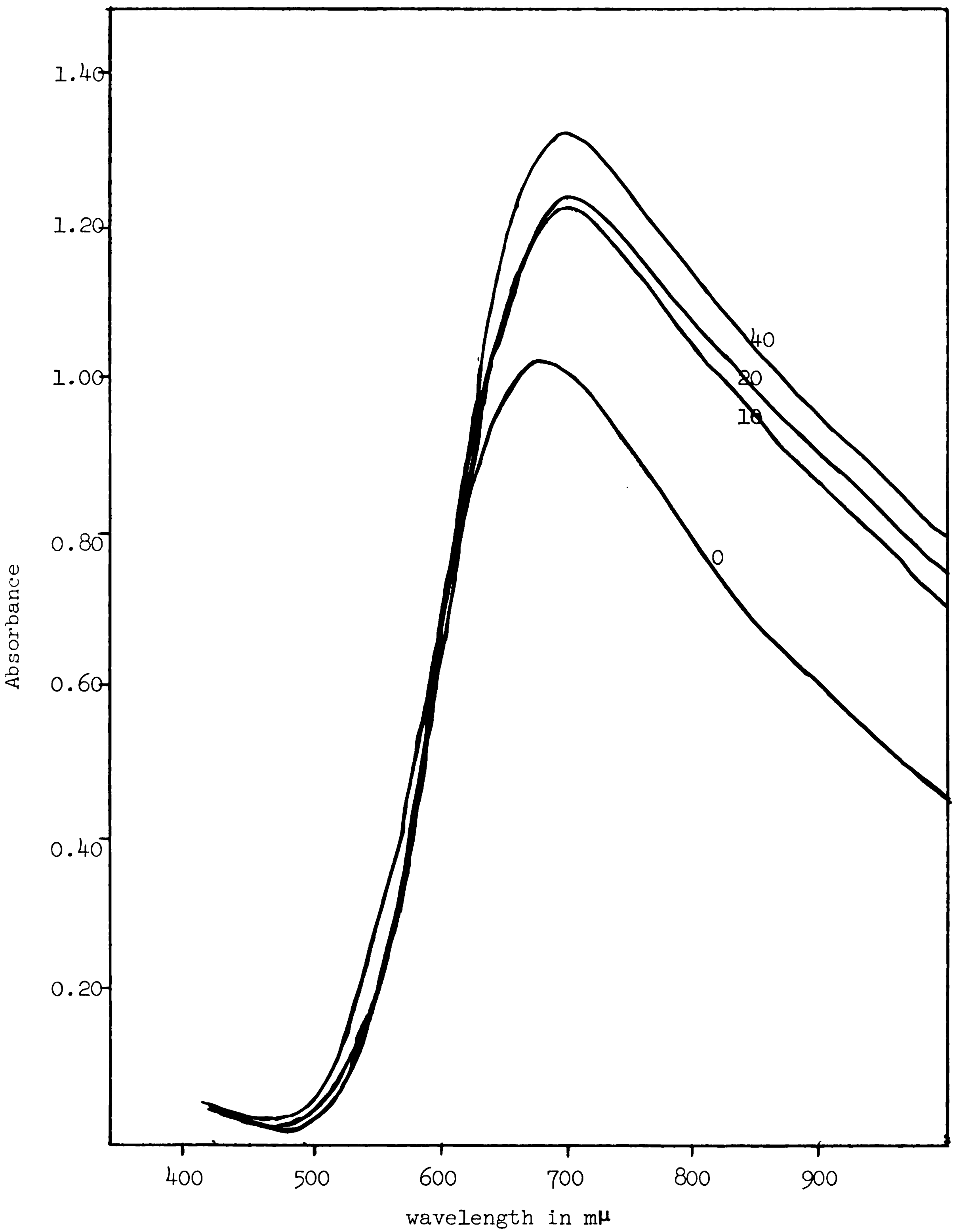

Figure 8. A spectrophotometric study of 1.0×10^{-2} $\underline{M}$ $Cu(PMT)_6(ClO_4)_2$ in nitromethane upon addition of PMT. The respective PMT/Cu^{2+} ratio is indicated on each curve.

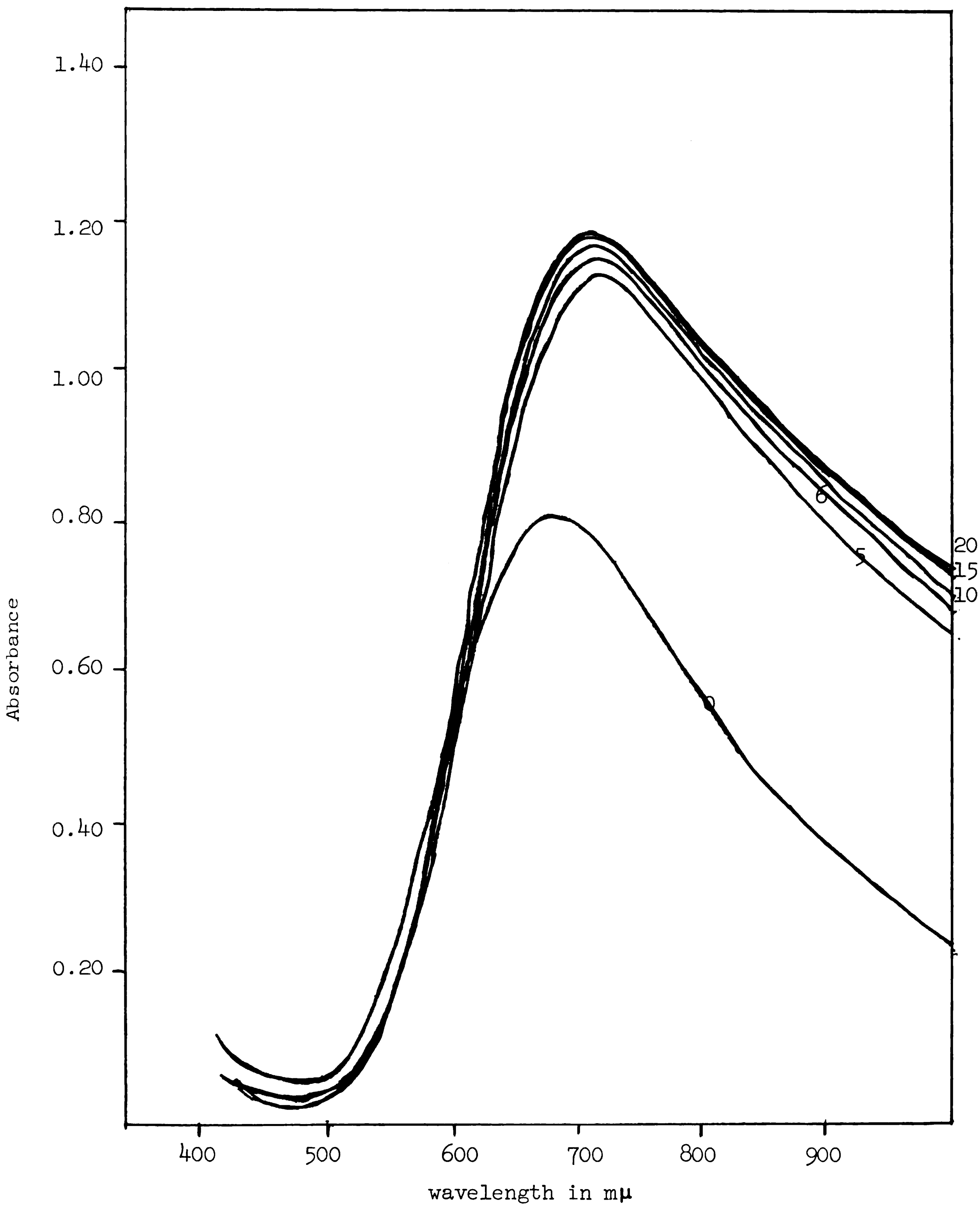

Figure 9. A spectrophotometric study of 1.0×10^{-2} $\underline{M}$ $Cu(PMT)_4(ClO_4)_2$ in nitromethane upon addition of PMT. The respective PMT/Cu^{2+} ratio is indicated on each curve.

Attempted Determination of the Stepwise Formation Constants by Spectrophotometric Methods

From the results obtained by the method of continuous variations (Figures 5,6) it can be assumed, due to the shifting of the maximum, that more than one absorbing species is present in solution. The method of Newman and Hume (85) was used in an attempt to calculate the successive formation constants (Appendix I). As shown above, however, an accurate limiting molar absorptivity could not be obtained and since this method is based on obtaining a limiting absorbance for the complex, the study was temporarily discontinued.

Visible and Reflectance Spectra of the Transition Metal Complexes of Pentamethylenetetrazole

Visible and Near Infrared Spectra

As shown in Figures 10-12 and Table II, the visible spectra of the complexes in nitromethane are essentially those expected for the respective transition metal ions in octahedral configurations. The spectra of hexakis(PMT)iron(II) and iron(III) were not run. The spectrum of hexakis(PMT)manganese(II) perchlorate could not be obtained due to its limited solubility and extremely low molar absorptivity (86) while hexakis(PMT)-zinc(II) perchlorate is colorless.

Cobalt(II) Perchlorate Hexahydrate and Hexakis(pentamethylenetetrazole)cobalt(II) Perchlorate

The spectra of cobalt(II) perchlorate hexahydrate and hexakis(PMT)cobalt(II) perchlorate are listed in Figure 10.

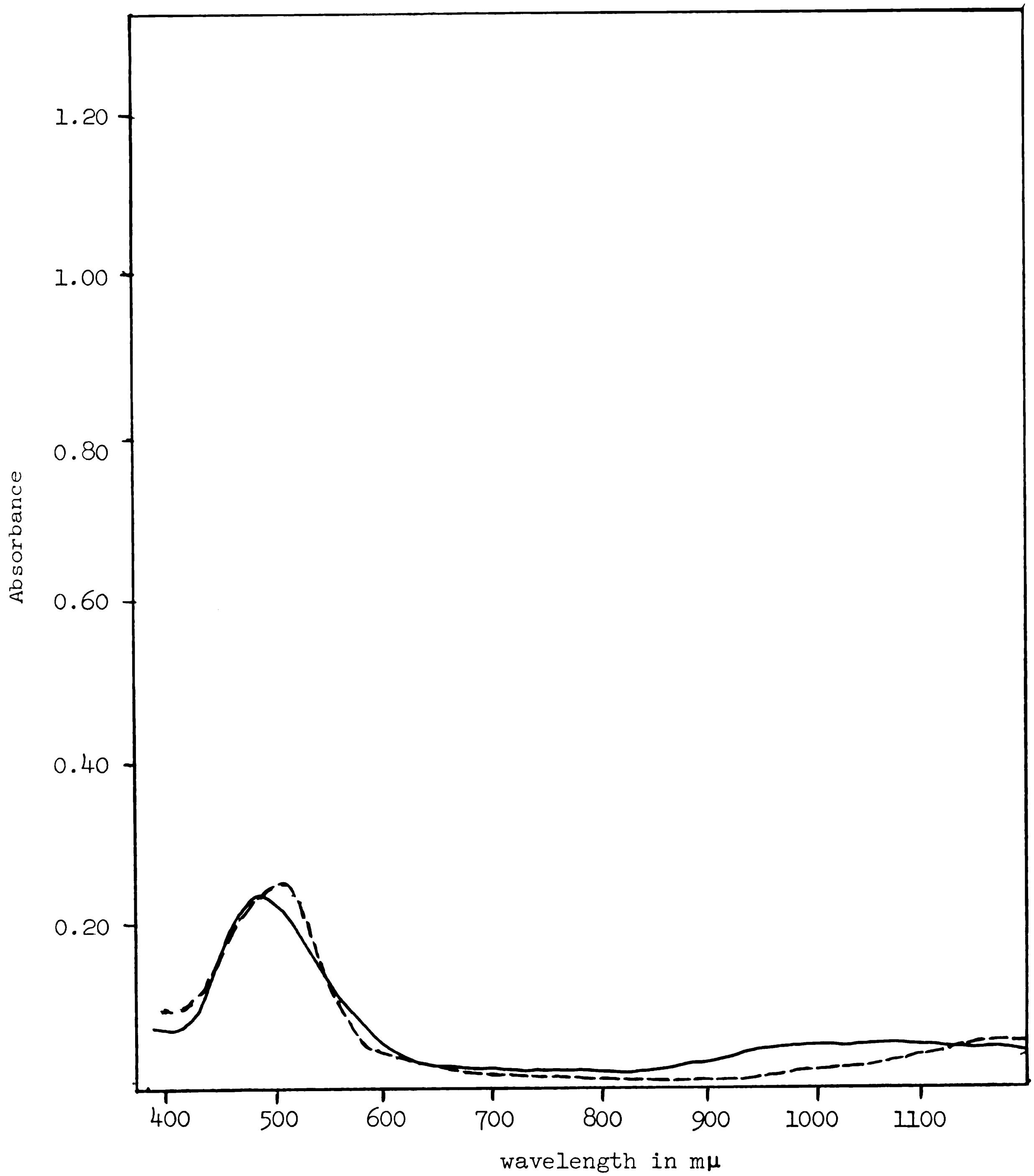

Figure 10. The visible and near infrared spectra of 1×10^{-2} $\underline{M}$ $Co(PMT)_6(ClO_4)_2$ (solid line, 1 cm cells) and 5×10^{-3} $\underline{M}$ $Co(ClO_4)_2 \cdot 6\ H_2O$ (broken line, 5 cm cells) in nitromethane.

The cobalt(II) perchlorate spectrum shows an unsymmetrical absorption band, due to a shoulder on the high frequency side at 19,800 cm^{-1} (504 mμ) and has a molar absorptivity of 10 while the hexakis(PMT)cobalt(II) perchlorate spectrum has a somewhat more symmetrical absorption band at 20,600 cm^{-1} (485 mμ) which has an apparent molar absorptivity of approximately 22. These spectra are typical of high spin octahedral complexes of cobalt(II) which has three spin-allowed d-d transitions from the ground state $^4T_1(F)$ to states $^4T_2(\nu_1)$, $^4A_2(\nu_2)$, and $^4T_1(P)(\nu_3)$ (87). The main band at approximately 20,000 cm^{-1} (500 mμ) is due to the $^4T_1(F)$-$^4A_2$ transition (ν_1), whereas the shoulder on the higher frequency side is the $^4T_1(F)$-$^4T_1(P)$ transition (ν_3). The $^4T_1(F)$-$^4T_2$ transition (ν_1) lies in the near infrared and is probably the weak broad band at approximately 9300 cm^{-1} (1075 mμ) with an apparent molar absorptivity 5 and 8320 cm^{-1} (1200 mμ) having a molar absorptivity 2 for hexakis(PMT)cobalt(II) and cobalt(II) perchlorate, respectively.

Nickel(II) Perchlorate Hexahydrate and Hexakis(pentamethylenetetrazole)nickel(II) Perchlorate

The spectra of nickel(II) perchlorate hexahydrate and hexakis(PMT)nickel(II) perchlorate are listed in Figure 11. The nickel(II) perchlorate spectrum shows an absorption band (ν_1) at 8850 cm^{-1} (1130 mμ) having a molar absorptivity 7.1 and a second broad band (ν_2) which is split into two bands at

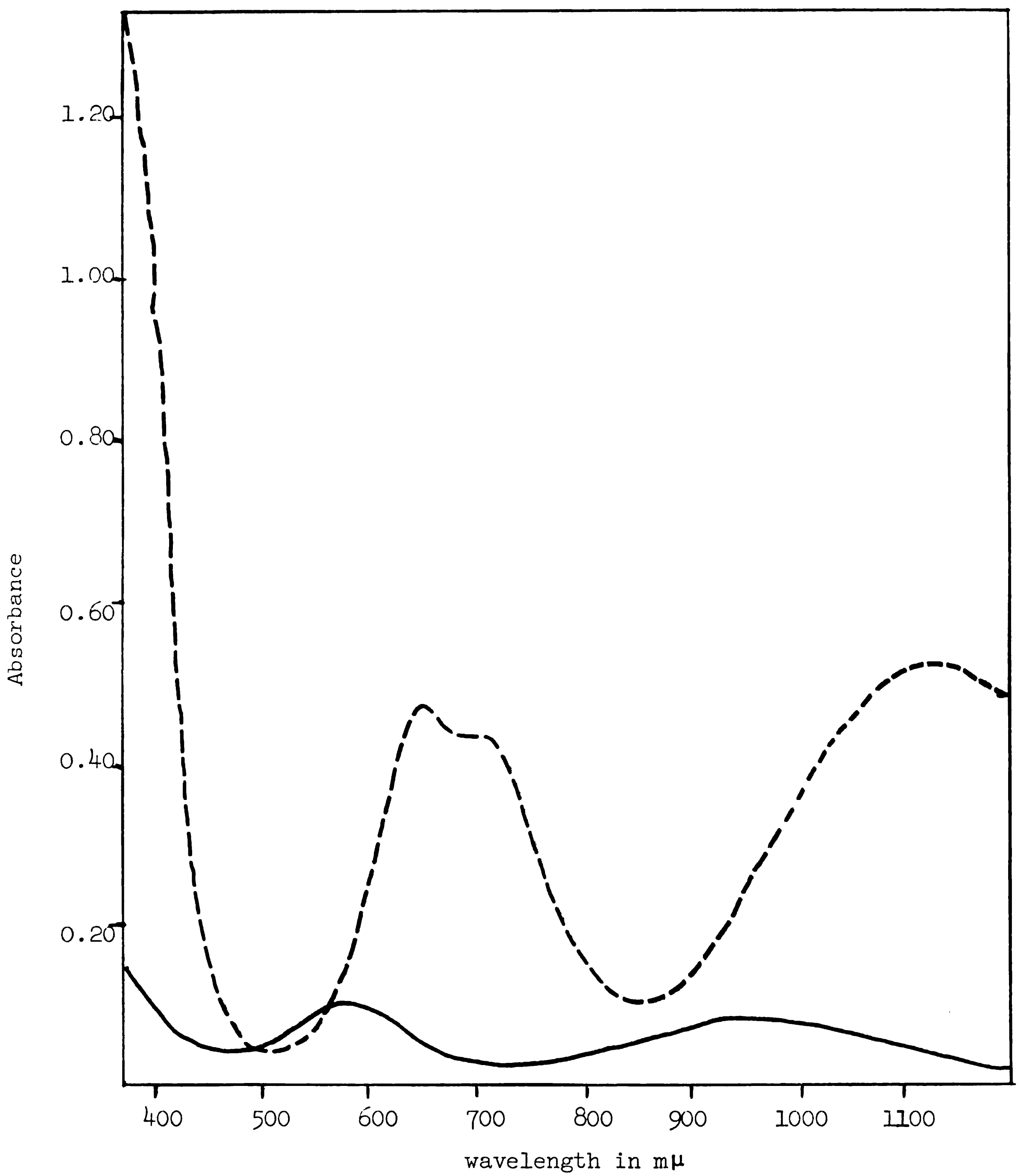

Figure 11. The visible and near infrared spectra of 1×10^{-2} $\underline{M}$ $Ni(PMT)_6(ClO_4)_2$ (solid line, 1 cm cells) and 6.72×10^{-3} $\underline{M}$ $Ni(ClO_4)_2 \cdot 6\ H_2O$ (broken line, 10 cm cells) in nitromethane. The spectrum obtained for $Ni(PMT)_6$-$(ClO_4)_2$ precipitated from water is identical to the solid line.

14,070 cm^{-1} (710 mμ) and 15,400 cm^{-1} (650 mμ) having respective molar absorptivities of 6.4 and 7.0. The lower frequency edge of ν_3 appears at 25,000 cm^{-1} (400 mμ), but ν_3 cannot be determined due to solvent cut-off at approximately 25,000 cm^{-1} (10 cm. cells). The hexakis(PMT)nickel(II) perchlorate spectrum in nitromethane consists of only two absorption bands ν_1 at 10,500 cm^{-1} (950 mμ) and ν_2 at 17,400 cm^{-1} (575 mμ) having respective molar absorptivities of 8.0 and 9.5. These spectra are characteristic of the spectra obtained for octahedrally coordinated complexes which have three spin-allowed d-d transitions from the ground state $^3A_2(F)$ to states $^3T_2(\nu_1)$, $^3T_1(\nu_2)$ and $^3T_1(P)(\nu_3)$. The ν_2 band of the nickel(II) perchlorate spectrum is split into two bands as a result of the spin-orbit coupling mixing the $^3T_2(F)$ and ^1Eg states which are very close in energy (88). The shifted ν_1 and ν_2 bands to higher energies indicate that the nickel(II) ion is in a stronger ligand field in hexakis(PMT)nickel(II) perchlorate complex than in nickel(II) perchlorate hexahydrate. As a result of the stronger ligand field, the $^3T_2(F)$ and ^1Eg state move farther apart which accounts for the lack of splitting of the ν_2 band in hexakis(PMT)nickel(II) perchlorate.

Copper(II) Perchlorate Hexahydrate, Tetrakis and Hexakis-(pentamethylenetetrazole)copper(II) Perchlorate

The spectra of copper(II) perchlorate hexahydrate, tetrakis and hexakis(PMT)copper(II) perchlorate (Figure 12) all

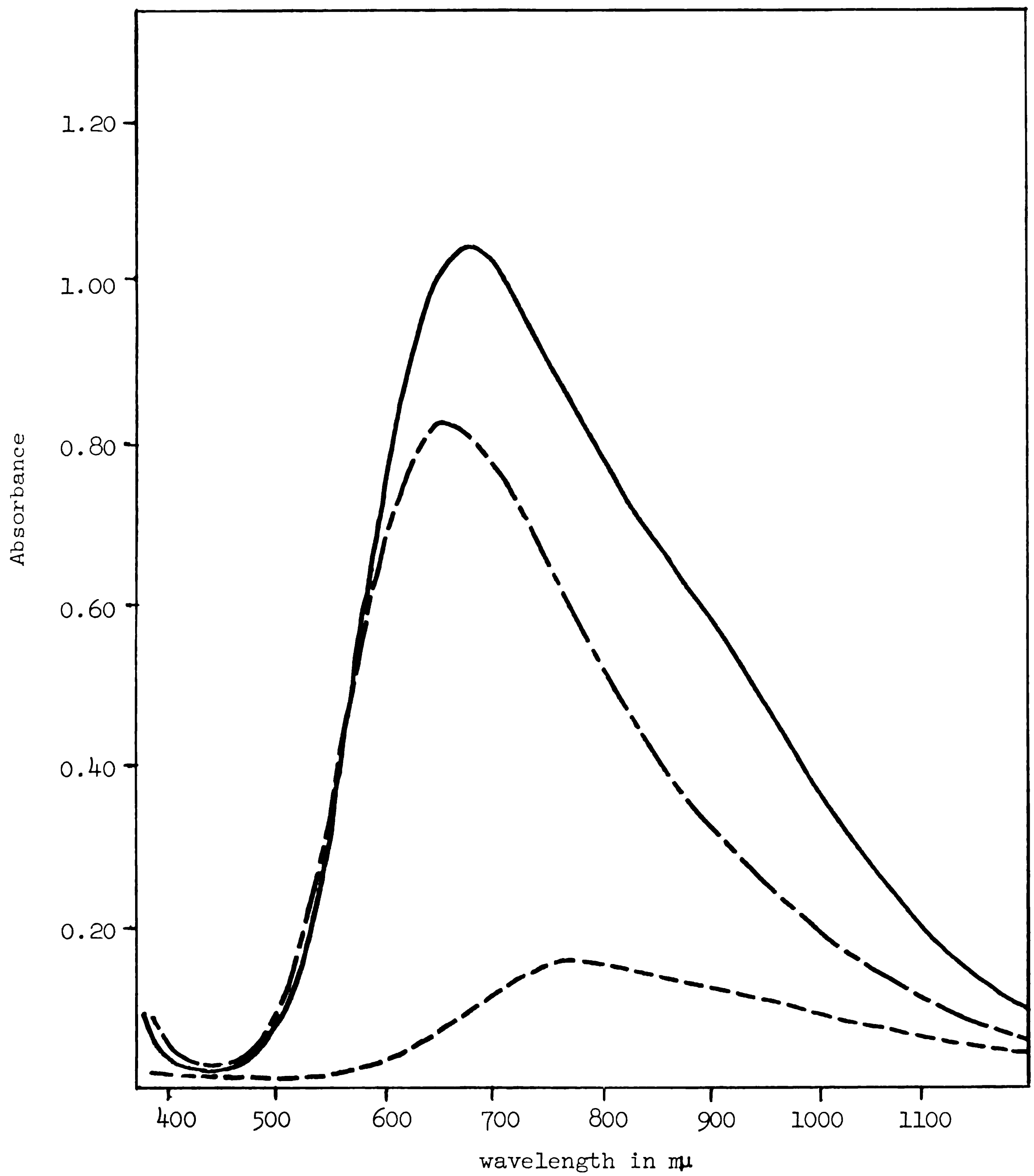

Figure 12. The visible and near infrared spectra of 1×10^{-2} $\underline{M}$ $Cu(PMT)_6(ClO_4)_2$ (solid line), $Cu(PMT)_4(ClO_4)_2$ (short-long-short broken line), and $Cu(ClO_4)_2 \cdot 6\ H_2O$ (broken line) in nitromethane using 1 cm cells.

Table II

Electronic Absorption Spectra (in cm^{-1}) of the Transition Metal Complexes of Pentamethylenetetrazole

Complex	State	λ max. (ε Molar for Solution)
$Co(ClO_4)_2 \cdot 6\ H_2O$	soln[b]	19,800 (~10), 9,310 (~ 5)
$Co(PMT)_6(ClO_4)_2$	soln[c]	20,600 (~22), ~8,300 (~5)
$Co(PMT)_6(ClO_4)_2$	solid	20,400, 8,500
$Ni(ClO_4)_2 \cdot 6\ H_2O$	soln[d]	15,400 (7.0), 14,070 (6.4), 8,850 (7.1)
$Ni(PMT)_6(ClO_4)_2$	soln[c]	17,400 (9.5), 10,500 (8.0)
$Ni(PMT)_6(ClO_4)_2$	solid	26,300, 16,000, 9,760
$Ni(PMT)_6(ClO_4)_2$[a]	soln[c]	17,400 (9.5), 10,500 (8.0)
$Ni(PMT)_6(ClO_4)_2$[a]	solid	26,300, 16,000, 9,760
$Cu(ClO_4)_2 \cdot 6\ H_2O$	soln[c]	12,900 (14.7)
$Cu(PMT)_6(ClO_4)_2$	soln[c]	14,530 (103)
$Cu(PMT)_6(ClO_4)_2$	solid	13,500
$Cu(PMT)_4(ClO_4)_2$[e]	soln[c]	14,920 (81)
$Cu(PMT)_4(ClO_4)_2$[e]	solid	16,000
$Fe(PMT)_6(ClO_4)_2$	solid	10,000

a. This complex was precipitated from water (see p.34)

b. 5.0×10^{-3} M in purified nitromethane - 5 cm cells

c. 1.0×10^{-2} M in purified nitromethane - 1 cm cells

d. 6.72×10^{-3} M in purified nitromethane - 10 cm cells

e. This complex was precipitated from acetic acid (see p. 27) show a single broad band at approximately 12,900 cm^{-1} (775 mμ), 14,920 cm^{-1} (670 mμ), and 14,530 cm^{-1} (687 mμ) having respective molar absorptivities of approximately 15, 82, and 113. These spectra are typical of copper(II) complexes which theoretically have only one allowed transition ($^2Eg-^2T_2(D)$). However, this band is probably made up of two or three overlapping symmetrical bands since the tetragonal distortion, usually associated with copper(II) ions, splits the E_g and T_{2g} levels so that more than one d-d transition is possible (89).

Reflectance Spectra

The absorption maxima found by reflectance measurements were essentially the same as those found in nitromethane solution (Figures 13-15). Absorption bands arising from PMT appear at approximately 8160, 7030, 5720 and 5200 cm^{-1} in the reflectance spectra of the respective complexes and are not listed in Table II.

Thermogravimetric Studies of the Transition Metal Complexes of Pentamethylenetetrazole

The thermogravimetric analyses were carried out in a nitrogen atmosphere with a heating rate of approximately 2°C per minute.

Tetrakis(pentamethylenetetrazole)copper(II) Perchlorate

The decomposition of tetrakis(PMT)copper(II) perchlorate began at approximately 126°C. The rate of the reaction was

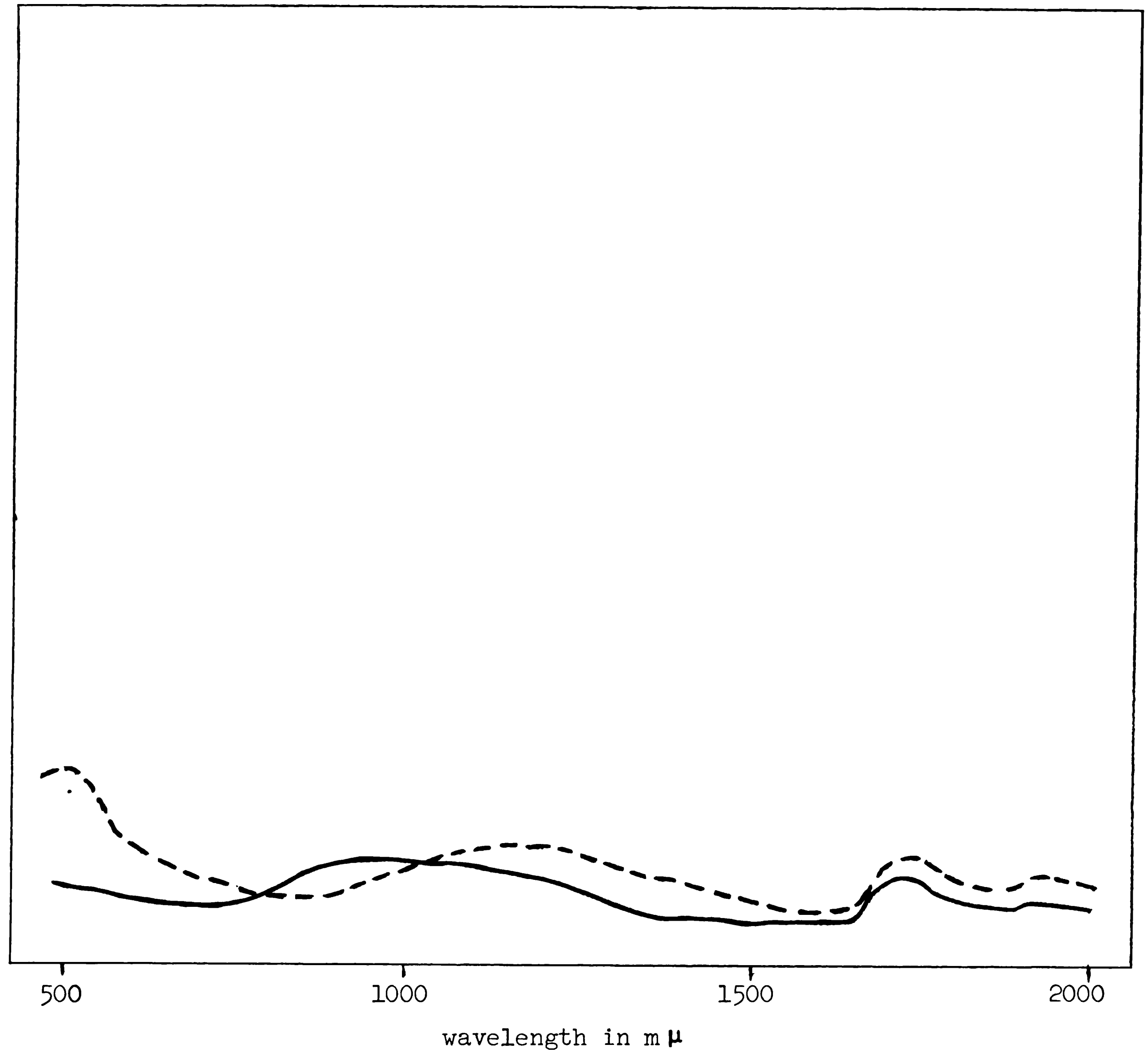

Figure 13. The reflectance spectra of $Fe(PMT)_6(ClO_4)_2$ (solid line) and $Co(PMT)_6(ClO_4)_2$ (broken line).

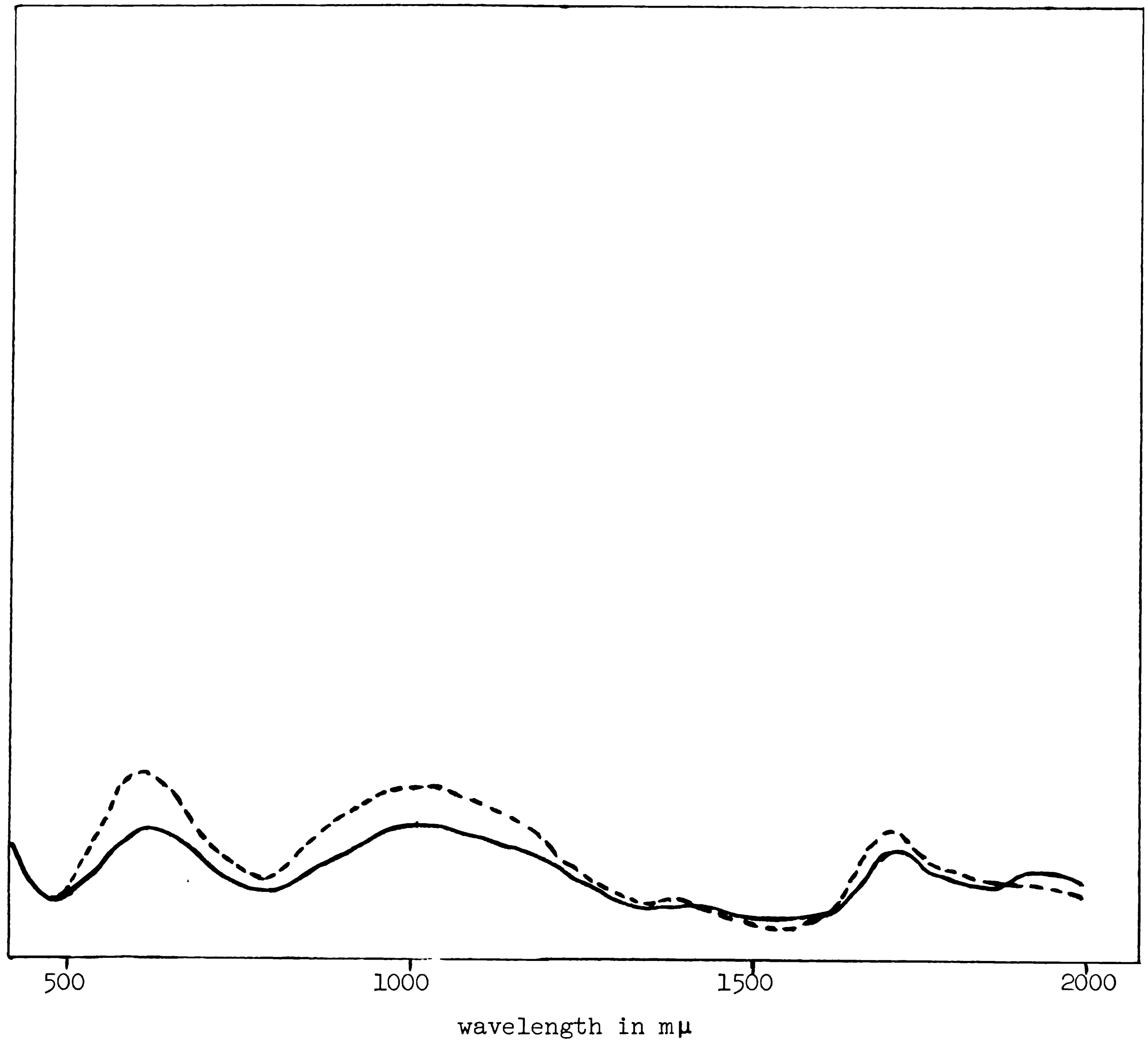

Figure 14. The reflectance spectra of $Ni(PMT)_6(ClO_4)_2$ precipitated from DMP (solid line) and $Ni(PMT)_6(ClO_4)_2$ precipitated from water.

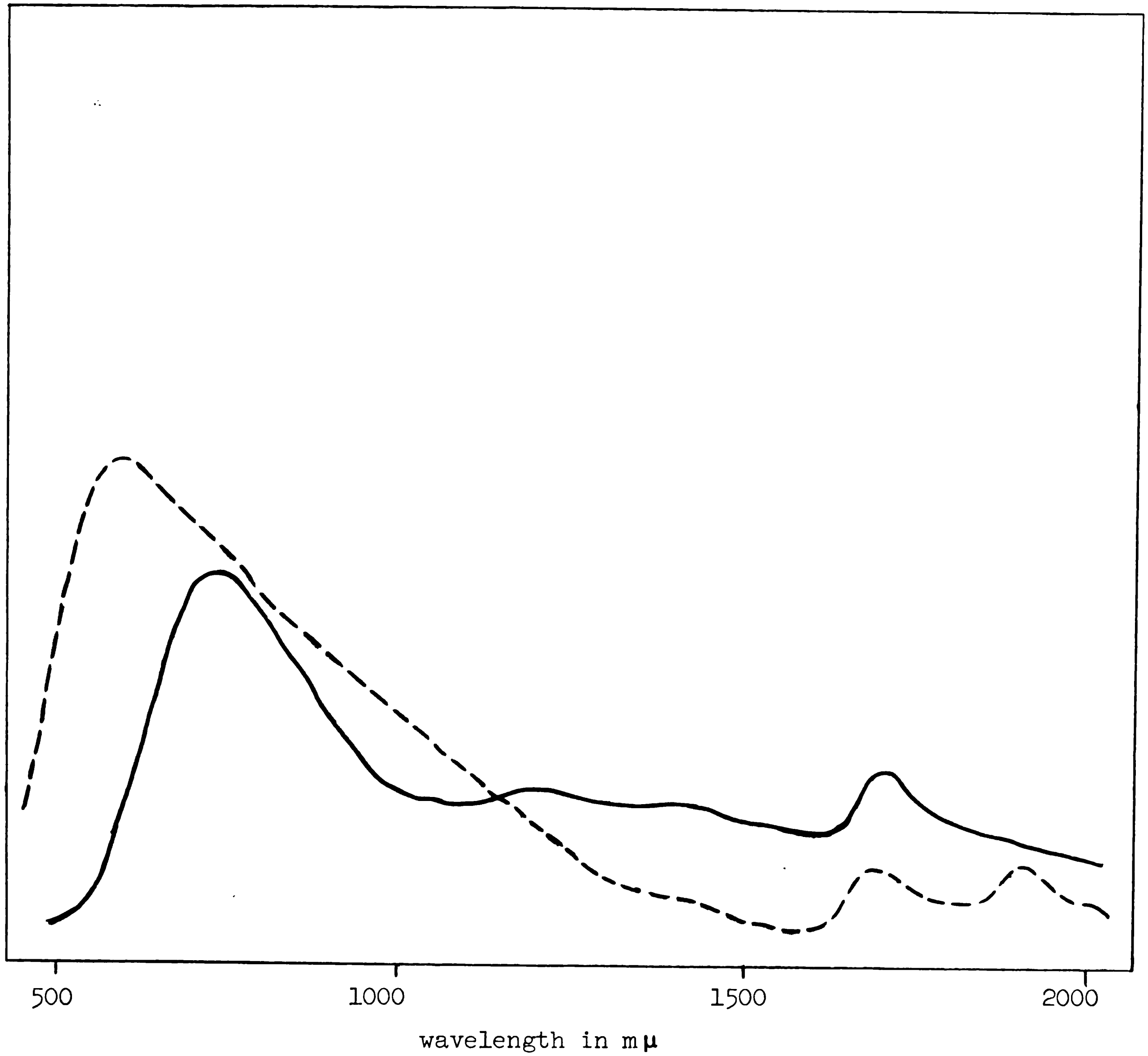

Figure 15. The reflectance spectra of $Cu(PMT)_6(ClO_4)_2$ (solid line) and $Cu(PMT)_4(ClO_4)_2$ (broken line).

slow until the temperature reached 180°C at which point the weight loss was 4%, beyond this point the reaction rate increased abruptly. The reaction was strongly exothermic, as indicated by the bulge in the volatilization curve. The sample then decomposed violently, and the momentum imparted to the sample holder broke the quartz spring from which the sample holder was suspended. As a result, the values recorded above that temperature are meaningless. Evidently this material should be handled with caution (Figure 16).

Hexakis(pentamethylenetetrazole)copper(II) Perchlorate

The decomposition of $Cu(PMT)_6(ClO_4)_2$ commenced at approximately 165°C. The rate of the reaction increased rapidly, and at 180°C the rate of volatilization reached explosive limits and the momentum imparted to the sample holder carried it past the point of 100% weight loss. The reaction was exothermic, judging by the increase in temperature at the end of the decomposition of the sample (Figure 16).

Hexakis(pentamethylenetetrazole)manganese(II) Perchlorate

The sample showed a small decrease in weight starting at approximately 30°C. At 150°C the weight decrease was 1.3%. This loss may be due to a small amount of residual solvent or other volatile material. Beyond 150°C the complex began to decompose and the rate of decomposition increased slowly with increasing temperature. At a weight loss of 30%, which

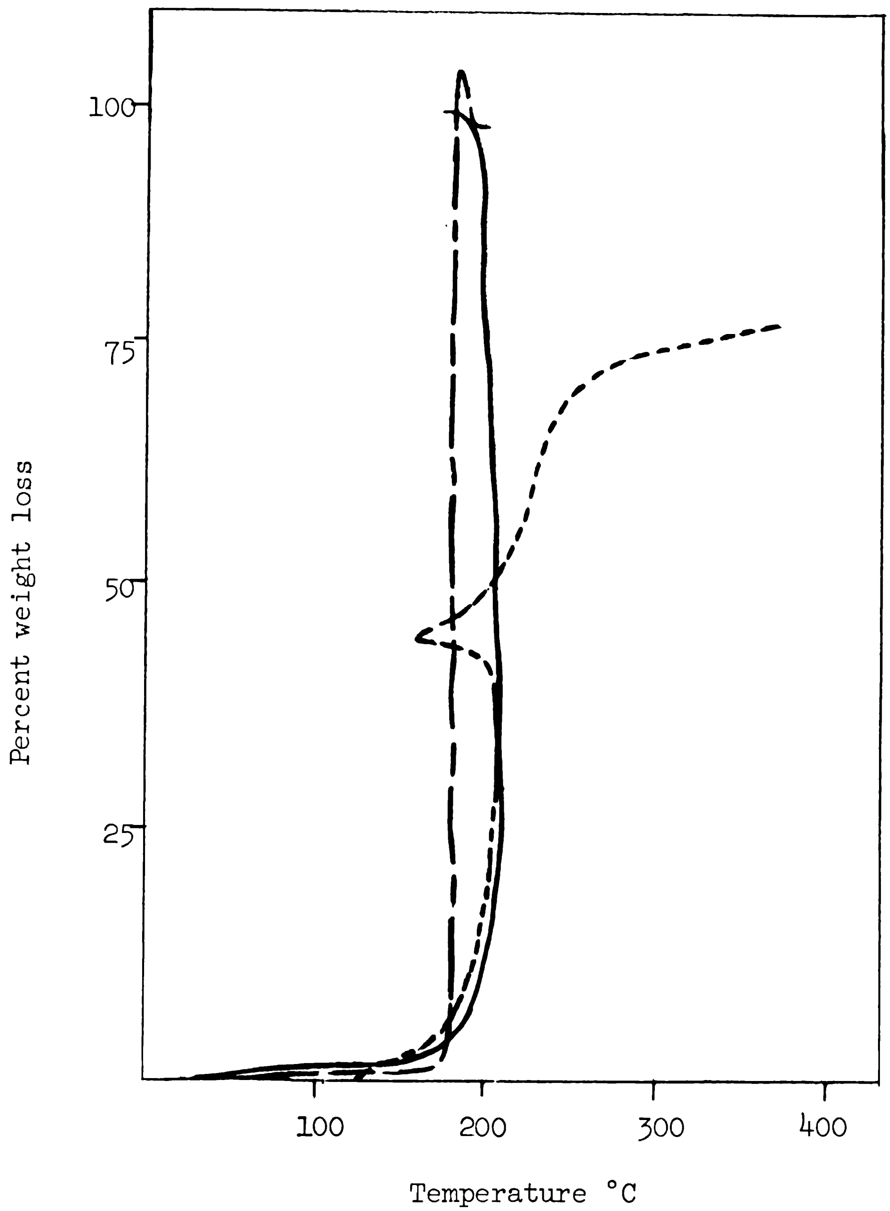

Figure 16. The thermogravimetric analysis of $Cu(PMT)_4(ClO_4)_2$ (solid line), $Cu(PMT)_6(ClO_4)_2$ (short-long-short broken line), and $Mn(PMT)_6(ClO_4)_2$ (broken line) in a nitrogen atmosphere with a heating rate of approximately 2°C per minute.

occurred at approximately 222°C, the decomposition of the material became increasingly endothermic. Between weight loss values of 42% and 48% an endothermic effect was evident reaching a maximum at a weight loss of 45.1%. The volatilization continued at a decreasing rate until, at approximately 390°C, a residue of 23.2% remained which corresponds to $Mn(ClO_4)_2$. At this temperature the rate was increasing, and further loss probably would have occurred if the run had been continued to higher temperatures (Figure 16).

Magnetic Susceptibility of the Transition Metal Complexes of Pentamethylenetetrazole

The magnetic susceptibilities of the transition metal complexes of PMT were determined by the Gouy method.

The Gouy susceptibility tube used in this study was constructed from 6 mm I.D. Pyrex tubing. The distance from the reference mark to the septum of the tube was 6.5 cm. The volume of the tube was determined by measuring the weight of distilled water (1.893 grams) needed to fill the tube to the reference mark. The volume was calculated by dividing the weight of water needed by the density of water at the ambient temperature of 23.3°C. The volume of the tube was calculated to be 1.898 ml.

The respective PMT complexes were then ground to the consistency of fine powder. The Gouy susceptibility tube was packed by placing a small quantity of the powdered sample in the tube and tapping it firmly on a stone surface sixty times. This process was repeated until the tube was filled to the calibration mark. This method was employed to minimize the errors resulting from a lack of uniform packing which, in general, is the main limitation on the accuracy of the determination.

This Gouy susceptibility tube was attached by a copper wire to the pan of a Mettler single-pan balance and suspended between the pole faces of an Alpha Scientific Laboratories model AL 7500M electromagnet. All changes in weight reported here are the averages of three successive readings on the same sample.

Mercury(II) tetrathiocynatocobaltate(II) was used as the apparatus calibrant. Figgis and Nyholm (90) report a gram susceptibility for this compound of 16.44 ($\pm$ 0.05%) x 10^{-6} at 20°C and that it obeys the Curie-Weiss law between 10 and 30°C.

The magnetic susceptibility of the complexes in Bohr magnetons, and the number of unpaired electrons in these complexes were calculated by the following method. The gram susceptibility X_g can be calculated from the relationship

$$\frac{\Delta W}{\rho X_g} = \frac{AH^2}{2} = c \qquad (1)$$

where:

$\frac{AH^2}{2}$ = Apparatus constant = c in grams

ΔW = Change in weight in grams of the calibrant in and out of the magnetic field

A = Cross-sectional area of Gouy tube in cm^2

H = Strength of the magnetic field in gauss

ρ = Density of the calibrant in $grams/cm^3$

X_g = Gram susceptibility of the calibrant in $cm^3/gram$

Volume susceptibility X can now be obtained from the equation:

$$X = X_g/\rho \qquad (2)$$

and the molar susceptibility, X_M then calculated by multiplying volume susceptibility by the molecular weight of the sample, MW

$$X_M = \frac{MWX_g}{\rho} \qquad (3)$$

The number of unpaired electrons were calculated from the following relationships:

$$X_M = \frac{NB^2 \mu\beta^2}{3\ kT} \qquad (4)$$

where:

N = Avogadro's number

B = 0.917×10^{-20} $erg\text{-}gauss^{-1}$

$\mu\beta$ = Magnetic moment

k = Boltzmann's constant

T = Absolute temperature

and

$$\mu\beta = [\,n(n+2)\,]^{\frac{1}{2}} \qquad (5)$$

where:

n = number of unpaired electrons in the unfilled shell.

Substitution of equation 5 into equation 4 and solving for n, yields the following expression for the number of unpaired electrons.

$$n = [-1 \pm 1 + (2.420 \times 10^{3})(X_M)]^{\frac{1}{2}} \qquad (6)$$

The respective magnetic moment in Bohr magnetons can also be calculated from equation 4 and is given by the equation.

$$\mu\beta = (2.4243 \times 10^{3} \cdot X_M)^{\frac{1}{2}} \text{ erg gauss}^{-1} \qquad (7)$$

The experimental magnetic susceptibility data for the respective complexes are listed in Table III. The calculated values for the magnetic moments in Bohr magnetons and the number of unpaired spins are listed in Table IV. All measurements were taken at an ambient temperature of 296.5°K.

Calculation of Magnetic Susceptibility of Hexakis(pentamethylenetetrazole)copper(II) Perchlorate

Using the data given in Table III the molar susceptibility was calculated in the following manner:

$$X_M = \frac{\Delta WMW}{\rho c} = \frac{-(0.00055)(1091.48)}{(0.6313)(5725)} = 1.6641 \times 10^{-4} \text{ cm}^3 \text{ mole}^{-1}$$

The experimental molar susceptibility was a negative number indicating diamagnetism. Therefore, diamagnetic correction values for PMT, perchlorate anion, and the central metal cations were incorporated in the following manner:

X_M (Corr.) = X_M (obs.) + aX_M(PMT) + $bX_M(ClO_4^-)$ + cX_M (metal)

The calculated X_M (obs.) can be a positive or negative value while the three correction susceptibilities are taken as positive values. The correction coefficients of the susceptibilities are the respective moles of each chemical species contained in the complex. Table V gives these molar diamagnetic susceptibilities.

$$X_M \text{ (corr.)} = (-1.6641 \times 10^{-4}) + (6)(2.22 \times 10^{-4}) + (2)(0.32 \times 10^{-4}) + (1)(0.128 \times 10^{-4})$$

$$X_M \text{ (corr.)} = 12.42 \times 10^{-4} \text{ cm}^3 \text{ mole}^{-1}$$

The number of unpaired electrons in the complex is calculated by substituting X_M (corr.) into equation 6.

$$n = -1 \pm [1+(2.420 \times 10^3)(12.42 \times 10^{-4})]^{\frac{1}{2}}$$

$$n = -1 + (4.01)^{\frac{1}{2}} = 1.00 \text{ unpaired electrons}$$

The experimental magnetic moment in Bohr magnetons of the complex is calculated using equation 7 and the corrected value of molar susceptibility.

$$\mu\beta = [(2.4243 \times 10^3)(12.42 \times 10^{-4})]^{\frac{1}{2}}$$

$$\mu\beta = 1.74 \text{ B.M.}$$

X-Ray Powder Diffraction Studies of the Transition Metal Complexes of Pentamethylenetetrazole

All the X-ray powder pattern photographs were obtained using a North American Philips Company, type 12045, X-ray generator and a type 52056, 114.6 mm. camera. Ilford brand

TABLE III

Magnetic Susceptibility Data of the Transition Metal Complexes of Pentamethylenetetrazole

Complex	Molecular Weight MW	Weight (grams) Field on	Weight (grams) Field off	Weight (grams) Change	Density* (grams/ml)
$Cu(PMT)_6(ClO_4)_2$	1091.4816	32.90388	32.90443	-0.00055	0.63013
$Fe(PMT)_6(ClO_4)_2$	1083.7886	32.39113	32.37311	0.01802	0.35020
$Mn(PMT)_6(ClO_4)_2$	1082.8796	35.55332	32.52392	0.02940	0.42965
$Co(PMT)_6(ClO_4)_2$	1086.8748	32.66621	32.64423	0.02198	0.49304
$Ni(PMT)_6(ClO_4)_2$	1086.6516	32.64123	32.63579	0.00544	0.48859
$Cu(PMT)_4(ClO_4)_2$	815.135	32.22515	32.22718	-0.00203	0.80017
$Fe(PMT)_6(ClO_4)_3$	1183.2392	32.58333	32.56613	0.01720	0.45189
$Zn(PMT)_6(ClO_4)_2$	1093.3116	32.69197	32.69716	-0.00519	0.52092
$Cu(PMT)_2ClO_4$	439.3374	32.37423	32.37752	-0.00329	0.35252
PMT	138.1734	33.13092	33.13785	-0.00693	0.75310

*(wt. field off - empty tube weight)/tube volume · Empty tube weight = 31.70842 g.; Tube volume = 1.89805 ml.

All measurements taken at an ambient temperature of 296.5°K.

The apparatus constant was calculated to be 5725 grams and held constant for all measurements.

TABLE IV

Calculated Magnetic Moments and Unpaired Spins of the Transition Metal Complexes of Pentamethylenetetrazole

Complex	χ_M Exp. ($\times 10^4$)	χ_M Corr. ($\times 10^4$)	n obs.	n calc.	a	b	c
$Cu(PMT)_6(ClO_4)_2$	- 1.664	12.424	1.00	1	1.74	1.73	1.70 - 2.20
$Fe(PMT)_6(ClO_4)_2$	97.423	111.510	4.29	4	5.20	4.90	5.10 - 5.70
$Mn(PMT)_6(ClO_4)_2$	129.421	143.511	4.98	5	5.90	5.92	5.65 - 6.10
$Co(PMT)_6(ClO_4)_2$	84.628	98.716	3.99	3	4.60	3.88	4.30 - 5.20
$Ni(PMT)_6(ClO_4)_2$	21.134	35.222	2.09	2	2.92	2.83	2.80 - 3.50
$Cu(PMT)_4(ClO_4)_2$	- 3.612	6.036	0.57	1	1.21	1.73	1.70 - 2.20
$Fe(PMT)_6(ClO_4)_3$	72.010	86.290	3.68	5	4.54	----	5.70 - 6.0
$Zn(PMT)_6(ClO_2)_2$	- 19.028	- 4.198	0	0	----	----	----------
$Cu(PMT)_2ClO_4$	- 7.162	- 2.402	0	0	----	----	----------

a. Experimental magnetic moments of the PMT complexes in Bohr magnetons.

b. Calculated spin-only magnetic moments in Bohr magnetons (91).

c. Literature experimental magnetic moments in Bohr magnetons (91).

TABLE V

Diamagnetic Correction Values

Material	χ_M ($\times 10^6$)	Reference
PMT	222.00	--
ClO_4^-	32.0	92
Cu^{2+}	12.8	92
Fe^{2+}	12.8	92
Mn^{2+}	14	93
Co^{2+}	12.8	92
Zn^{2+}	15.0	92
Fe^{3+}	10	93
Cu^{+}	12	93
Ni^{2+}	12.8	92

(35 x 355 mm) Industrial G X-ray film was used for recording the diffraction patterns. The respective samples were first ground to the consistency of fine powder and packed into either 0.3 or 0.5 mm thin walled glass capillary tubes. The samples were then irradiated five to eight hours with nickel filtered $Cu_{K\alpha}$ radiation. All powder diffraction patterns were obtained at X-ray generator instrument settings of 40 kilovolts and 20 milliamps.

The spacings of the powder diffraction pattern lines were obtained using a Picker X-ray reader and the value of two theta calculated by dividing the difference between the d(hkl) and d($\overline{hkl}$) reflections of the same line by two. The respective d values were obtained by graphical interpolation in which two theta was plotted as a function of the interplanar distance, d (94).

Hexakis(pentamethylenetetrazole)-Transition Metal Perchlorates

Evaluation of the experimental data (Table VI) shows that within experimental error the same respective d spacings and relative intensities are observed in all of these complexes. It seems reasonable to conclude, therefore, that these complexes are isomorphous (95).

Likewise an excellent agreement of the respective d-spacing values and relative intensities (Table VI) indicates that the hexakis(PMT)nickel(II) perchlorate complex prepared in 2,2-dimethoxypropane is identical to the one precipitated from aqueous solution.

An anomaly is noted between the hexakis(PMT)iron(II) and hexakis(PMT)iron(III) perchlorate complexes. The data (Table VI) indicate that the two complexes are isomorphous which is contrary to what one would predict since the iron(III) complex must fit an extra perchlorate ion into the same crystal structure. No explanation of this observation can be given at this time.

Mixed complexes of 99% zinc(II) and 1% copper(II) or 1% manganese(II) were prepared for Electron Spin Resonance (ESR) studies, and they appeared to be isomorphous with the other complexes of this series (Table VII). The ESR data indicated, however, that only the manganese(II) was inserted into the zinc(II) complex lattice. The absence of the appropriate copper(II) ESR signal indicated that the copper(II) cation could not be inserted into the zinc(II) lattice structure (Appendix II).

The transition metal complexes of PMT prepared in DMP using a 4:1 ratio of PMT to transition metal perchlorate (see p. 37), with the exception of tetrakis(PMT)copper(II) perchlorate, are isomorphous since they possess the same relative intensities and d-spacings (Table VIII). Comparison of these d-spacings and relative intensities of Tables VI-VIII shows that the complexes prepared using an

8:1 and 4:1 ratio of PMT to transition metal perchlorate are isomorphous. Therefore, the complexes prepared with a 4:1 ratio of PMT to transition metal perchlorate are actually the hexakis(PMT)transition metal perchlorate complexes. The standard deviations of each of the respective lines within these three series (Tables VI-VIII) are tabulated in Table IX. The maximum deviation from the standard mean value is noted in the right hand column.

Tetrakis(pentamethylenetetrazole)copper(II) Perchlorate

Identical tetrakis(PMT)copper(II) perchlorate complexes were obtained by precipitation from anhydrous acetic acid (see p. 27), or from nitromethane (see p. 28) with an excess of PMT and from DMP with a 4:1 ratio of PMT to copper(II) perchlorate. The excellent agreement of each of the respective d-spacings and the corresponding relative intensities confirm this fact (Table X).

Bis(pentamethylenetetrazole)copper(I) Perchlorate

The bis(PMT)copper(I) perchlorate complexes prepared by the addition of a 2:1 ratio of PMT to copper(II) perchlorate in DMP (see p. 25) and the complex prepared by adding hot water to the evaporated residue of a mixture of a 2:1 ratio of PMT to copper(II) perchlorate in a nitromethane solution (see p. 26) are the same complex.

TABLE VI

Relative Intensities *versus* d-spacings for the Hexakis-(Pentamethylenetetrazole) Transition Metal Perchlorate Complexes[a]

$Fe(PMT)_6(ClO_4)_3$		$Fe(PMT)_6(ClO_4)_2$		$Ni(PMT)_6(ClO_4)_2$[b]		$Ni(PMT)_6(ClO_4)_2$	
I	d	I	d	I	d	I	d
80	11.75	80	11.65	80	11.78	80	11.68
---	-----	---	-----	---	-----	---	-----
---	-----	---	-----	---	-----	20	9.38
---	-----	---	-----	---	-----	---	-----
10	7.11	10	7.13	20	7.18	40	7.15
50	6.78	50	6.78	60	6.75	50	6.74
10	6.41	10	6.41	20	6.41	20	4.20
---	-----	10	6.17	---	-----	20	6.05
10	5.87	10	5.89	20	5.84	20	5.87
---	-----	10	5.39	---	-----	20	5.39
60	5.07	50	5.07	60	5.05	70	5.06
---	-----	---	-----	---	-----	---	-----
100	4.65	100	4.67	100	4.63	100	4.64
40	4.44	40	4.45	50	4.42	60	4.44
---	-----	---	-----	---	-----	---	-----
---	-----	---	-----	20	4.10	---	-----
20	3.92	30	3.93	80	3.90	30	3.91
40	3.81	40	3.81	70	3.81	70	3.80
---	-----	---	-----	---	-----	---	-----
---	-----	---	-----	---	-----	---	-----
20	3.49	30	3.49	30	3.47	40	3.48
20	3.40	30	3.42	20	3.37	40	3.39
---	-----	10	3.25	20	3.24	---	-----
20	3.19	20	3.20	30	3.18	30	3.18
---	-----	---	-----	---	-----	---	-----
---	-----	---	-----	---	-----	---	-----
50	3.00	50	3.00	40	2.98	50	2.98
50	2.88	50	2.89	40	2.88	50	2.88

a. These complexes were prepared with an 8:1 ratio of PMT to transition metal perchlorate in DMP (see p. 29).

b. This complex was precipitated from water (see p. 34).

TABLE VI (continued)

$Mn(PMT)_6(ClO_4)_2$ I	d	$Co(PMT)_6(ClO_4)_2$ I	d	$Zn(PMT)_6(ClO_4)_2$ I	d	$Cu(PMT)_6(ClO_4)_2$ I	d
80	11.78	80	11.66	80	11.78	80	11.63
---	-----	---	-----	---	-----	---	-----
---	-----	---	-----	---	-----	10	9.39
---	-----	---	-----	---	-----	30	7.36
20	7.18	30	7.12	30	7.15	---	-----
40	6.81	40	6.77	50	6.78	60	6.74
20	6.44	20	6.45	20	6.42	20	6.45
20	6.10	20	6.10	20	6.13	---	-----
20	5.90	20	5.89	20	5.87	40	5.82
30	5.41	20	5.38	20	5.37	---	-----
70	5.08	70	5.08	70	5.07	50	5.09
---	-----	---	-----	---	-----	30	4.96
100	4.69	100	4.65	100	4.66	100	4.66
40	4.44	40	4.44	50	4.44	40	4.40
---	-----	---	-----	---	-----	20	4.26
20	4.16	---	-----	---	-----	---	-----
40	3.96	40	3.93	30	3.91	30	3.99
50	3.81	60	3.81	60	3.81	70	3.85
---	-----	---	-----	---	-----	40	3.68
---	-----	---	-----	---	-----	10	3.54
40	3.50	40	3.48	40	3.47	40	3.47
40	3.41	40	3.41	30	3.39	---	-----
---	-----	---	-----	---	-----	---	-----
20	3.20	30	3.18	20	3.19	---	-----
---	-----	---	-----	---	-----	20	3.14
---	-----	---	-----	---	-----	20	3.06
50	3.01	50	2.99	70	2.95	40	2.98
50	2.90	50	2.89	70	2.88	50	2.90

TABLE VII

Relative Intensities *versus* d-spacings for the Isomorphous Replacement of 1% Copper(II) and 1% Manganese(II) in the Hexakis-(Pentamethylenetetrazole)Zinc(II) Perchlorate Complex Lattice[a]

1% $Mn(PMT)_6(ClO_4)_2$ 99% $Zn(PMT)_6(ClO_4)_2$		1% $Cu(PMT)_6(ClO_4)_2$ 99% $Zn(PMT)_6(ClO_4)_2$		$Cu(PMT)_6(ClO_4)_2$[b]	
I	d	I	d	I	d
95	11.79	80	11.72	90	11.75
---	-----	10	10.13	10	10.12
---	-----	10	9.30	10	9.25
---	-----	---	-----	---	-----
20	7.14	30	7.14	20	7.15
50	6.80	40	6.75	40	6.75
10	6.42	20	6.44	20	6.43
10	6.10	20	6.09	10	6.10
---	-----	---	-----	---	-----
10	5.41	20	5.39	20	5.40
70	5.07	60	5.07	60	5.08
---	-----	---	-----	---	-----
100	4.67	100	4.64	100	4.65
40	4.45	40	4.45	40	4.45
---	-----	---	-----	---	-----
---	-----	---	-----	---	-----
60	3.94	40	3.94	50	3.93
70	3.82	50	3.81	60	3.80
---	-----	---	-----	---	-----
---	-----	---	-----	---	-----
40	3.49	30	3.48	30	3.48
40	3.41	30	3.40	40	3.40
5	3.27	---	-----	---	-----
30	3.20	20	3.18	30	3.18
---	-----	---	-----	---	-----
---	-----	---	-----	---	-----
60	3.01	50	3.00	60	3.00
60	2.90	60	2.89	60	2.90
20	2.73	---	-----	10	2.75
10	2.58	---	-----	10	2.57

a. These complexes were prepared with an 8:1 ratio of PMT to transition metal perchlorates in DMP (see p. 29).

b. Crystalline form of $Cu(PMT)_6(ClO_4)_2$ (see p. 29).

TABLE VIII

Relative Intensities *versus* d-spacings for the Hexakis-(Pentamethylenetetrazole)-Transition Metal Perchlorate Complexes[a]

$Mn(PMT)_6(ClO_4)_2$		$Fe(PMT)_6(ClO_4)_3$		$Fe(PMT)_6(ClO_4)_2$	
I	d	I	d	I	d
90	11.65	95	11.78	90	11.72
---	-----	---	-----	---	-----
---	-----	---	-----	---	-----
---	-----	---	-----	---	-----
30	7.10	5	7.17	10	7.15
---	-----	40	6.76	30	6.78
10	6.41	10	6.37	10	6.42
---	-----	---	-----	---	-----
10	5.93	10	5.88	10	5.88
---	-----	---	-----	10	5.42
70	5.08	60	5.07	70	5.08
---	-----	---	-----	---	-----
100	4.66	100	4.64	100	4.66
30	4.47	35	4.45	60	4.44
---	-----	---	-----	---	-----
20	4.17	---	-----	---	-----
40	3.95	15	3.92	---	-----
50	3.81	60	3.81	70	3.80
---	-----	---	-----	---	-----
---	-----	---	-----	---	-----
30	3.43	15	3.48	30	3.48
20	3.40	10	3.39	10	3.40
---	-----	---	-----	---	-----
15	3.18	10	3.19	15	3.18
---	-----	---	-----	---	-----
---	-----	---	-----	---	-----
50	3.01	50	3.00	50	3.00
50	3.89	50	2.89	50	2.89
10	2.74	10	2.72	20	2.73
10	2.58	---	-----	10	2.56

a. These complexes were prepared with a 4:1 ratio of PMT to transition metal perchlorate in DMP (see p. 37).

TABLE VIII (continued)

$Co(PMT)_6(ClO_4)_2$		$Ni(PMT)_4(ClO_4)_2$		$Zn(PMT)_6(ClO_4)_2$	
I	d	I	d	I	d
90	11.78	80	11.79	95	11.79
---	-----	---	-----	---	-----
---	-----	---	-----	---	-----
---	-----	---	-----	---	-----
5	7.16	5	7.16	10	7.16
30	6.78	40	6.80	60	6.75
10	6.37	10	6.37	10	6.37
---	-----	---	-----	---	-----
10	5.87	10	5.84	5	5.87
---	-----	---	-----	---	-----
60	5.06	60	5.06	70	5.07
---	-----	---	-----	---	-----
100	4.65	100	4.64	100	4.64
30	4.44	40	4.44	30	4.44
---	-----	---	-----	---	-----
---	-----	---	-----	---	-----
20	3.92	10	3.91	20	3.93
40	3.80	30	3.81	50	3.81
---	-----	---	-----	---	-----
---	-----	---	-----	---	-----
10	3.48	10	3.48	30	3.49
10	3.39	5	3.39	20	3.40
---	-----	---	-----	5	3.27
10	3.18	5	3.18	10	3.19
---	-----	---	-----	---	-----
---	-----	---	-----	---	-----
40	3.00	30	2.99	40	2.99
40	2.88	30	2.88	40	2.89
5	2.73	10	2.72	10	2.72
---	-----	10	2.55	10	2.57

TABLE IX

Standard Deviation Calculations for the Tabulated d-spacings of all the Hexakis-(Pentamethylenetetrazole)-Transition Metal Complexes (Tables VI, VII, and VIII)

Line	N	Σ	Mean Ave.	σ	a
1	16	187.73	11.73	0.06	11.63
2	---	------	-----	----	-----
3	---	------	-----	----	-----
4	---	------	-----	----	-----
5	15	107.20	7.15	0.04	7.10
6	15	101.57	6.77	0.02	6.81
7	16	102.56	6.41	0.03	6.37
8	7	42.74	6.10	0.04	6.17
9	14	82.22	5.87	0.03	5.93
10	8	43.16	5.40	0.02	5.37
11	16	81.13	5.07	0.01	5.09
12	---	------	-----	----	-----
13	16	74.45	4.65	0.02	4.69
14	16	71.05	4.44	0.02	4.40
15	---	------	-----	----	-----
16	---	------	-----	----	-----
17	15	58.95	3.93	0.02	3.99
18	16	60.98	3.81	0.01	3.85
19	---	------	-----	----	-----
20	---	------	-----	----	-----
21	16	55.66	3.48	0.02	3.43
22	15	50.97	3.40	0.01	3.42
23	4	13.03	3.26	0.01	3.24
24	15	47.80	3.19	0.01	3.20
25	---	------	-----	----	-----
26	---	------	-----	----	-----
27	16	47.89	2.99	0.02	2.95
28	16	46.21	2.89	0.01	2.88
29	7	19.09	2.73	0.01	2.72
30	5	12.84	2.57	0.01	2.55

a. Maximum d-spacing deviation from the mean.

TABLE X

Relative Intensities *versus* d-spacings for the Tetrakis-(Pentamethylenetetrazole)-Copper(II) Perchlorate Complex

$Cu(PMT)_4(ClO_4)_2$ [a]		$Cu(PMT)_4(ClO_4)_2$ [b]		$Cu(PMT)_4(ClO_4)_2$ [c]		$Cu(PMT)_4(ClO_4)_2$ [d]	
I	d	I	d	I	d	I	d
40	12.45	40	12.52	40	12.47	30	12.50
30	8.90	30	8.86	30	8.90	30	8.91
90	7.93	80	7.96	90	7.90	80	7.96
40	7.25	30	7.27	40	7.27	40	7.25
30	6.26	20	6.25	20	6.25	20	6.25
10	5.82	---	-----	---	-----	5	5.80
30	5.12	20	5.12	20	5.10	30	5.09
10	4.91	20	4.73	20	4.80	20	4.85
100	4.44	100	4.44	100	4.43	100	4.45
20	4.19	20	4.29	20	4.25	20	4.28
10	4.18	---	-----	---	-----	10	4.18
90	3.95	60	3.97	80	3.96	80	3.96
10	3.77	---	-----	---	-----	10	3.78
90	3.61	70	3.62	90	3.60	80	3.60
10	3.47	10	3.47	10	3.48	10	3.46
10	3.28	---	-----	---	-----	10	3.28
5	3.11	---	-----	---	-----	10	3.10
50	2.95	50	2.95	50	2.95	50	2.95
20	2.77	10	2.70	20	2.75	10	2.74
20	2.67	10	2.67	20	2.67	10	2.67
---	-----	10	2.37	---	-----	10	2.35

a. This complex was prepared by adding a 4:1 ratio of PMT to a copper(II) perchlorate mixture of 2,2-dimethoxypropane (see p. 37).

b. This complex was precipitated by adding an 8:1 ratio of PMT to copper(II) perchlorate in anhydrous acetic acid (see p. 27).

c. This complex was isolated by the evaporation of nitromethane method (see p. 28).

d. This complex was prepared starting from $Cu(PMT)_6(ClO_4)_2$ (see p. 29).

TABLE XI

Relative Intensities *versus* d-spacings for the Bis-(Pentamethylenetetrazole)-Copper(I) Perchlorate Complex

$Cu(PMT)_2ClO_4$ [a]		$Cu(PMT)_2ClO_4$ [b]	
I	d	I	d
95	12.65	95	12.65
100	10.65	100	10.65
10	9.61	---	-----
20	8.10	30	8.10
5	7.15	---	-----
---	-----	5	6.75
40	6.51	50	6.49
15	6.17	10	6.14
5	5.69	10	5.73
---	-----	10	5.47
60	5.34	80	5.35
40	4.88	60	4.87
70	4.69	80	4.70
30	4.31	30	4.31
30	4.13	40	4.13
70	4.05	90	4.03
10	3.94	20	3.85
10	3.56	20	3.55
20	3.45	40	3.45
50	3.24	70	3.24
20	3.07	20	3.07
20	2.98	20	2.98
20	2.92	20	2.92

a. This complex was prepared by adding hot water to the evaporated residue of a 2:1 ratio of PMT to copper(II) perchlorate in nitromethane solution (see p. 26).

b. This complex was prepared by the addition of a 2:1 ratio of PMT to copper(II) perchlorate in 2,2-dimethoxypropane (see p. 25).

This is shown by the excellent agreement between their respective d values and relative intensities (Table XI).

Electron Spin Resonance Studies of the Transition Metal Complexes of Pentamethylenetetrazole

This work and the interpretation of the data was performed by Dr. Henry A. Kuska in this laboratory. A more complete description of the results is listed in Appendix II.

The ESR investigation of these complexes in nitromethane solutions presented considerable difficulty because the solutions were equilibrium mixtures of the dissociation products of the respective complexes. The exact species depended on the concentration of PMT. In order to avoid this difficulty solid solutions of the complexes were investigated. Since X-ray studies showed the hexakis-(PMT) complexes to be isomorphous, solid solutions of 99% diamagnetic $Zn(PMT)_6(ClO_4)_2$ and 1% paramagnetic $Cu(PMT)_6(ClO_4)_2$ or $Mn(PMT)_6(ClO_4)_2$ were prepared. A modification of the DMP method (see p. 29) was employed where 1% by weight of either copper or manganese perchlorate hexahydrate was added to the zinc perchlorate hexahydrate and the mixture was then dehydrated with DMP and reacted with PMT. The second method employed was to use the undiluted complex directly.

The ESR data of these solid solutions indicated that these complexes are nearly octahedral or tetragonal in symmetry and that the metal-nitrogen bond is approximately 91% ionic.

Nuclear Magnetic Resonance Studies of the Transition Metal Complexes of Pentamethylenetetrazole

Pentamethylenetetrazole

The NMR spectrum of PMT in pyridine shows three absorbances at 5.54, 6.96 and 8.29 τ having the respective areas of 1:1:3 (Figure 17).

Hexakis(pentamethylenetetrazole)zinc(II) Perchlorate

The NMR spectrum of diamagnetic hexakis(PMT)zinc(II) perchlorate in deuterated water is very similar to that of PMT in appearance and has three absorbances at 6.57, 7.70 and 8.59 τ. The respective areas of the absorbances are 1:1:3 (Figure 17).

Bis(pentamethylenetetrazole)copper(I) Perchlorate

The NMR spectrum of diamagnetic bis(PMT)copper(I) perchlorate in pyridine shows the presence of the PMT moiety in the complex. The NMR absorbances appear at values of 5.42, 7.20 and 8.33 τ having respective areas of 1:1:3 (Figure 17).

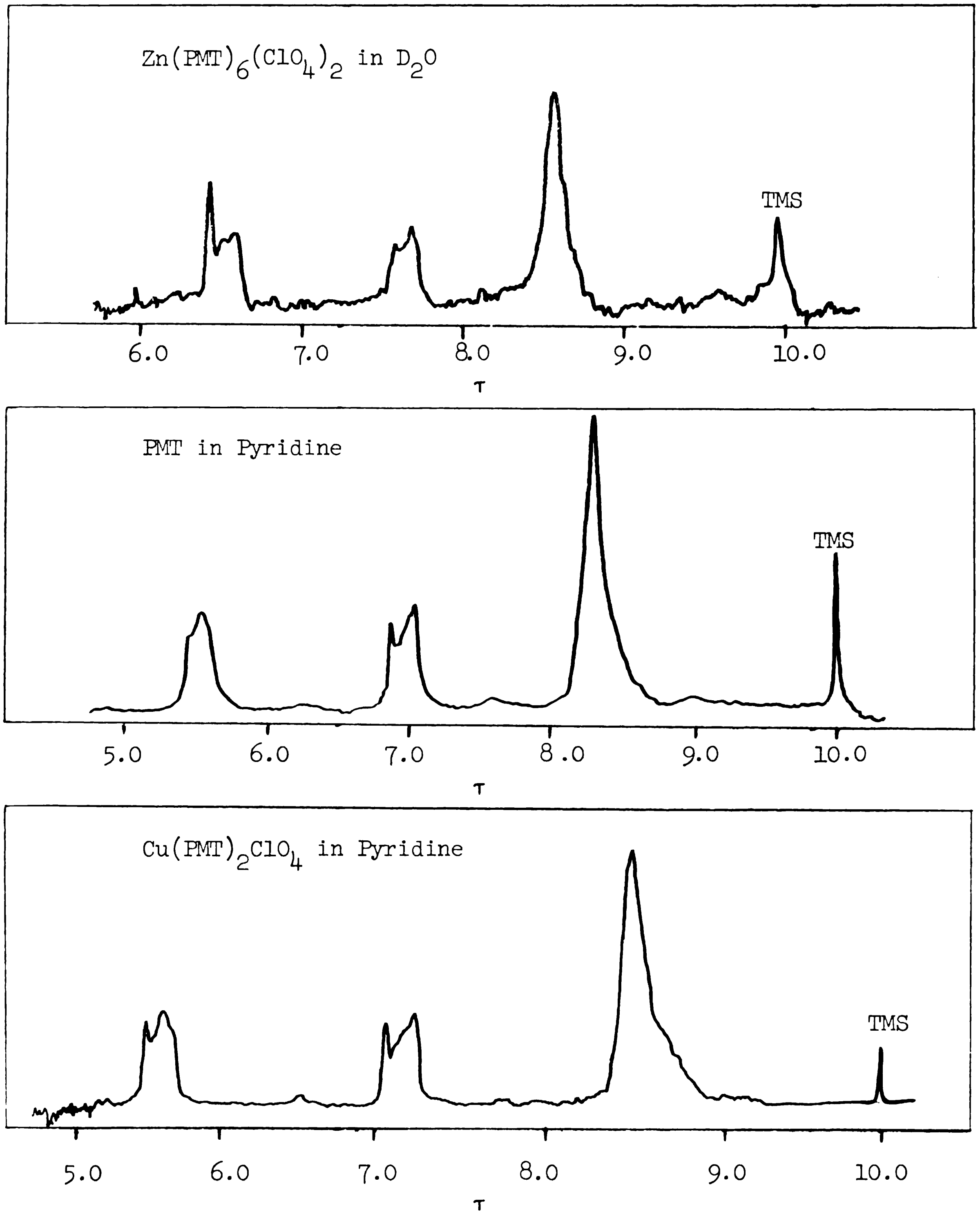

Figure 17. NMR absorption spectra. Tetramethylsilane was used as the internal standard.

Tetrakis and Hexakis(pentamethylenetetrazole) Transition Metal Perchlorate Complexes

All of the metal complexes of PMT prepared are paramagnetic with the exception of hexakis(PMT)zinc(II) and bis(PMT)-copper(I) perchlorate which are diamagnetic and yield predicted NMR spectra. The NMR spectra of hexakis(PMT)-manganese(II), iron(II), iron(III), cobalt(II), nickel(II), copper(II) and tetrakis(PMT)copper(II) perchlorate were run and no absorbances were detected within the entire sweep width of the Varian A-60 Proton Spectrophotometer (-1000 to 2000 cps). Since paramagnetic ions have been responsible for large shifts of proton absorbances (96), one possible explanation for the lack of the predicted NMR spectra is that the absorbances are shifted beyond the sweep width limits of the instrument.

Infrared Absorption Studies of the Transition Metal Complexes of Pentamethylenetetrazole (5000-680 cm^{-1} region)

Infrared spectra were obtained for PMT and for all the complexes prepared in this study (Figures 18-27 and Table XII). All the spectra of the complexes were obtained in Nujol mulls while PMT was obtained both in mull and in a pressed KBr pellet. The bands arising from Nujol appear at approximately 2940(s), 1460(s), 1381(s), 1100(w), and

725(w) cm^{-1} and are not listed in Table XII. Potassium bromide pellets were not used due to the suspected formation of the corresponding transition metal bromide-PMT mixed complexes. When the hexakis(PMT)cobalt(II) and copper(II) perchlorate complexes were pressed at approximately 8 tons pressure, the resulting disks were blue and green respectively. Gill, et al. (97) reported the same colors for the tetrahedrally coordinated complexes of bis-(pyridine)cobalt(II) and copper(II) bromide.

Each sample was mulled by weighing 100 milligrams of the complex and 200 milligrams of Nujol into a plastic mulling capsule containing a plastic ball. The capsule was rapidly agitated for two minutes using a Wig-L-Bug (Cresent Dental Mfg. Co.). The mulled sample was then transferred to a sodium chloride plate and inserted into the instrument.

The infrared spectra were interpreted relative to the spectrum of PMT and the literature values for the various perchlorate bands. No attempts were made in this study to assign the bands of PMT or any of the complexes prepared.

Hexakis(pentamethylenetetrazole) Transition Metal Perchlorates

Comparison of the spectra of PMT (Figure 18) with those of the hexakis(PMT) transition metal perchlorates (Figures 19-25) show little change in the PMT spectrum upon

TABLE XII

Infrared Absorption Bands (in cm^{-1}) of Transition Metal Complexes of Pentamethylenetetrazole (Nujol Mulls)

PMT	$Mn(PMT)_6(ClO_4)_2$ a	$Mn(PMT)_6(ClO_4)_2$ b	$Fe(PMT)_6(ClO_4)_2$ a	$Fe(PMT)_6(ClO_4)_2$ b
-----	-----	-----	-----	-----
-----	-----	3445s	-----	-----
-----	-----	-----	-----	3370m
-----	-----	-----	-----	-----
-----	-----	1700w	-----	1700w
-----	-----	1640m	-----	1625w
-----	-----	-----	-----	-----
1530m	1530m	1540m	1532m	1535m
-----	1348w	1346w	1348w	1348sh
1319w	1335sh	1338sh	1340sh	1335sh
1310sh	1313w	1315w	1314w	1315w
1272w	1292w	1293w	1295w	1295w
-----	1259w	1260w	1259w	1260w
1248m	1242sh	1242sh	-----	1240sh
1190w	1188w	1190sh	1189w	1189sh
1174w	1170sh	-----	1171sh	-----
1118m	-----	-----	-----	-----
1099w	-----	-----	-----	-----
-----	~1091vs	~1090vs	~1098vs	~1090vs
1090w	-----	-----	-----	-----
1079w	-----	-----	-----	-----
-----	1029w	1032w	1028w	1030sh
994m	1008m	1008m	1008m	1007w
-----	-----	-----	-----	-----
964m	964m	968m	968m	969m
-----	-----	920w	-----	932w
-----	898sh	-----	-----	900sh
895m	892m	893m	882m	892m
864m	868m	868m	868m	868m
833w	831m	832m	832w	831m
798m	801m	801m	801m	802m
743w	746m	746m	747m	746m
719w	721m	721w	722m	722w
675m	677m	676m	678m	677m
-----	-----	668sh	-----	699sh
631m	632sh	632sh	633sh	632sh

a. This complex was prepared in DMP with an 8:1 ratio of PMT to transition metal perchlorate (see p. 29).

b. This complex was prepared in DMP with a 4:1 ratio of PMT to transition metal perchlorate (see p. 37).

TABLE XII (continued)

$Fe(PMT)_6(ClO_4)_3$		$Ni(PMT)_6(ClO_4)_2$		
a	b	a	c	b
-----	-----	-----	-----	-----
-----	-----	-----	-----	-----
-----	-----	-----	-----	3400s
-----	-----	-----	-----	-----
-----	-----	-----	-----	1690w
-----	-----	-----	-----	1645w
1598w	-----	-----	-----	-----
1530m	1535m	1520m	1532m	1535m
1345w	1348w	1350sh	1350sh	1348w
1335sh	1335sh	1335sh	1338sh	1335sh
1312w	1315w	1312w	1313w	1318w
1293w	1296w	1295w	1295w	1299w
1260w	1260w	1260w	1260w	1260w
1240sh	1245sh	1240sh	1240sh	1248sh
1187w	1192w	-----	-----	1198sh
1171sh	1174w	1170sh	1170sh	-----
-----	-----	-----	-----	-----
-----	-----	-----	-----	-----
1082vs	~1090vs	~1092vs	~1088vs	~1090vs
-----	-----	-----	-----	-----
-----	-----	-----	-----	-----
1028sh	1030w	1029w	1029w	1030sh
1005w	1010m	1012m	1011m	1012w
-----	-----	-----	-----	-----
966m	968m	967m	966m	968m
-----	-----	-----	-----	930w
-----	900sh	898sh	898sh	-----
892m	893m	891m	890m	894m
866m	868m	868m	867m	869m
831w	833m	832w	831w	832w
801m	803m	802m	802m	803m
744m	747m	747m	746m	746m
722w	722w	719w	722w	722w
676m	677m	677m	677m	679m
668sh	670sh	-----	668sh	669sh
-----	-----	-----	-----	-----

c. This complex was precipitated from aqueous solution (see p. 34).

TABLE XII (continued)

$Co(PMT)_6(ClO_4)_2$ a	$Co(PMT)_6(ClO_4)_2$ b	$Zn(PMT)_6(ClO_4)_2$ a	$Zn(PMT)_6(ClO_4)_2$ b	$Cu(PMT)_6(ClO_4)_2$ a
-----	-----	-----	-----	-----
-----	3460s	-----	3480w	-----
-----	-----	-----	-----	-----
-----	-----	-----	-----	-----
-----	1710w	-----	-----	-----
-----	1640m	-----	1635w	-----
-----	-----	-----	-----	-----
1532m	1535m	1530m	1535m	1530m
1345w	1352w	1344w	1350sh	1350sh
1335sh	1336sh	1335w	1337sh	1338sh
1312w	1318w	1313w	1317w	1317w
1293w	1295w	1292w	1296w	1298sh
1260w	1263w	1258w	1261w	1358w
1240sh	1244sh	1240w	1243sh	1240sh
1189w	-----	1190w	1190w	1193sh
1171w	-----	1173w	1174w	1172w
-----	-----	-----	-----	-----
-----	-----	-----	-----	-----
~1087vs	~1090vs	~1080vs	~1094vs	~1089vs
-----	-----	-----	-----	-----
-----	-----	-----	-----	-----
1026w	1032sh	1029w	1030w	1028w
1006m	1009m	1010m	1010m	1010m
-----	-----	-----	-----	-----
965m	970m	965m	670m	967m
-----	932w	-----	-----	-----
896sh	900sh	898sh	899sh	904w
891m	892m	890m	892m	892m
867m	869m	867m	869m	868m
832m	833m	830m	832w	832m
801m	803m	800m	802m	802m
746m	748m	747m	746m	744m
722m	722w	721m	722m	721w
677m	678m	678m	677m	678m
-----	668sh	670sh	668sh	-----
633sh	-----	632sh	-----	-----

TABLE XII (continued)

	$Cu(PMT)_4(ClO_4)_2$		$Cu(PMT)_2ClO_4$	
d	b	e	f	g
-----	-----	-----	3615w	3630w
-----	3500w	3495w	-----	-----
-----	-----	-----	-----	-----
-----	-----	-----	-----	-----
1680w	-----	-----	-----	-----
-----	-----	1625w	-----	1640w
-----	1605sh	1570w	1615w	-----
1540m	1540sh	1540m	1540m	1540m
1341w	1342w	1348w	1346sh	1348sh
1322w	-----	1325w	-----	-----
1305m	1305w	1308w	1303w	1303w
-----	-----	-----	-----	-----
1267m	1268m	1270w	1268w	1268w
1242sh	1247sh	1250sh	1249sh	1249sh
1205w	1203w	1209w	1204w	1204w
-----	-----	-----	-----	-----
-----	-----	-----	1142m	1139m
-----	-----	-----	-----	-----
~1091vs	~1087vs	~1095vs	~1088vs	~1090vs
-----	-----	-----	-----	-----
-----	-----	-----	-----	-----
1020sh	1020sh	1020sh	-----	-----
-----	-----	-----	-----	-----
-----	-----	-----	972m	972m
969m	968m	973m	964sh	964sh
924w	925sh	926w	-----	-----
-----	-----	-----	-----	-----
896m	897m	900m	899w	899w
867m	868m	870m	868w	868w
835sh	-----	840w	839w	839w
801m	800m	802m	805w	805w
743m	741m	744m	738w	738w
721w	722m	722m	722w	720w
674m	673m	677m	679w	678w
664sh	669sh	659w	-----	-----
633sh	635sh	636sh	635sh	635sh

d. This complex was precipitated from anhydrous acetic acid (see p. 27).
e. This complex was precipitated from nitromethane (see p. 28).
f. This complex was prepared in nitromethane (see p. 26).
g. This complex was precipitated from DMP (see p. 25).

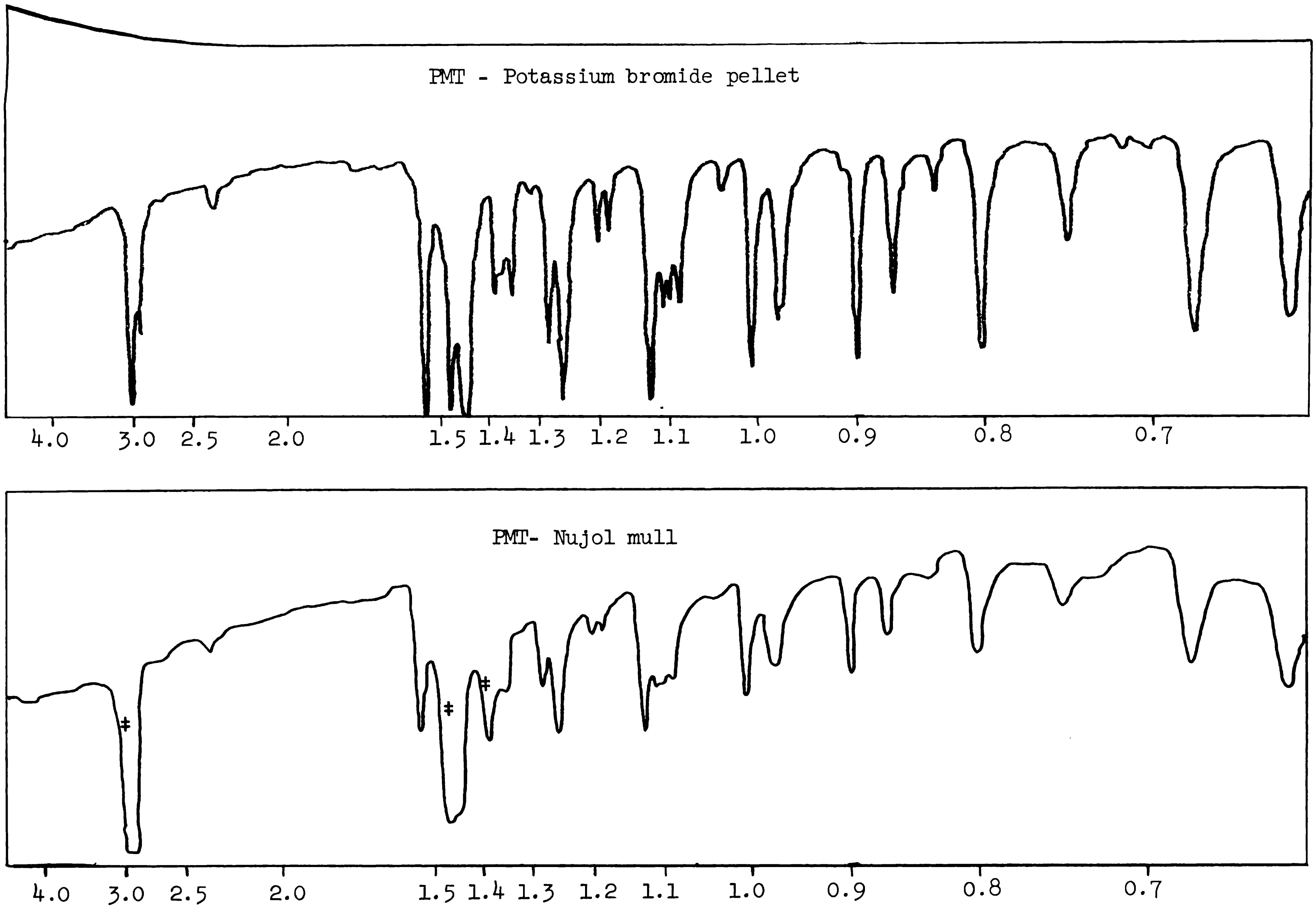

Figure 18. Infrared Absorption Spectra (in $cm^{-1} \times 10^{-3}$) of PMT.

‡ - Nujol bands

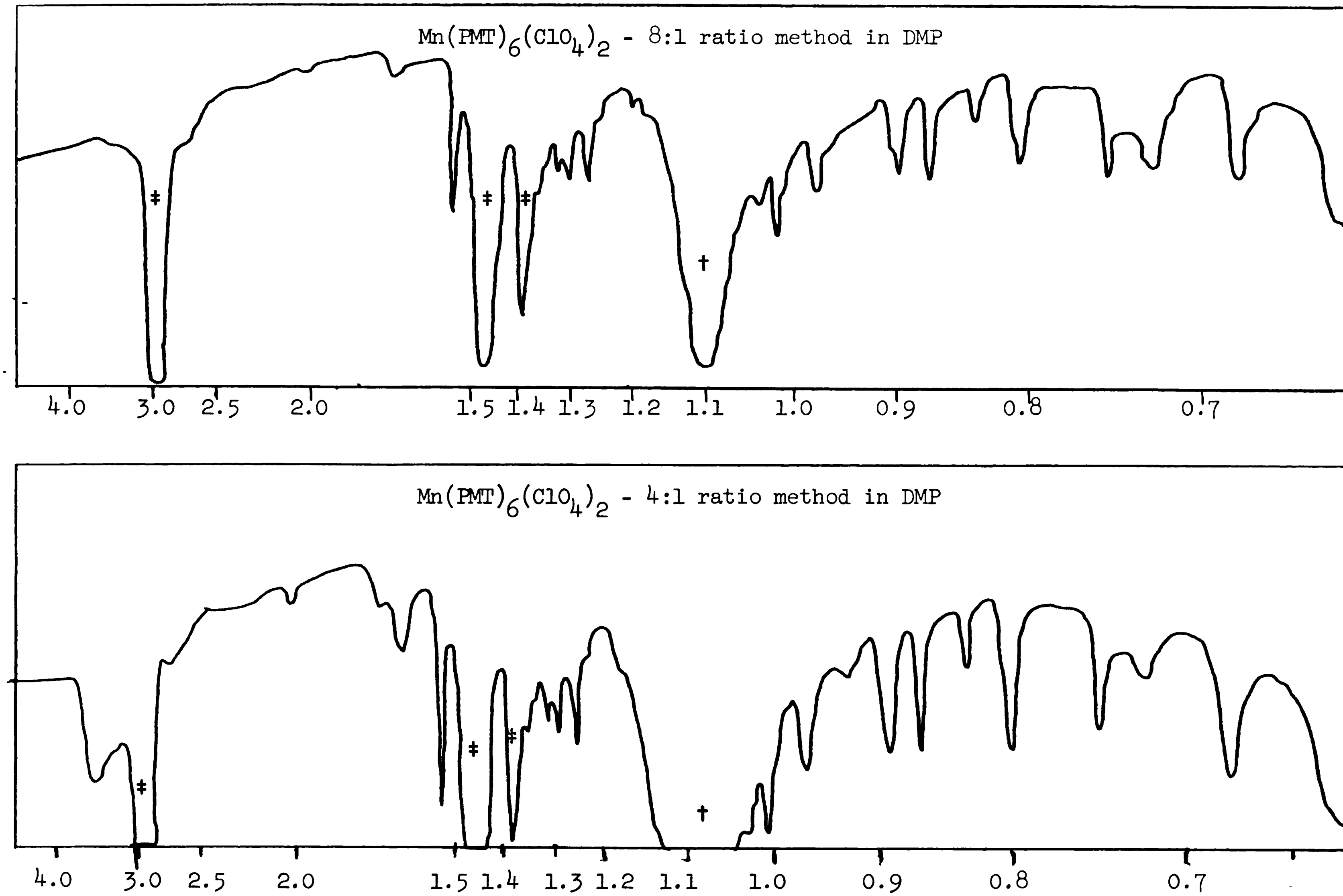

Figure 19. Infrared Absorption Spectra (in $cm^{-1} \times 10^{-3}$). Nujol mull.

‡ - Nujol bands † - Perchlorate band

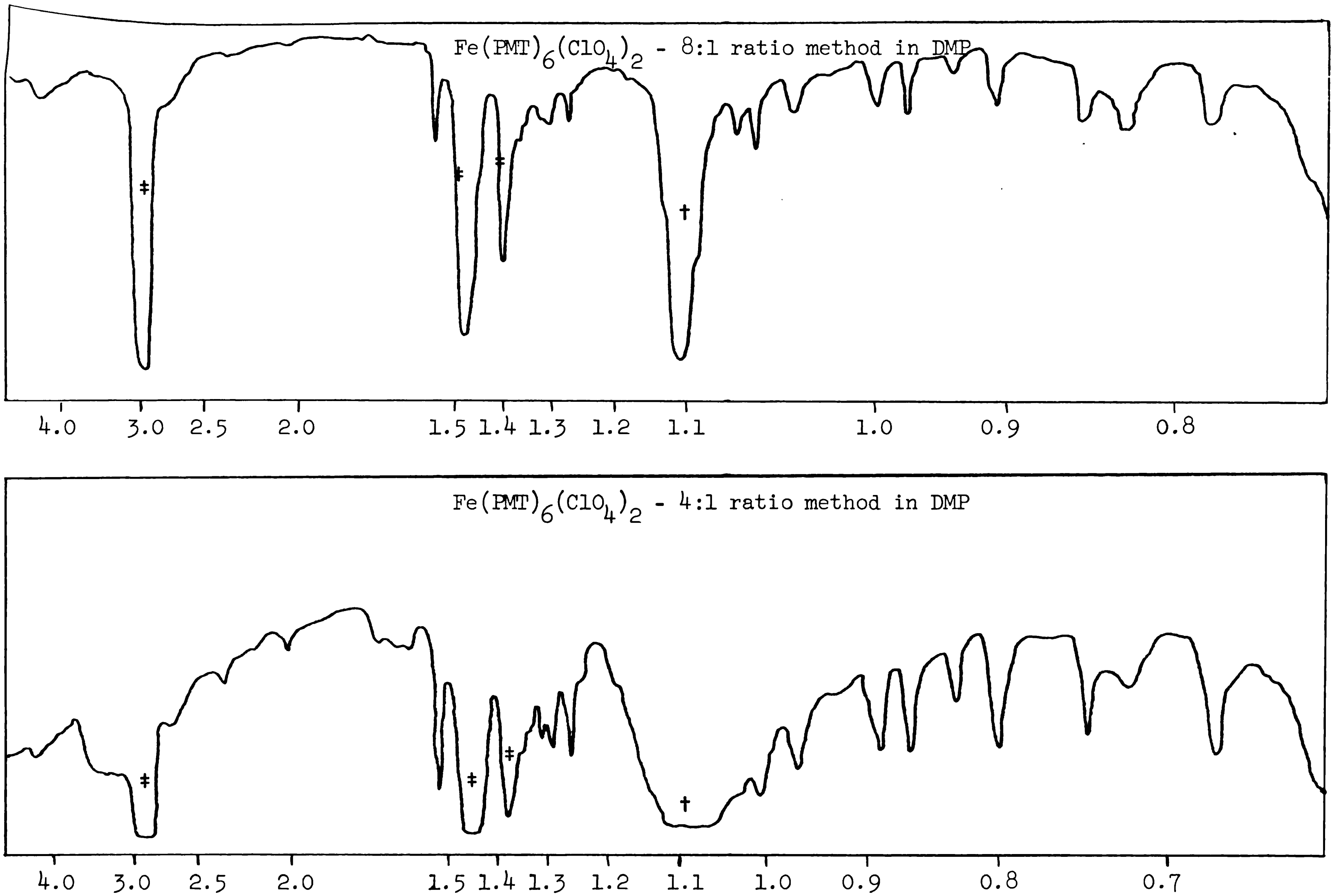

Figure 20. Infrared Absorption Spectra (in $cm^{-1} \times 10^{-3}$). Nujol mull.

‡ - Nujol bands † - Perchlorate band

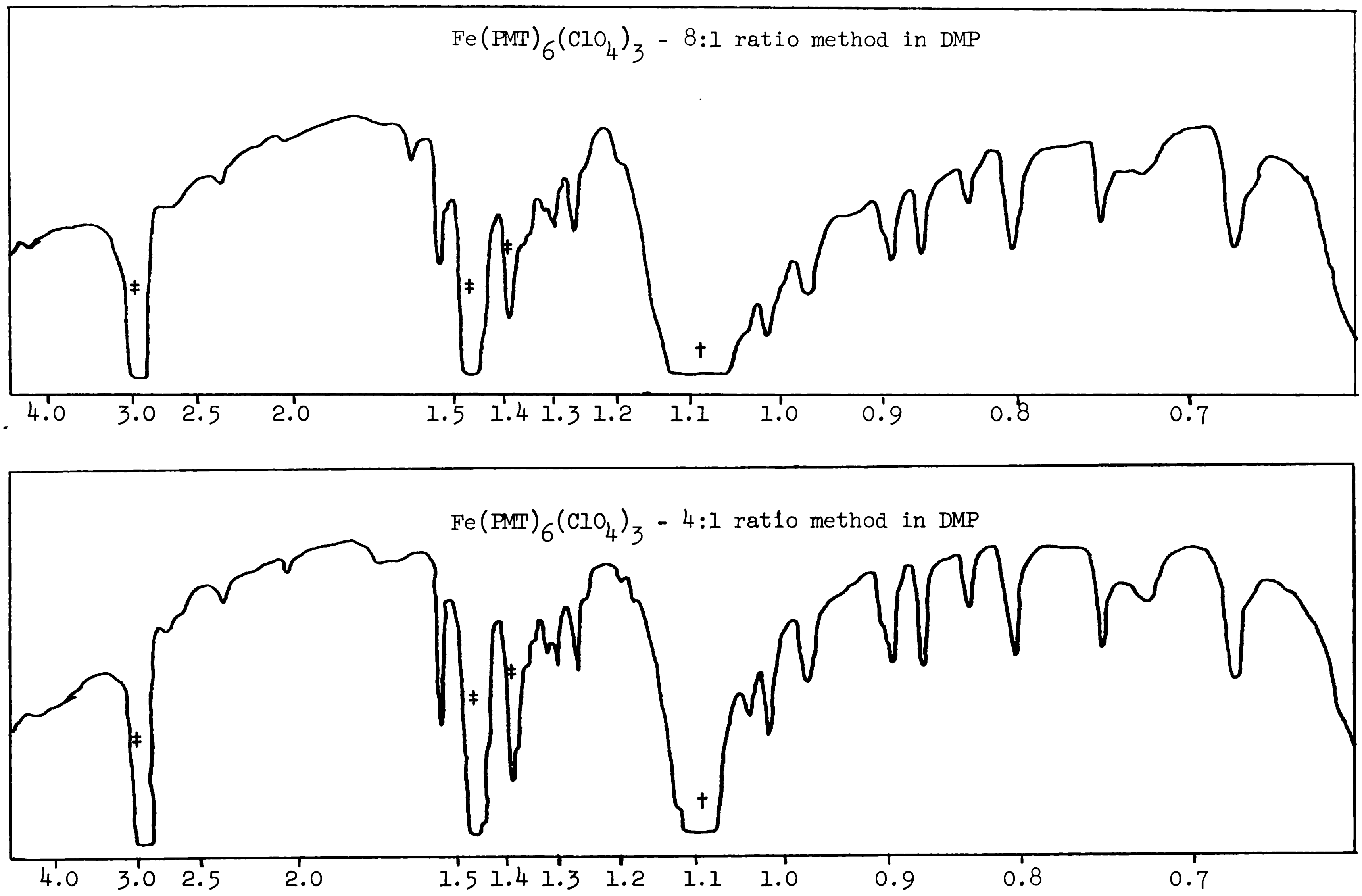

Figure 21. Infrared Absorption Spectra (in $cm^{-1} \times 10^{-3}$). Nujol mull.

‡ - Nujol bands † - Perchlorate band

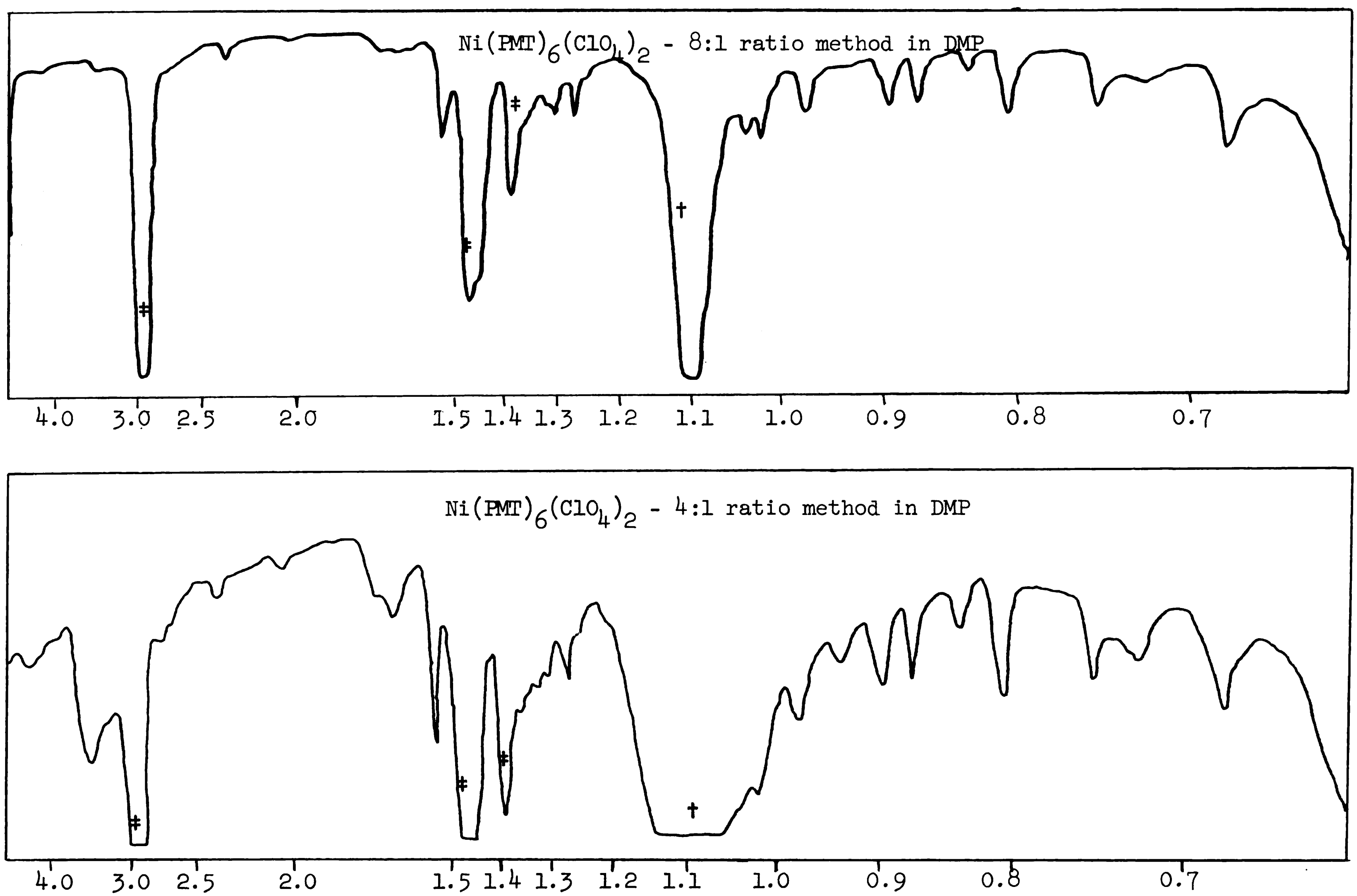

Figure 22. Infrared Absorption Spectra (in $cm^{-1} \times 10^{-3}$). Nujol mull.

‡ - Nujol bands ✝ - Perchlorate band

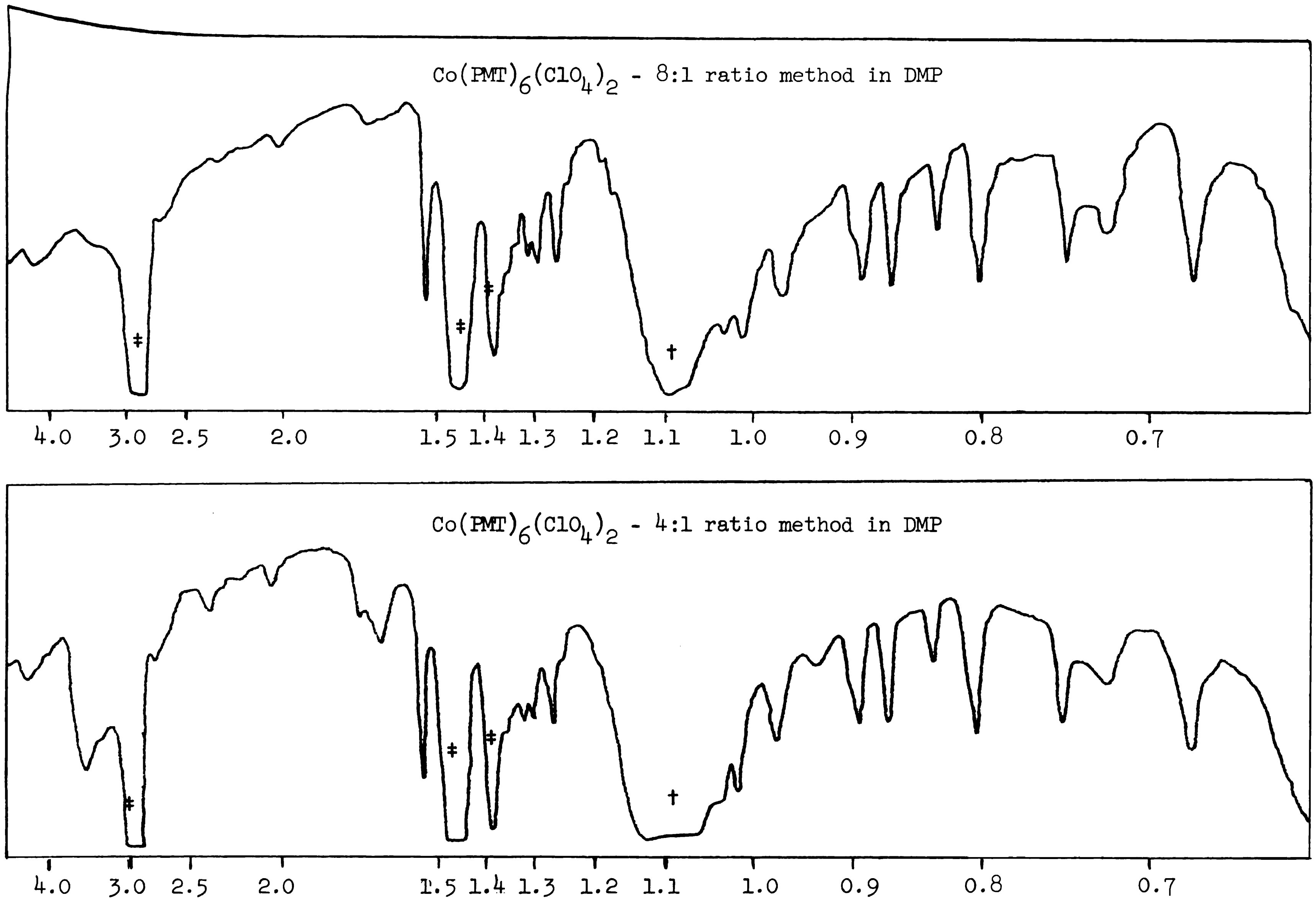

Figure 23. Infrared Absorption Spectra (in $cm^{-1} \times 10^{-3}$). Nujol mull.

‡ - Nujol bands   † - Perchlorate band

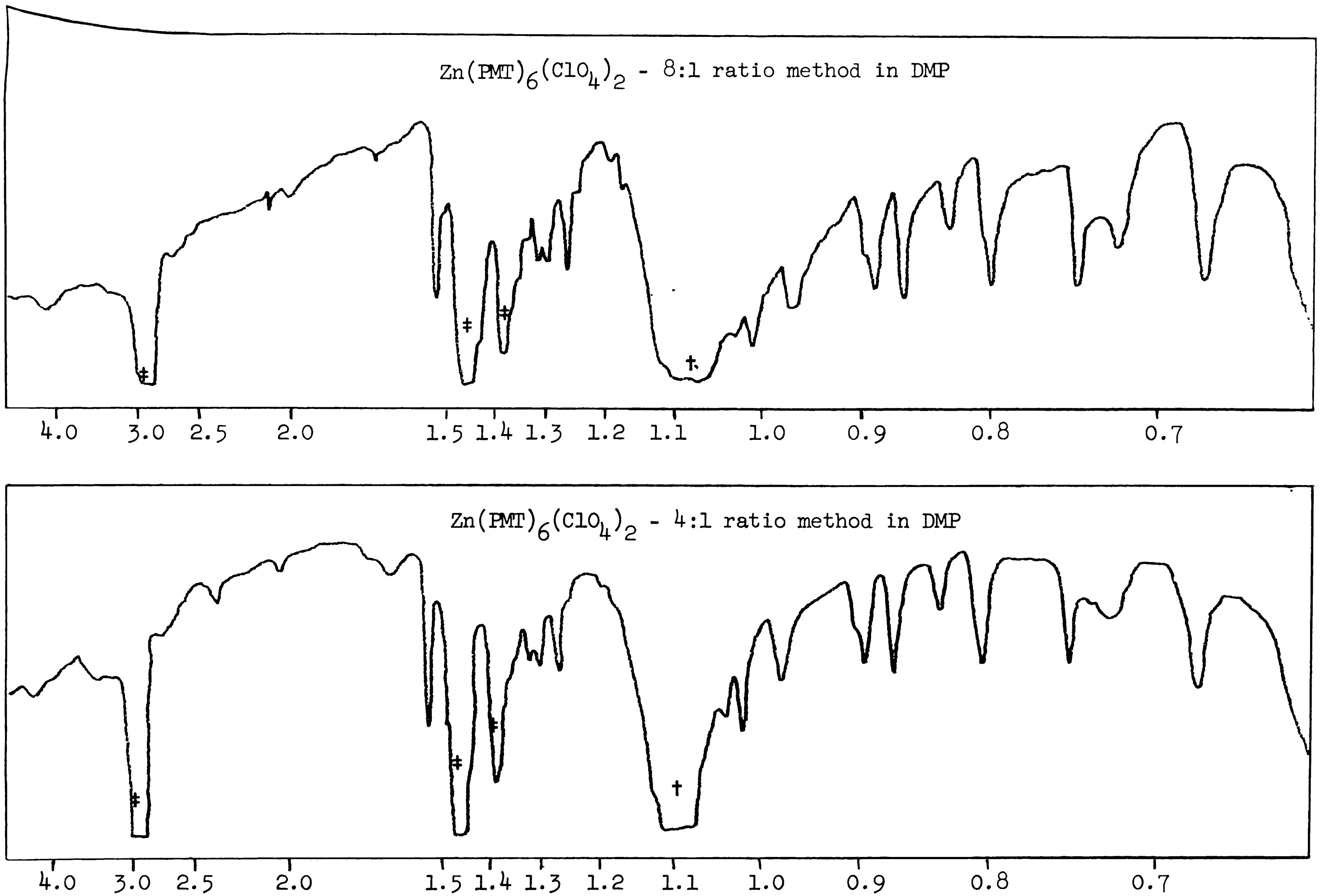

Figure 24. Infrared Absorption Spectra (in $cm^{-1} \times 10^{-3}$). Nujol mull.

‡ - Nujol bands † - Perchlorate band

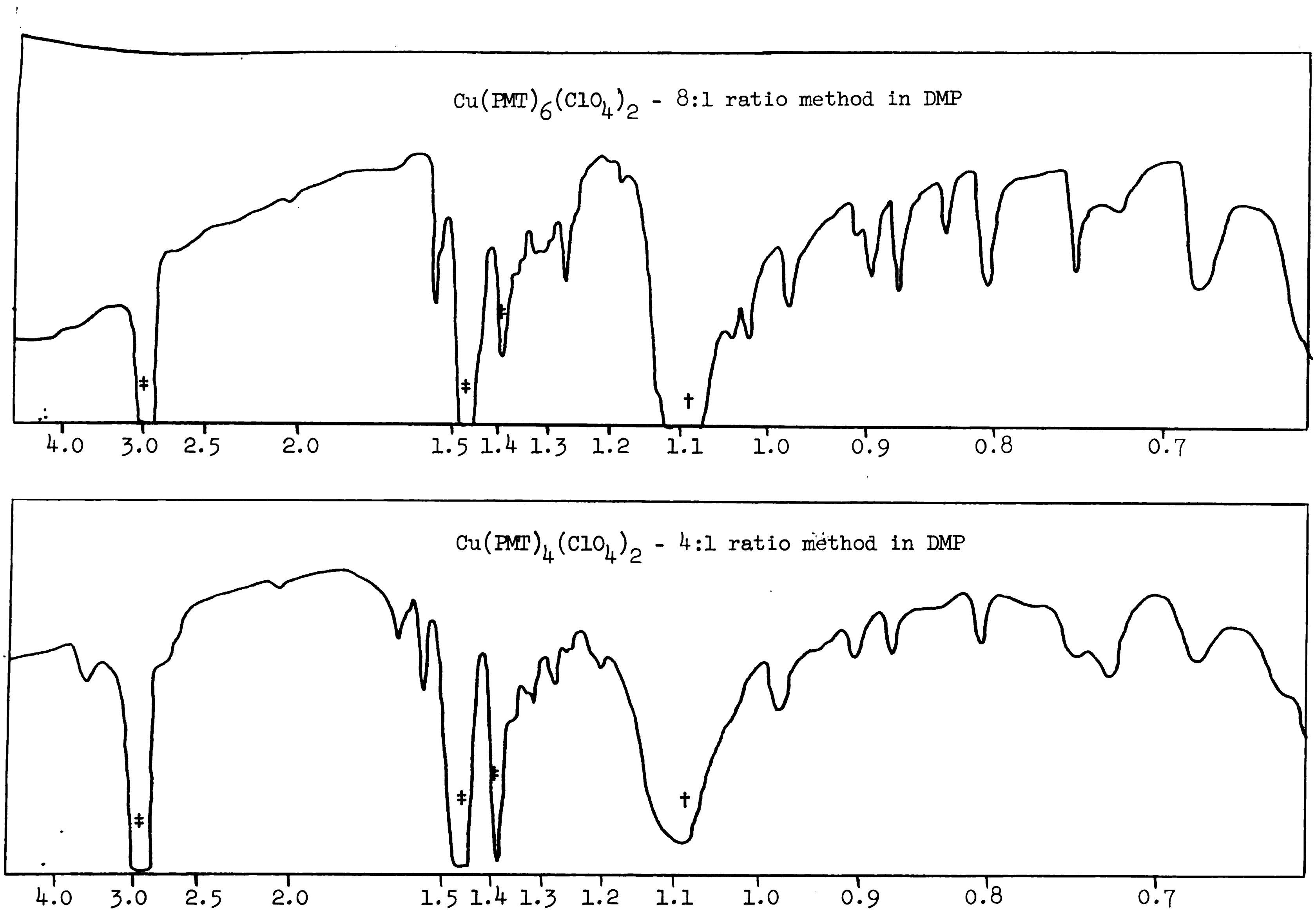

Figure 25. Infrared Absorption Spectra (in $cm^{-1} \times 10^{-3}$). Nujol mull.

‡ - Nujol bands † - Perchlorate band

complexation. There are small (± 3 cm^{-1}) absorption shifts which vary with the central metal ion. However, little information with regard to complexation could be obtained from these spectra.

Some evidence concerning the nature of the coordination of the central metal ion can be obtained from the perchlorate absorptions. The perchlorate ion has a regular tetrahedral structure and belongs to the point group Td, having nine vibrational degrees of freedom distributed between four normal modes of vibration. These normal modes are: the symmetric stretch ν_1 which is theoretically infrared inactive and usually appears as a very weak band at 932 cm^{-1} due to the distortion of the ion in the crystal field (83); the symmetric bend ν_2 which is infrared inactive and is assigned a frequency of 460 cm^{-1} from the Raman spectra; the asymmetric stretch ν_3 which appears at approximately 1100 cm^{-1} in the infrared spectra of ionic perchlorate as a very broad, strong band with a poorly defined maximum; and the asymmetric bending mode ν_4 at 620 cm^{-1} which is beyond the range of the Beckman IR5 and is discussed in the far infrared section of this study.

If, in the process of complexation, the perchlorate group changes from an ionic to a perchlorato group, the oxygen atom involved in the partial covalent bonding with the central metal ion is no longer equivalent to the other three oxygen atoms, and the symmetry of the perchlorate group is lowered to C_{3v}. As a result, the broad degenerate ν_3 band present in the spectra of the ionic perchlorates splits into two well-defined bands with maxima between 1200 and 1000 cm^{-1} and the chlorine coordinated oxygen (Cl—o*) stretching frequency ν_2 increases in intensity and appears as a medium or strong band at about 950-925 cm^{-1} (98,99).

Inspection of the spectra shows that, in all cases, the broad degenerate ν_3 band at approximately 1090 cm^{-1} is not split and the ν_1 symmetric stretching frequency, when it appears, is very weak. This suggests that the perchlorate group in these complexes is ionic and it appears that the PMT ligands are arranged octahedrally around the central metal ion and prevent coordination by the perchlorate group (83).

Tetrakis(pentamethylenetetrazole)copper(II) Perchlorate

Comparison of the spectra of PMT (Figure 18) with those of tetrakis(PMT)copper(II) perchlorate (Figures 25,26), prepared by different methods, shows good correspondence of the various bands. Again little information is obtainable from the slight shifts of the bands of PMT on coordination. The perchlorate ν_3 asymmetric stretch is again

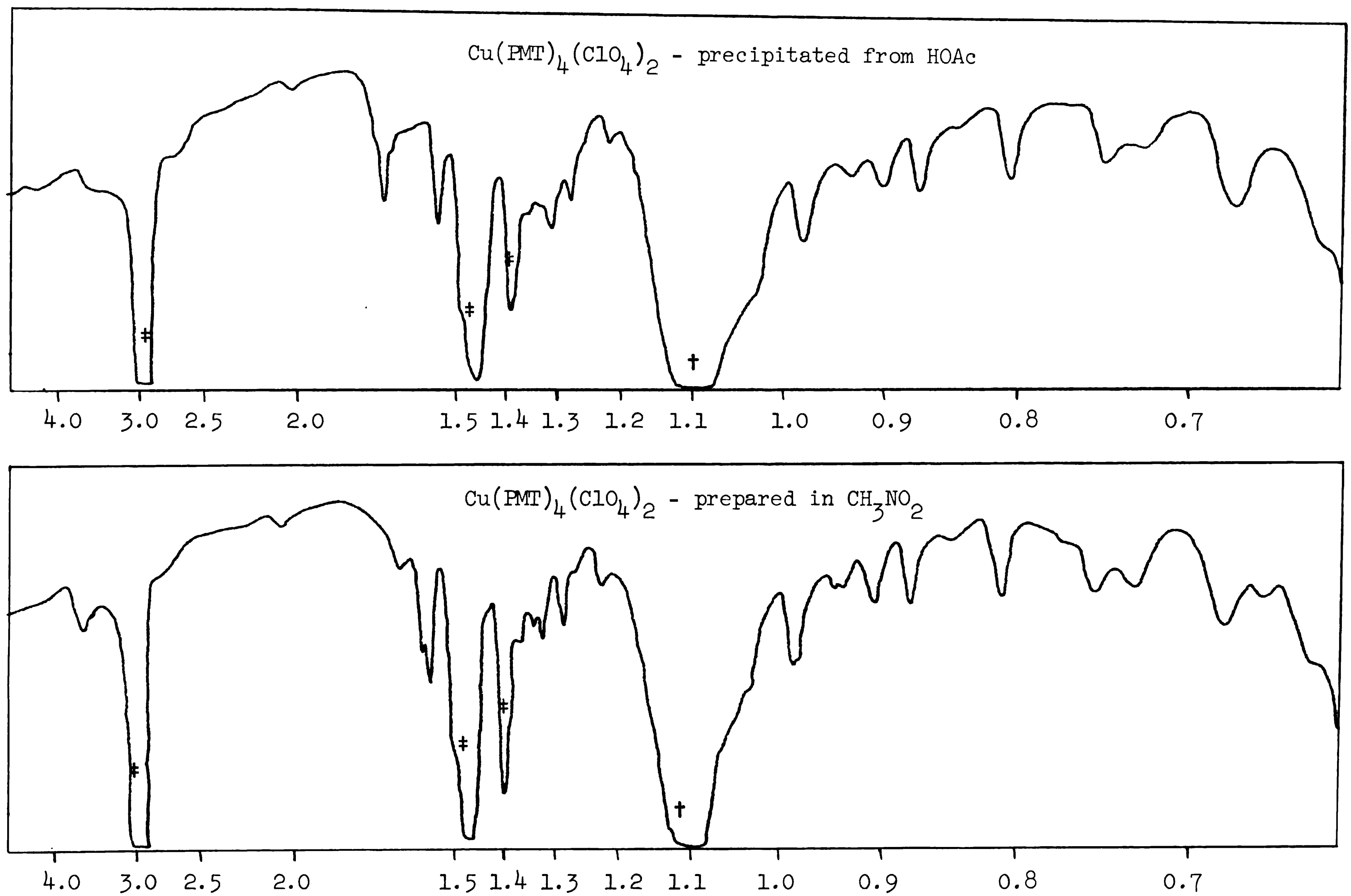

Figure 26. Infrared Absorption Spectra (in $cm^{-1} \times 10^{-3}$). Nujol mull.

‡ - Nujol bands † - Perchlorate band

unsplit, and the ν_1 symmetric stretch may be present as a weak band at approximately 925 cm^{-1}. It appears that this complex may have a square-coplanar configuration around the copper ion with the perchlorate groups above and below this plane. A regular octahedral arrangement will be distorted by the Jahn-Teller effect to give slightly longer bonds between the perchlorate groups and the copper ion. This will result in less covalent character in the copper-oxygen bond; and since the perchlorate group will be more ionic, the asymmetric stretching ν_3 mode will appear unsplit.

<u>Bis(pentamethylenetetrazole)copper(I) Perchlorate</u>

The spectra of bis(PMT)copper(I) perchlorate (Figure 27) are very similar to spectra of the hexakis and tetrakis(PMT) transition metal perchlorates (Figures 19-26) and compare favorably with the spectra of PMT (Figure 18). The complex is ionic based on the absence of splitting of the ν_3 asymmetrical stretch and the absence of the ν_1 symmetric stretching mode at approximately 925 cm^{-1}.

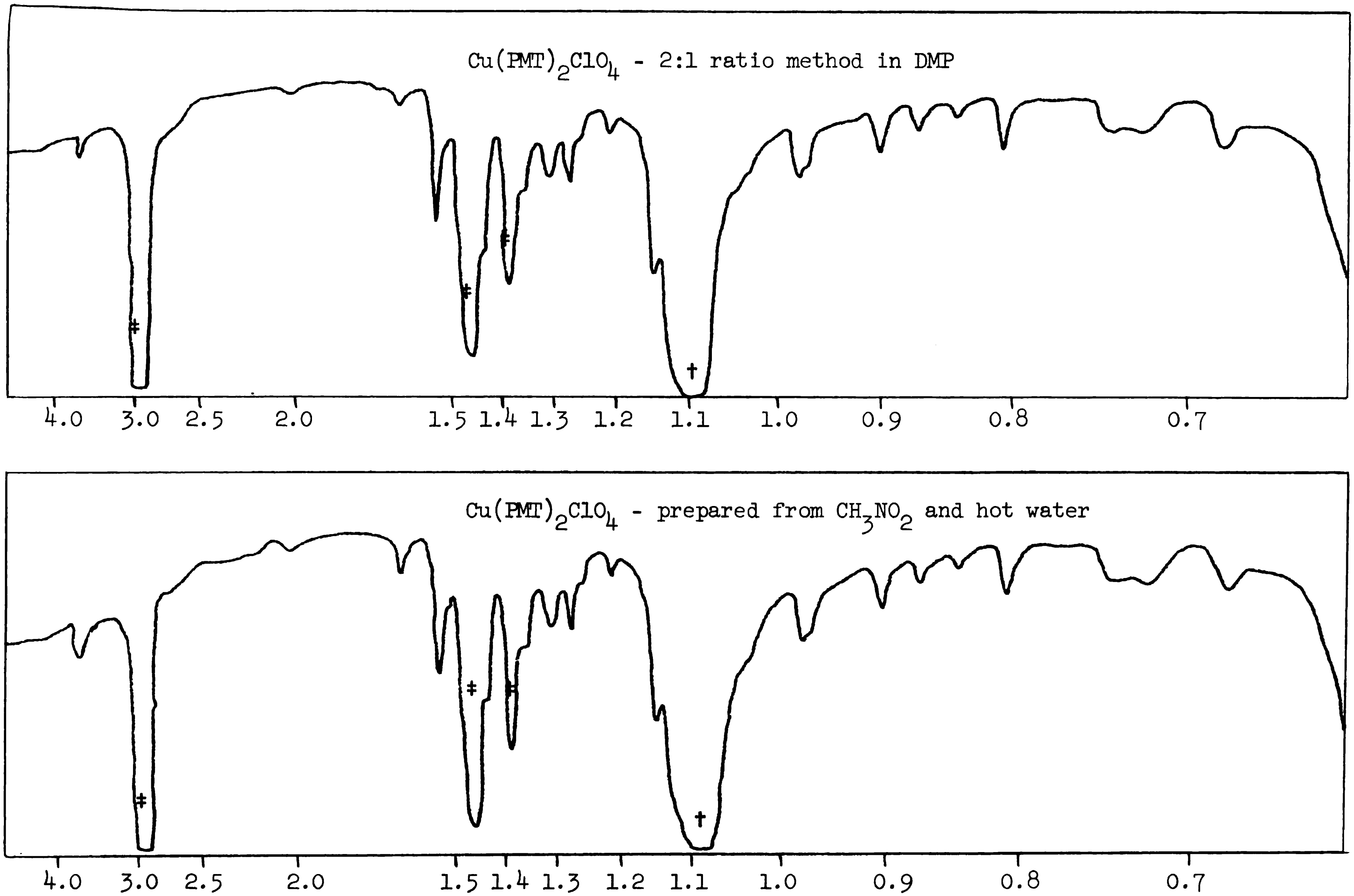

Figure 27. Infrared Absorption Spectra (in $cm^{-1} \times 10^{-3}$). Nujol mull.

‡ - Nujol bands ✝ - Perchlorate band

Far Infrared Studies of the Transition Metal Complexes of Pentamethylenetetrazole ($680\text{-}180\ cm^{-1}$ region)

A Perkin-Elmer model 301 far infrared double beam spectrometer was used to obtain all of the far infrared spectra. All the spectra were obtained with the complexes dispersed in Nujol which is nearly ideal for use in the cesium bromide (700-320 cm^{-1}) and polyethylene (320-100 cm^{-1}) regions because it has only one weak band at 725 cm^{-1} (100).

The samples were prepared by the same techniques explained in the infrared studies section (see p. 83). Selected mulled samples were allowed to age for 24 hours and showed no change in absorption in the 320-170 cm^{-1} region. It was, therefore, assumed that the mulled complexes would be stable for the time required to run the sample (about six hours).

The spectra in the cesium bromide and polyethylene regions were obtained by use of air and polyethylene of the same thickness as references. Since water vapor absorbs strongly below 320 cm^{-1} (101), the entire system was continually flushed with dry nitrogen.

In order to obtain a spectrum of a complex from 700-100 cm^{-1}, it was necessary to change gratings, mirrors, choppers and reststrahlen filters several times. It was found convenient to obtain the spectra of all the complexes in one region before modifying the instrument for the next region. For this reason the relative intensities of bands for the same complex in different regions probably do not have any significance. The breaks in the spectra due to these changes are shown on the figures by interruptions in the traces.

Pentamethylenetetrazole

The far infrared spectrum of PMT shows nine absorption bands in the 700-100 cm^{-1} spectral region (Table XIII, Figure 28). All the bands, except the one at 670 cm^{-1}, are probably due to the pentamethylene ring since they are absent in the spectra of 1 and 5-methyl, 5-ethyl, 5-*n*-propyl and 5-*n*-pentyl tetrazole (Figures 28-30). The absorption bands in the 500 cm^{-1} region for the 5-ethyl, 5-*n*-propyl and 5-*n*-pentyl tetrazole probably result from the rocking vibration of the alkyl groups.

Anhydrous Sodium and Silver Perchlorate

These compounds show a strong band due to the perchlorate ion in the vicinity of 620 cm^{-1} (Figure 31). This value agrees with the literature value of 620-630 cm^{-1} (100).

Hexakis-(Pentamethylenetetrazole)-Transition Metal Complexes

When PMT is complexed with the transition metal perchlorates, three new bands appear in the far infrared spectrum of PMT

TABLE XIII

Far Infrared Spectra (in cm^{-1}) of Transition Metal Complexes of Pentamethylenetetrazole

PMT	$Mn(PMT)_6(ClO_4)_2$	$Fe(PMT)_6(ClO_4)_2$	$Co(PMT)_6(ClO_4)_2$	$Ni(PMT)_6(ClO_4)_2$
672	674	674	675	675
628	628 sh	628 sh	628 sh	628 sh
---	620	620	620	620
499	499	499	499	499
440	441	444	444	446
390	394	395	396	398
352	368	369	372	370
339	339	339	340	339
266	285	290	294	303
---	---	---	---	---
---	277	279	281	286
239	245	247	250	252
---	198	211	221	233

TABLE XIII (continued)

$Cu(PMT)_6(ClO_4)_2$	$Zn(PMT)_6(ClO_4)_2$	$Fe(PMT)_6(ClO_4)_3$	$Cu(PMT)_4(ClO_4)_2$	$Cu(PMT)_2ClO_4$
675	675	674	673	678
628 sh	628 sh	630 sh	634	632 sh
619	619	620	618	620
499	499	499	500	501
448	443	443	452	459
401	396	394	392	386
372	370	372	---	371
340	337	340	---	---
300	292	290	288	---
276	---	---	---	---
288	279	278	---	281
256	247	247	266	255
237	211	212		199

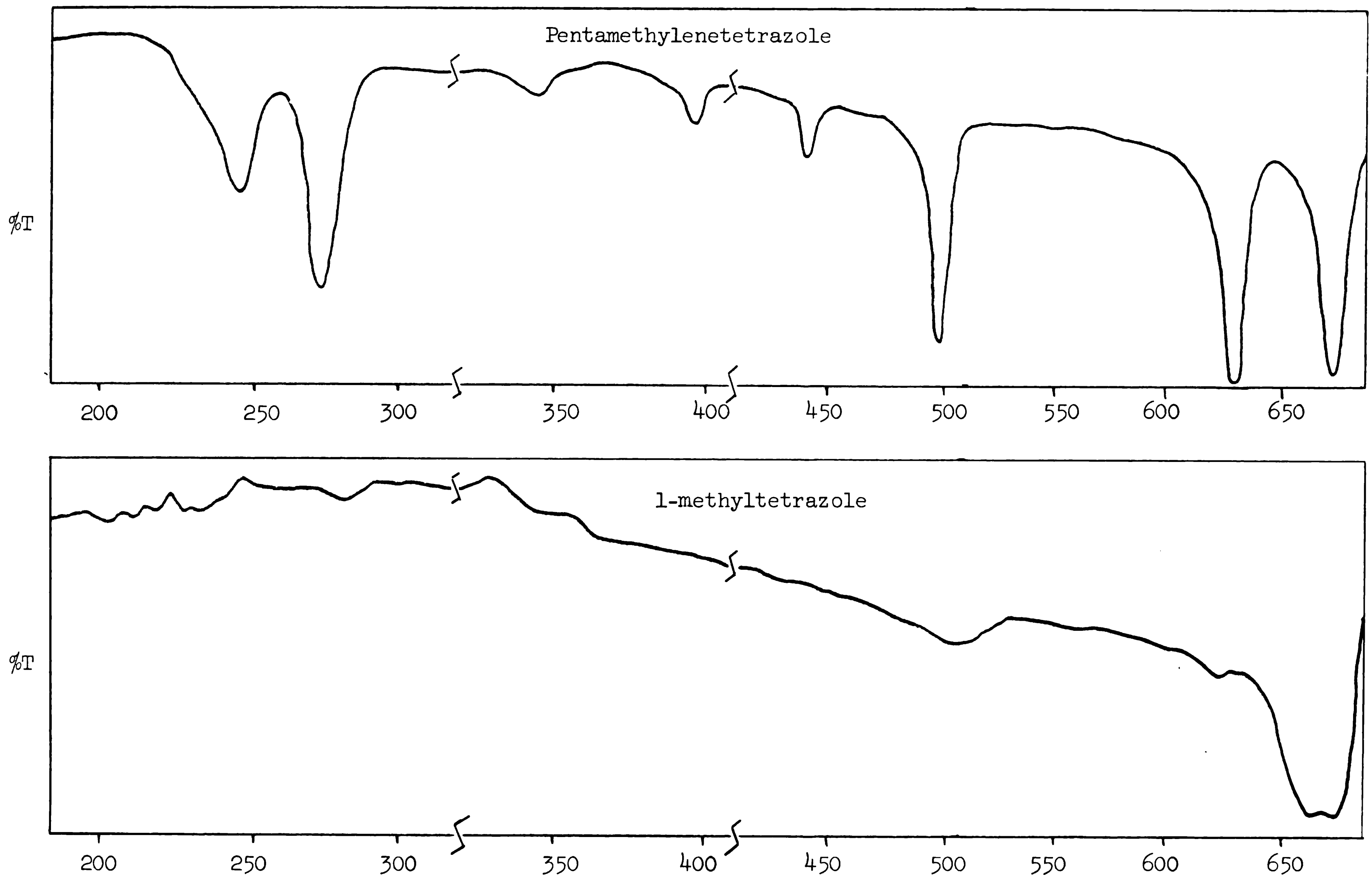

Figure 28. Far Infrared Absorption Spectra (in cm^{-1}). Nujol mull.

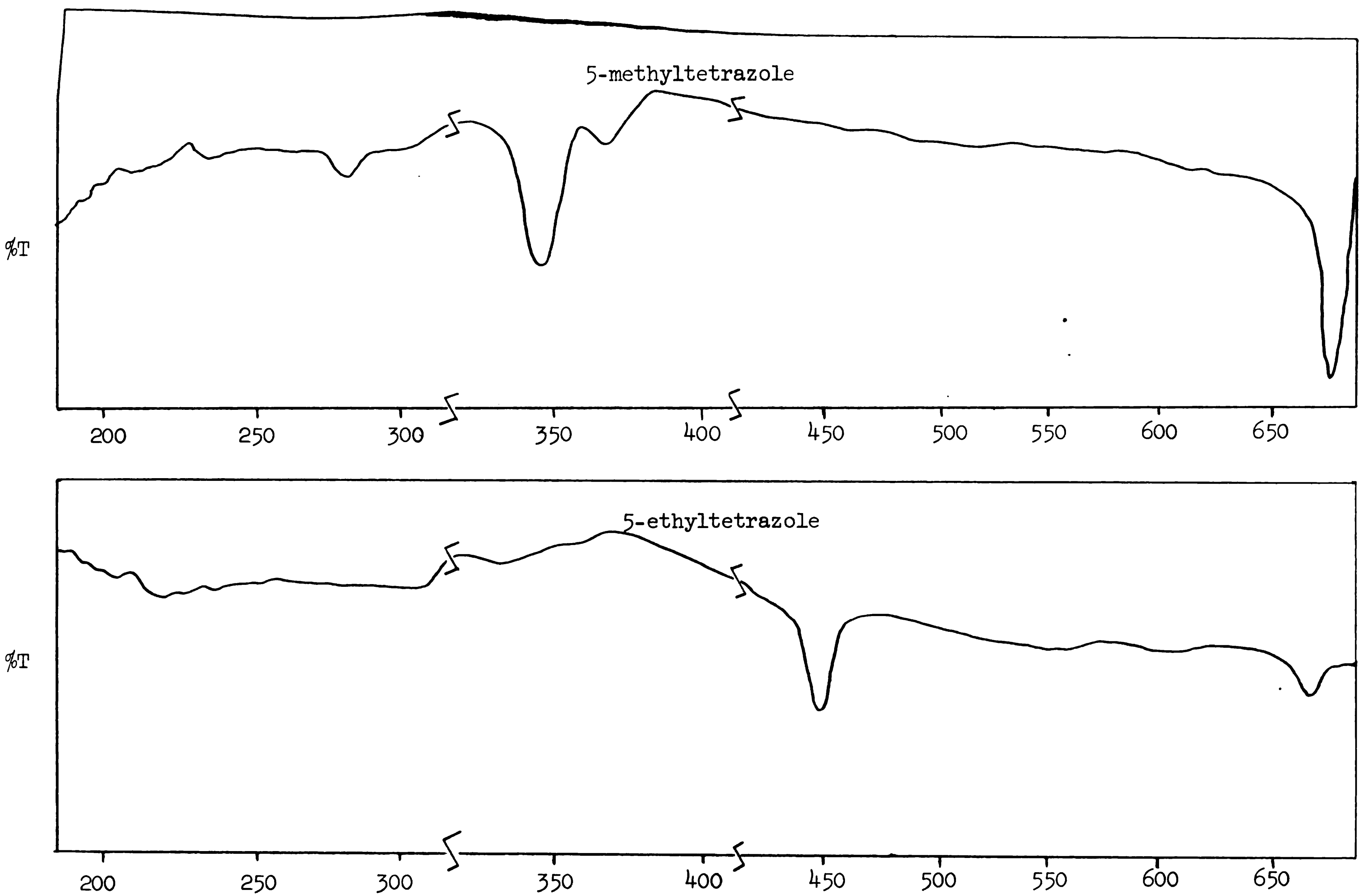

Figure 29. Far Infrared Absorption Spectra (in cm^{-1}). Nujol mull.

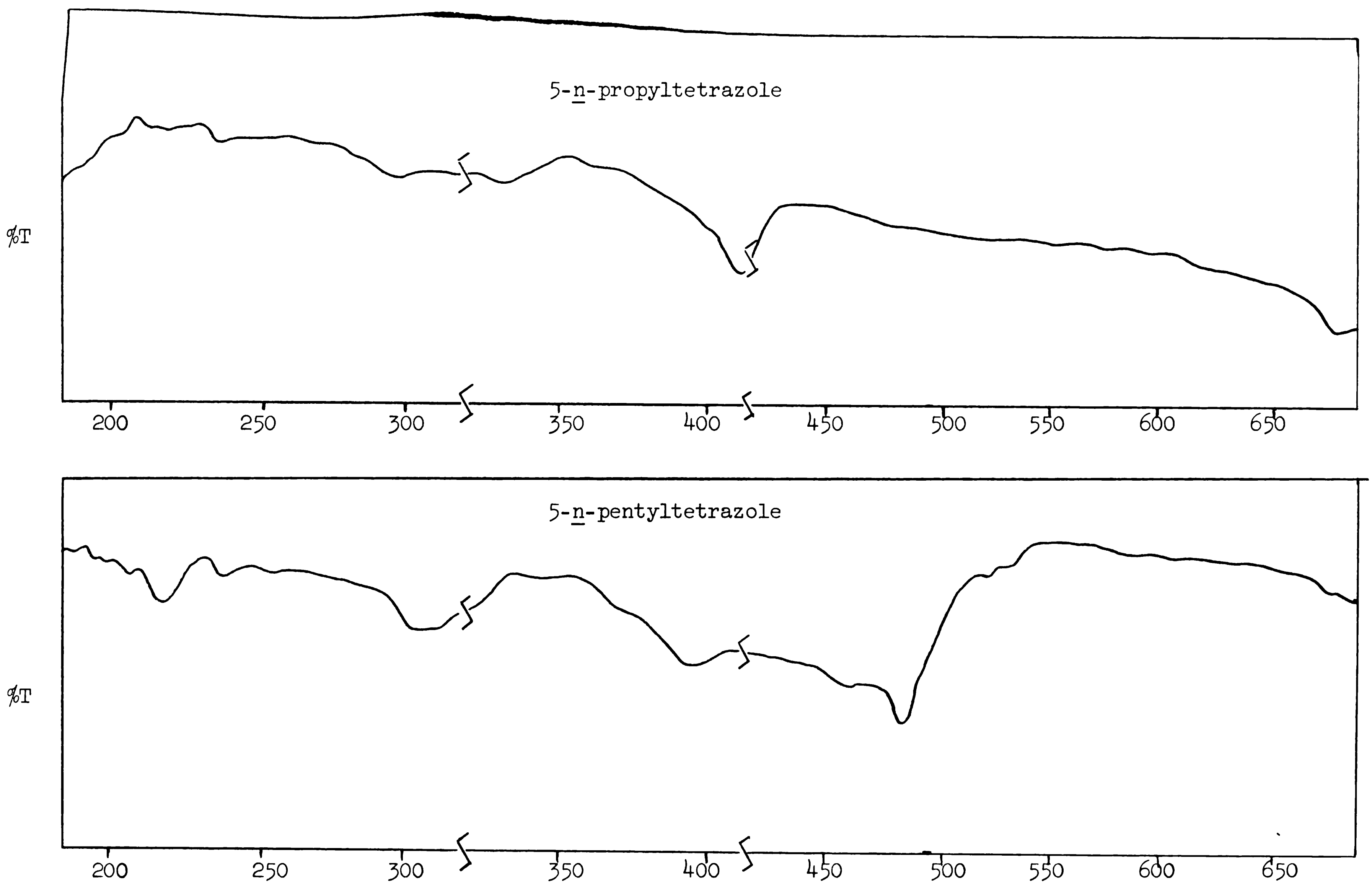

Figure 30. Far Infrared Absorption Spectra (in cm^{-1}). Nujol mull.

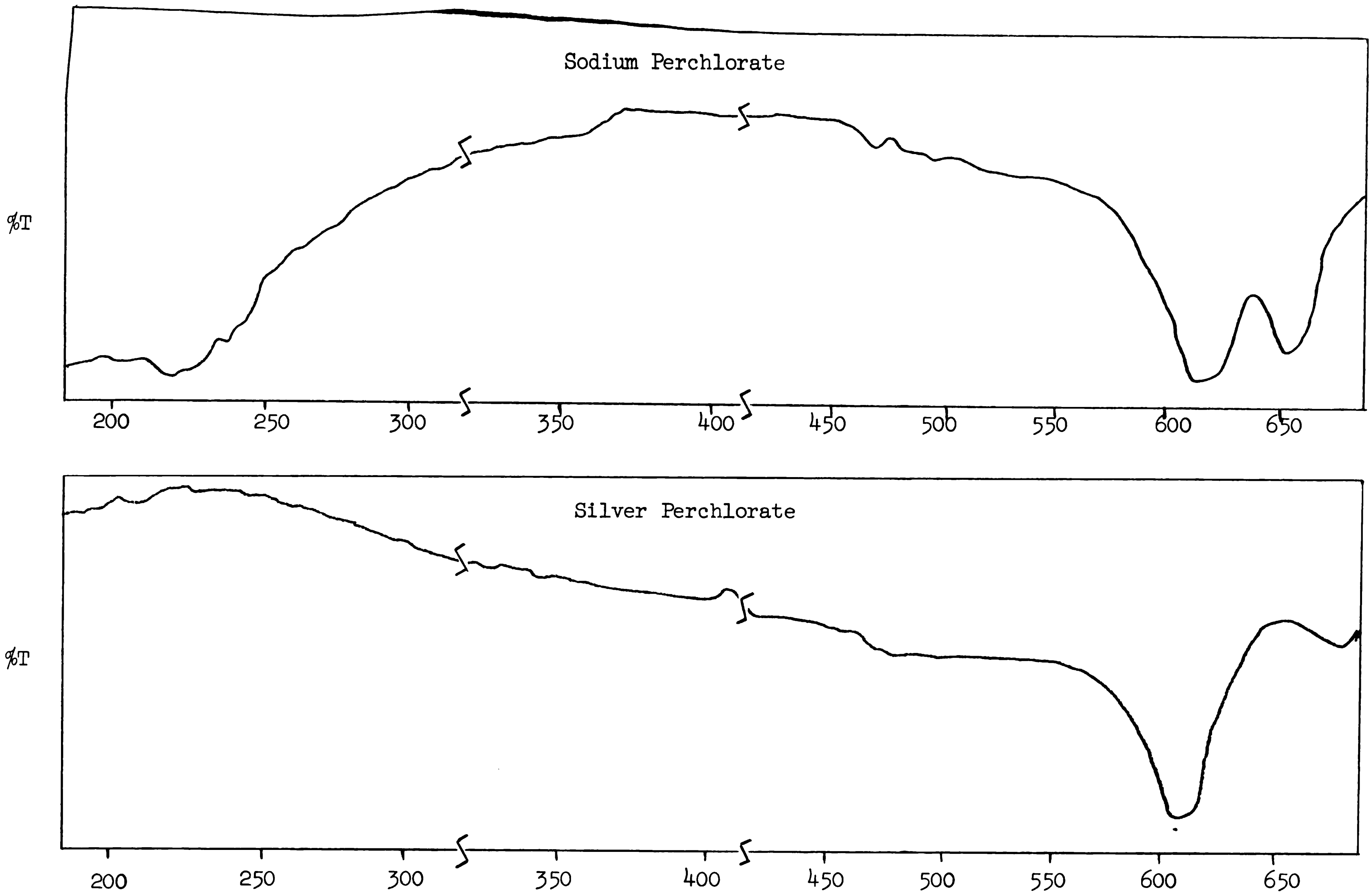

Figure 31. Far Infrared Absorption Spectra (in cm^{-1}). Nujol mull.

(Table XIII, Figures 32-35). The appearance of the perchlorate band is apparent as the broadening of the 628 cm^{-1} band. The other two new bands are located in the 302-276 cm^{-1} and 236-198 cm^{-1} regions. Since they are not present in the spectrum of PMT, they evidently result from the coordination of PMT with the metal ions.

The frequency of the metal-nitrogen asymmetrical stretch can vary from approximately 250 to 450 cm^{-1}. Sharp _et al_. (102) suggested that in complexes formed between transition metal halides and substituted anilines the bands found near 400 cm^{-1} could be tentatively assigned to the nitrogen-metal vibrations. Jungbauer and Curran (103), in their study of aniline complexes, speculated that bands found in the 450-370 cm^{-1} region may be associated with the metal-nitrogen stretching vibrations. Bands tentatively assigned to the metal-nitrogen stretch have been found in the 267-249 cm^{-1} region for 2,2'-bipyridyl amine complexes of cobalt(II), copper(II), zinc(II) and palladium(II) (104). Goldstein _et al_. (105) assigned the asymmetric stretch to the 254 $\pm$ 13 cm^{-1} band of complexes of copper(II) halides and heterocyclic bases. Clark and Williams (106) found that the spectra of many octahedrally coordinated metal-pyridine complexes show a band in the 215-240 cm^{-1} region which was considered to originate from a metal-nitrogen vibration. Sharp _et al_. (107)

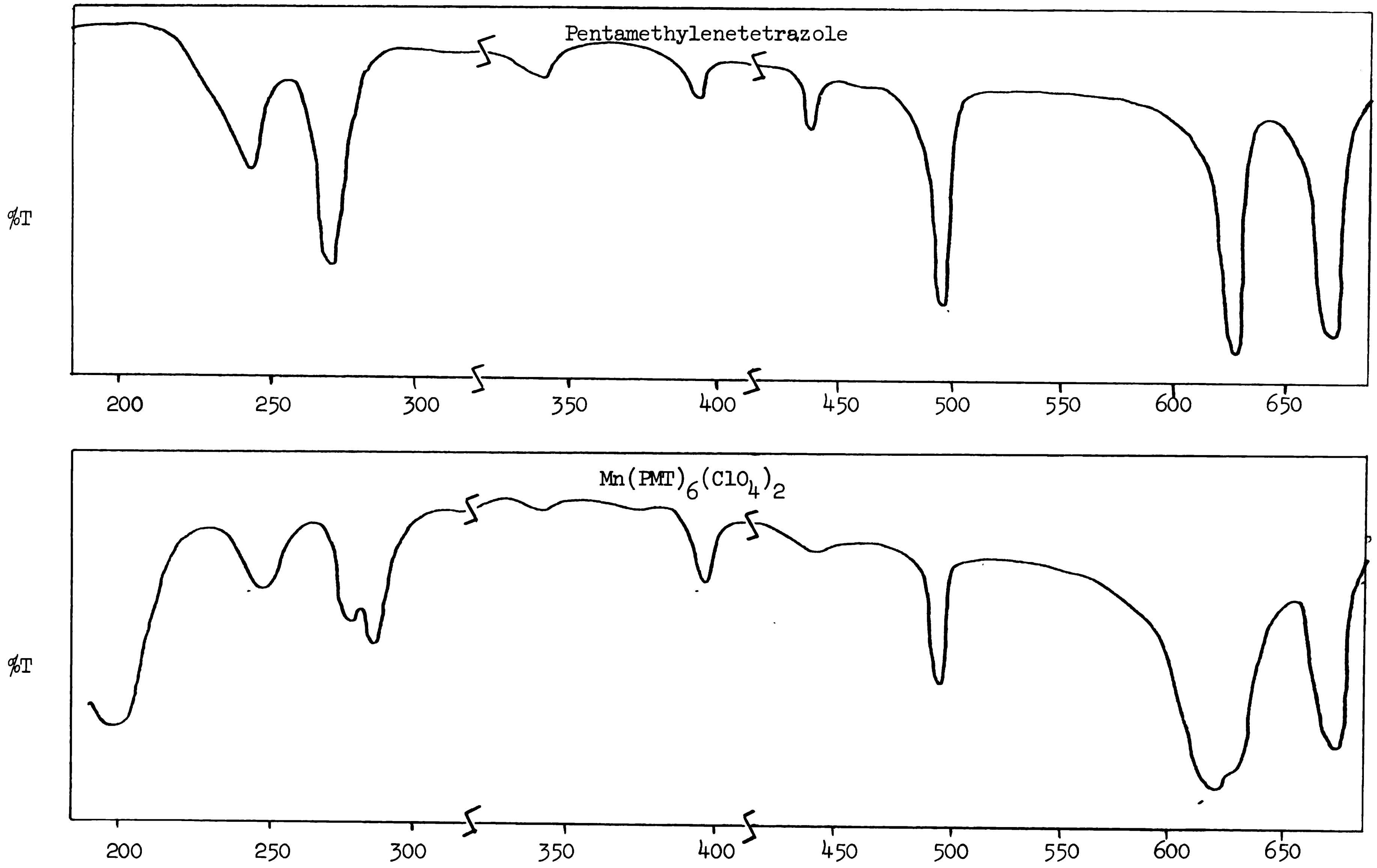

Figure 32. Far Infrared Absorption Spectra (in cm^{-1}). Nujol mull.

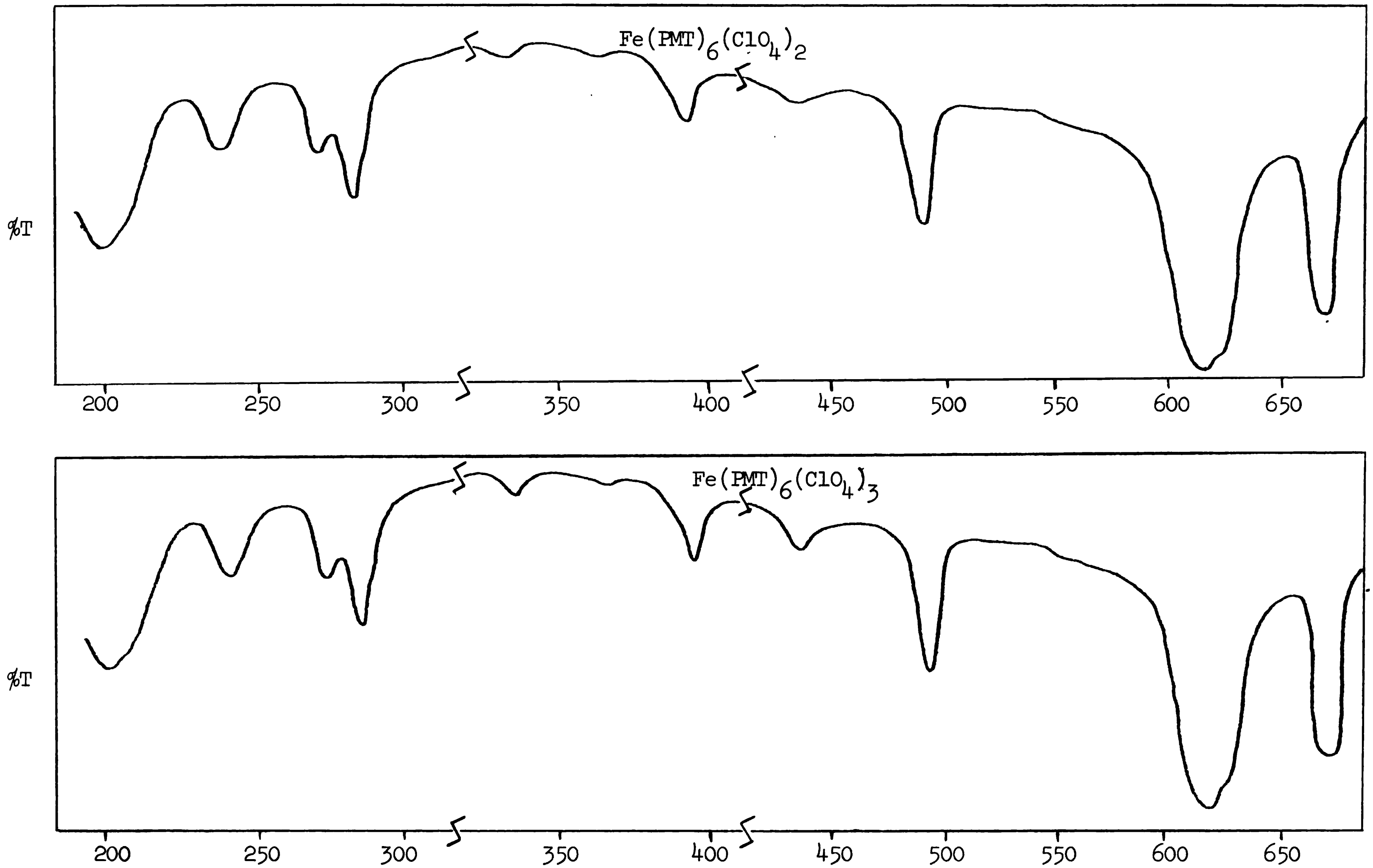

Figure 33. Far Infrared Absorption Spectra (in cm^{-1}). Nujol mull.

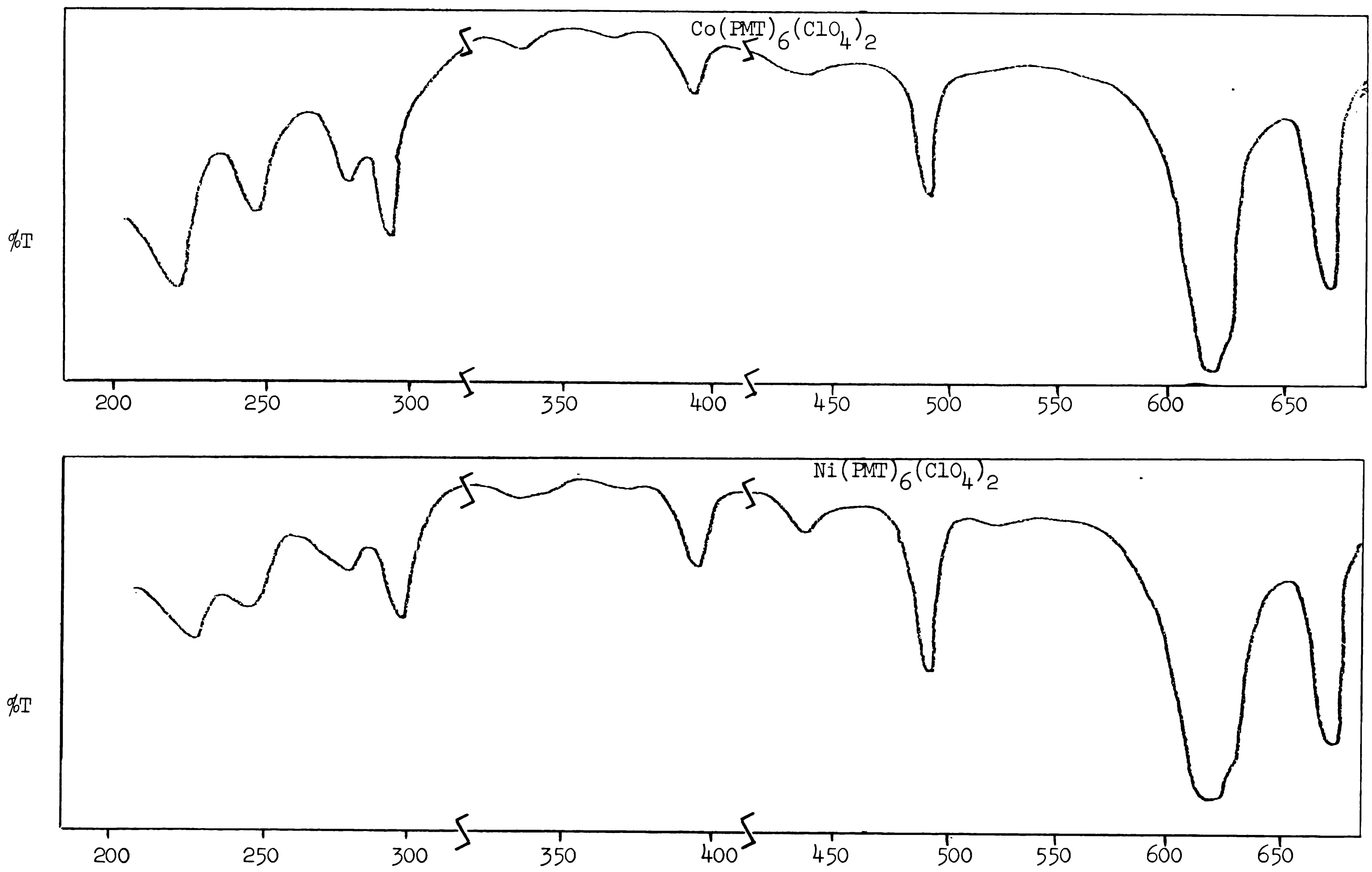

Figure 34. Far Infrared Absorption Spectra (in cm^{-1}). Nujol mull.

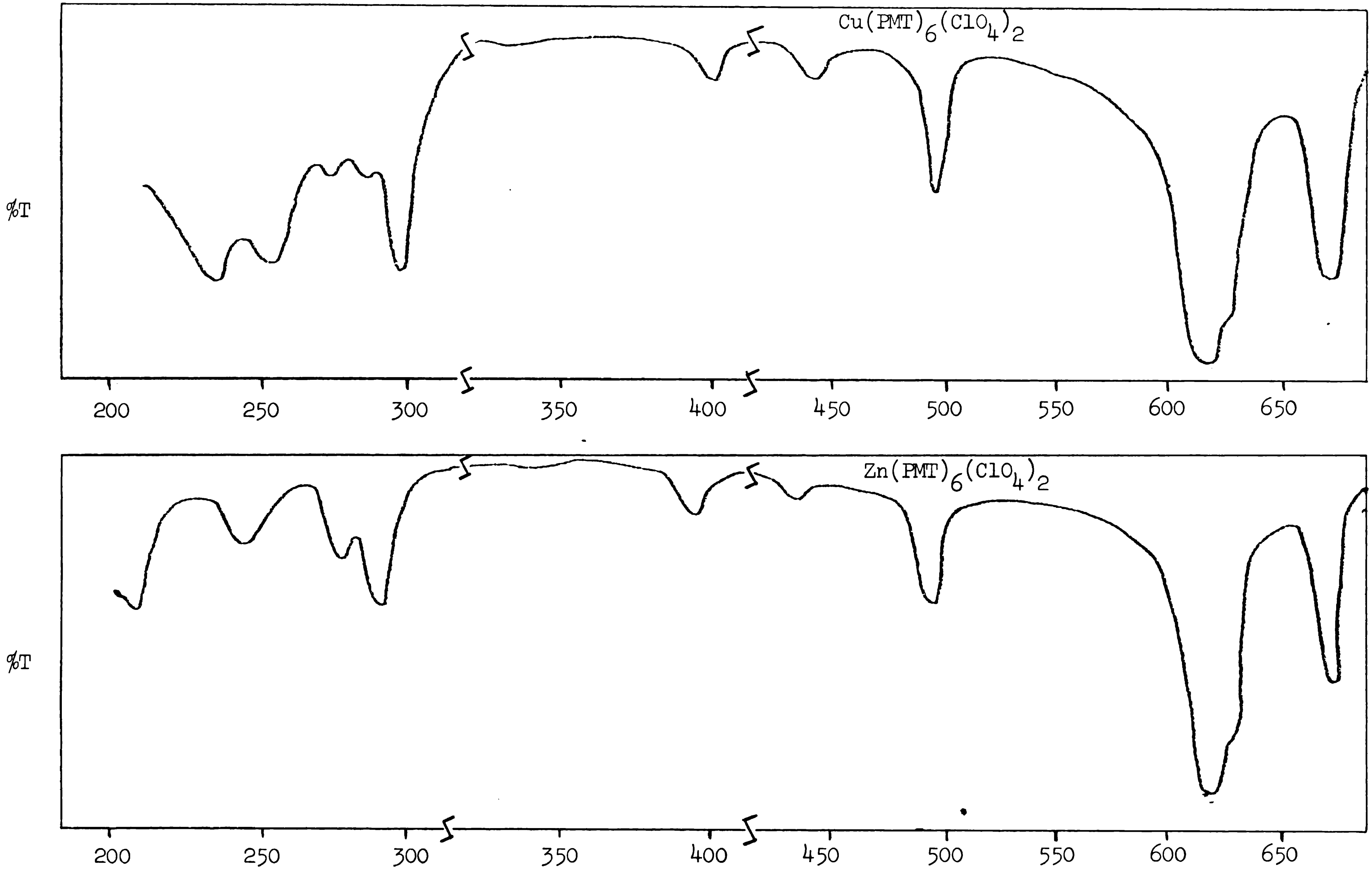

Figure 35. Far Infrared Absorption Spectra (in cm^{-1}). Nujol mull.

investigating some transition metal halide complexes with substituted pyridines found that all spectra show broad bands, often at low intensity, near 240 cm^{-1} which they assigned to the metal-nitrogen stretch. Therefore, the low intensity band, which appears in the 277-288 cm^{-1} region has been very tentatively assigned to the asymmetric stretch of the metal-nitrogen bond. The lowest frequency band in the 236-198 cm^{-1} region was tentatively assigned to the metal-ligand deformation (105).

Inspection of the spectra shows a shifting of all the bands in the 320-180 cm^{-1} region, except for the 300 cm^{-1} band of the copper(II) complex and all of the bands of the zinc(II) complex, to higher energies. The frequencies increase with a decrease in ionic radius (increasing in polarizing ability) of the metal. This same type of systematic band shift has been noted in pyridine complexes of divalent transition metal halides (108). The shift on coordination of the 266 and 239 cm^{-1} bands of PMT follows the general tendency for the fundamental modes of the complexed base to be at a slightly higher frequency than those of the free base. This could arise from a general "tightening-up" of the pentamethylene ring of the ligand on coordination (105).

The copper(II) complex shows an additional weak band at 276 cm^{-1}. This may be another metal-nitrogen stretch with a greater bond distance. This could indicate two different Cu-N bond distances and would be in accord with the proposed tetragonal structure of the complex. All of the hexakis-transition metal complexes give rise to essentially the same type of spectrum which implies that their bonding must be very similar.

Tetrakis(pentamethylenetetrazole)copper(II) Perchlorate

The far infrared spectrum of this complex is similar to the hexakis(PMT)copper(II) perchlorate complex in the 700-350 cm^{-1} region. In the 350-180 cm^{-1} region, however, the absorptions are much broader, and there is considerable overlap of the bands making correlation with the spectrum of hexakis(PMT)copper(II) perchlorate difficult (Table XIII, Figure 36). The slight shoulder at 294 cm^{-1} could be the metal-nitrogen asymmetric stretch. The absorptions at 288 and 266 cm^{-1} could correlate with the 266 and 239 cm^{-1} bands of PMT respectively while the 246 cm^{-1} shoulder probably arises from the bending of the metal-ligand bond.

Bis(pentamethylenetetrazole)copper(I) Perchlorate

The far infrared spectrum of this complex shows the characteristic PMT spectrum in the region of 700-400 cm^{-1} (Table XIII, Figure 36). From 400-180 cm^{-1} there is little resemblance to the other coordinated complexes or to PMT. The wide, broad band at approximately 380 cm^{-1} is

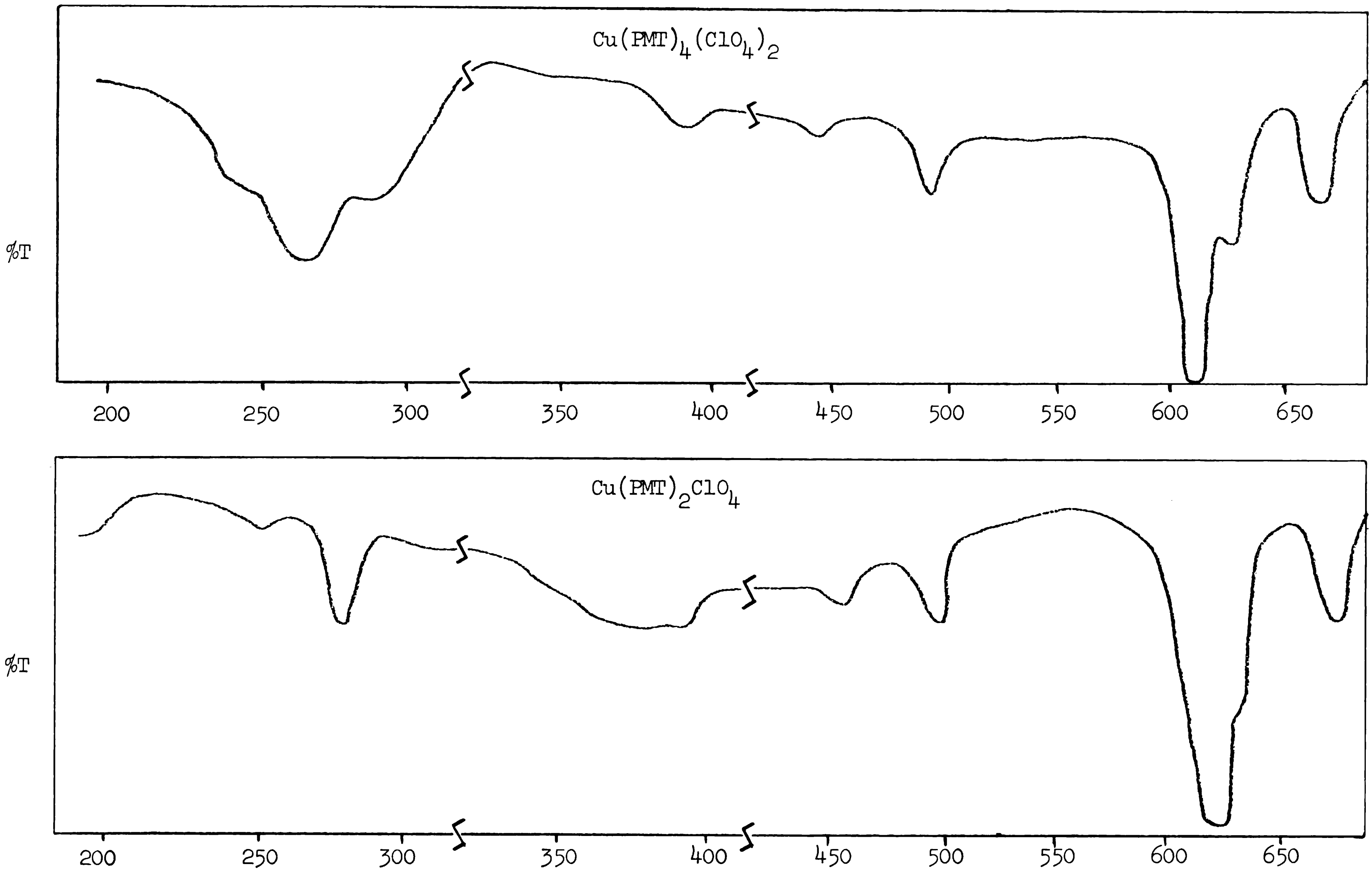

Figure 36. Far Infrared Absorption Spectra (in cm^{-1}). Nujol mull.

new and has not yet been tentatively assigned. In the 300-180 cm^{-1} region there is a band at 281 cm^{-1} and what appear to be bands at 255 and 198 cm^{-1}. The 281 and 255 cm^{-1} bands could be assigned to the 266 and 239 cm^{-1} bands of PMT. An alternative possibility for the 281 band is the metal-nitrogen asymmetric stretch. The 198 cm^{-1} band probably corresponds to the metal-ligand bending mode.

III. SUMMARY AND CONCLUSIONS

This investigation consisted primarily of the preparation and characterization of a new series of six coordinated complexes of pentamethylenetetrazole with manganese(II), iron(II), iron(III), cobalt(II), nickel(II), copper(II), and zinc(II) perchlorate. Tetrakis(PMT)-copper(II) and bis(PMT)copper(I) perchlorate were also prepared and characterized. The hexakis-transition metal and bis(PMT)copper(I) complexes were obtained as micro-crystalline powders while the tetrakis(PMT)copper(II) and hexakis(PMT)nickel(II) complexes were obtained as crystals from acetic acid solution and water respectively. One of the experimental difficulties was that no method for the purification of the solids, other than washing with the solvent or ether, could be devised.

Some general information about the configurations of all these complexes can be obtained from their respective infrared spectra. The infrared region (5000-650 cm^{-1}) yields little information concerning the complexation of the PMT ligand to the metal. More precise information is obtained, however, from the symmetric stretch ν_1 (~932 cm^{-1}) and asymmetric stretch ν_3 (~1090 cm^{-1}) of the perchlorate ion. Since all the spectra (Figures 18-27) show that the ν_3 band is not split and there is no infrared activation of the theoretically infrared inactive ν_1 band, one can conclude that the perchlorate ion associated with these complexes is not coordinated to the central metal ion.

The far infrared spectra of the complexes, however, are of more interest because the metal-nitrogen stretching frequency would be found in this region, and it could provide direct evidence of metal-nitrogen coordinate bond. The unsymmetrical stretch has previously been located only for ammonia complexes of trivalent metals where they occur in the 500 cm^{-1} region (109).

Powell and Sheppard (110) have assigned an extremely weak band at 502 cm^{-1} to the metal-nitrogen unsymmetrical stretch in hexakis-amminecobalt(III) chloride. Corresponding bands are clearly seen in tetramminepalladium(II) bromide and tetramminepalladium(II) tetrachloropalladate-(II) (111). Coates and Parkin (112), explaining the weakness of this band, suggest the formation of two neutral species in the limit of the extension of the metal-ligand bond. Therefore, upon vibration there is a small change in dipole moment with bond length of the metal-nitrogen bond.

The frequency of the metal-nitrogen asymmetrical stretch can vary from approximately 250 to 450 cm^{-1} (102-107) while the metal-ligand deformation mode has been located in the 200 cm^{-1} region (105). In the spectra of our complexes (Figures 28-36) two new bands appear in the

277-288 cm^{-1} and 236-198 cm^{-1} region. Since they are not present in the spectrum of PMT, they evidently result from the coordination of PMT with the respective metal ions. The 266 cm^{-1} PMT band appears to be split into two bands, one of slightly higher and another of lower frequency. The exact position of these bands varies with the respective complex. Likewise, a new band appears in the 236-198 cm^{-1} region. The low frequency band of the new doublet is tentatively assigned to the asymmetrical stretch of the metal-nitrogen bond while the 236-198 cm^{-1} band is tentatively assigned to the metal-ligand deformation vibration. These assignments are based on studies of the metal-nitrogen stretch and deformation frequencies described in the literature (100-108).

Bis(pentamethylenetetrazole)copper(I) Perchlorate

This complex is prepared starting with copper(II) perchlorate hexahydrate. Therefore, a reduction takes place. This fact has been confirmed by a positive chemical test for copper(I) ion, ESR studies, magnetic susceptibility studies, elemental analysis and, more recently, by polarographic studies in acetonitrile which give only a single wave for the reduction of copper(I) to elemental copper (113). While copper is clearly the reduction product, the nature of the oxidation product is rather obscure; and no explanation of the reduction and oxidation mechanism can be made at this time.

Hexakis(pentamethylenetetrazole)nickel(II) Perchlorate

In general, hexacoordinated nickel complexes are blue or green in color except where the nickel(II) ion is strongly coordinated. When this is the case, a pink color is observed (114). The complete X-ray structure determination on hexammine nickel(II) chloride, bromide, iodide, and perchlorate have been obtained (114). A small deviation from regular octahedral arrangements of the attached groups, so that the axial bonds are slightly longer, has been observed in some cases. Drago *et al*. (115) prepared and characterized hexakis methyl-, ethyl-, *n*-propyl-, and isopropyl-amine nickel(II) perchlorate complexes and determined their spectra. However, they were unable to prepare the six-coordinate nickel(II) complexes of dimethyl- and trimethylamine. Weinland, Effinger and Beck (116) reported the preparation and isolation of hexakis(pyridine)nickel(II) perchlorate in the form of blue prismatic crystals, however, there is some doubt that this complex was actually prepared. Drago and Rosenthal (117), however, could only report the existence of hexakis-(pyridine)nickel(II) ion in nitromethane solution by adding an excess of pyridine. As the pyridine/nickel molar ratio is increased, the color changes from a blue-green to a deeper blue, and the electronic absorption bands shift to slightly longer wavelengths with an increase in the molar absorptivity of each respective band. Bjerrum (118), in his classic study of the nickel(II)-ammine system in aqueous solution, found that the electronic absorption bands shift to higher energies; at the same time, the absorption increases uniformly to the tetrammine complex. When still more ammonia is introduced in the tetrammine complex, the absorption decreases via the pentammine to the hexammine complex while the absorption maximum continues to move toward higher energies. Quagliano <u>et</u> <u>al</u>. (119) found that on addition of an excess of 3,4 or 3,5-lutedine to a yellow dichloromethane solution of tetrakis(3,4-lutedine)-nickel(II) perchlorate, the blue hexakis (3,4 or 3,5-lutedine)nickel(II) perchlorate complex forms in solution. However, attempts to isolate the solid complex failed as it reverted back to the respective tetrakis (3,4 or 3,5-lutedine) complex. Krause and Wickenden (120) prepared and characterized hexakis(acetonitrile)nickel(II) perchlorate, bis(perchlorato)tetrakis(acetonitrile)nickel(II), and bis(perchlorato)bis(acetonitrile)nickel(II). The latter two complexes were prepared by heating hexakis(acetonitrile)-

nickel(II) perchlorate under vacuum until 2 and 4 moles of acetonitrile were removed. A coordination number of six for the nickel(II) ion was supported by the visible electronic spectral data and magnetic susceptibilities.

The classic spectrum for octahedral complexes is obtained for hexakis(PMT)nickel(II) perchlorate (Figure 11) with the ν_1 and ν_2 absorption bands located at 10,500 (955 mμ, apparent ϵ_{max} 8.0) and 17,400 cm^{-1} (575 mμ, apparent ϵ_{max} 9.5). The highest frequency absorption band, located at approximately 25,000 cm^{-1} is shifted to higher energies on complexation and is not observed due to solvent absorption at approximately 25,650 cm^{-1} (390 mμ).

This spectrum compares well with that of tris(ethylenediamine)nickel(II) ion (88) indicating that PMT is a stronger ligand than water. This may explain the reason why hexakis(PMT)nickel(II) perchlorate can be precipitated from aqueous solution. The ratio ν_2/ν_1 for the complex is 1.66 which is the same as that observed for tris(ethylenediamine)nickel(II) ion and compares well with the calculated value of 1.8 which is one of the distinguishing features of octahedrally coordinated complexes (121).

The reflectance spectrum of the solid complex is in good agreement with these results and shows absorbances at 9,760 (ν_1, 1025 mμ), 16,000 (ν_2, 625 mμ) and 26,300 cm^{-1} (ν_3, 380 mμ).

When a nickel(II) atom is surrounded by six identical groups such as the hexammine or hexaquo nickel(II) ions, the orbital contribution in excess of the "spin only" value of 2.83 B.M. is small; and magnetic moments of the order of 3.1 to 3.2 B.M. are observed (114). Magnetic susceptibility measurements indicates that the hexakis(PMT)-nickel(II) perchlorate complex has a magnetic moment of 2.92 B.M. corresponding to two unpaired electrons, as expected for the octahedral complex. The two unpaired electrons located in the 3d shells force the use of outer orbital sp^3d^2 hybridization, therefore the bonding is ionic and octahedral configuration is indicated.

The crystals of the hexakis(PMT)nickel(II) complex precipitated from aqueous solution were of sufficient purity and definition so that single crystal studies are being performed on it by Dr. R. C. Srivastava of this laboratory. Preliminary evaluation of the data indicates that the space group is $P6_3/m$ with the following unit cell dimensions:

$$a_o = b_o = 26.99 \text{ Å}, \; c_o = 7.60 \text{ Å}$$

and density measurements indicate that there are four hexakis(PMT)nickel(II) perchlorate molecules per unit cell.

Hexakis(pentamethylenetetrazole)cobalt(II) Perchlorate

The cobalt(II) ion usually forms octahedral and tetrahedral complexes. Planar complexes, however, have been prepared in solution with chelating type ligands. For example, bis(aminooxalato)cobalt(II), bis(dimethylglyoximato)copper(II) and bis(o-aminophenol)cobalt(II) all contain only one unpaired electron (87). Addition of ammonia to an aqueous solution of cobalt(II) causes formation of the octahedral hexammine cobalt(II) ion, and several crystalline complexes have been isolated. Bjerrum (122) calculated the overall formation constant for the hexammine cobalt(II) ion to be 1.29×10^5 with stepwise formation constants for k_5 and k_6 of 1.51 and 0.24 respectively. In a continuation of this study, Bjerrum calculated the overall formation constant of the octahedral tris(ethylenediamine)cobalt(II) complex to be 6.6×10^{13} (the stepwise formation constant k_3 is 1.2×10^3). This is a considerably larger formation constant than that calculated for hexammine cobalt(II) ion.

The cobalt(II) ion has a d^7 electronic configuration, and its ground state configuration in an octahedral field may be either low or high spin with 1 or 3 unpaired electrons respectively. High spin octahedrally coordinated cobalt(II) ions should, therefore, have three spin-allowed d-d transitions, which are experimentally seen. The high-spin octahedral spectra are characterized by three absorption bands of low molar absorptivity found at approximately 8,350 (ν_1), 17,850 (ν_2) and 20,000 (ν_3)cm^{-1} (1196, 560 and 500 mμ respectively) (123). The most intense band is ν_2 having a molar absorptivity of approximately 10 while ν_3 usually appears as a shoulder on the high frequency side of the ν_2 band. Tetrahedral cobalt(II) complexes also have three spin-allowed d-d transitions. The most intense transition occurs from the $^4A_2$ ground state to the $^4T_1(P)$ state, and its absorption band occurs at approximately 14,500 cm^{-1} (690 mμ, ϵ_{max} 600). The other two transitions, i.e., the $^4A_2$-$^4T_2$ and $^4A_2$-$^4T_1(F)$, occur at approximately 4000 and 7200 cm^{-1} (2500 and 1390 mμ respectively) and usually are weak bands (123).

The classic spectrum for octahedral complexes is also obtained in nitromethane for hexakis-(PMT)-cobalt(II) perchlorate (Figure 10) having a weak broad absorption band, ν_1, at 9300 cm^{-1} (1075 mμ, ϵ_{max} 5) and a more intense unsymmetrical band at 20,600 cm^{-1} (485 mμ, ϵ_{max} 22) which is made up of ν_2 and ν_3. From the shifting of these absorptions to higher energies relative to the spectrum of cobalt(II) perchlorate hexahydrate (Figure 10), it appears that in this system PMT may be a slightly stronger ligand than water.

The reflectance spectrum of the solid complex correlates closely with the respective spectrum obtained in nitromethane having absorption maxima at approximately 20,600 and 8,775 cm^{-1} (485 and 1040 mμ respectively) in which the absorption maxima at 20,600 cm^{-1} is probably made up of ν_2 and ν_3.

The magnetic moment of hexakis(PMT)cobalt(II) perchlorate was calculated to be 4.60 B.M. which agrees well with literature experimental magnetic moments ranging from 4.30 to 5.20 B.M. (91). While the spin-only magnetic moment is 3.89 B.M. for three unpaired electrons, the higher moments obtained are due to high orbital contributions (87).

Since six coordinate inner orbital complexes of cobalt(II) are unlikely, as they would require the promotion of one or two electrons to the 4d level, the hexakis-(PMT)cobalt(II) perchlorate complex probably forms an outer-orbital complex utilizing sp^3d^2 hybridized orbitals (124).

Hexakis and Tetrakis(pentamethylenetetrazole)copper(II) Perchlorate

The stereochemistry of copper(II) is unusual in that a regular octahedral environment of the copper(II) ion rarely, if ever, occurs. The copper(II) ion usually exists in a distorted octahedral configuration having four short and two longer bond distances, a square coplanar configuration, or in a tetrahedral configuration. The vast majority of the copper(II) compounds are of the distorted octahedral or its limiting case, the square coplanar configuration.

Copper(II) compounds with a d^9 electronic configuration with a single unpaired electron are normally paramagnetic and, theoretically, they should have only one transition from the ground state ^2Eg to the only excited state, $^2T_{2g}$. The ^2Eg state, however, is highly susceptible to a Jahn-Teller configuration instability which predicts that distortion of the regular octahedron will occur whenever the resulting splitting of the energy yields additional stabilization. Therefore, if the octahedron is elongated along the z axis by increasing the metal-ligand distances, the degeneracy of the $^2T_{2g}$ and ^2Eg levels is removed. For this reason, regular octahedrally coordinated copper(II) complexes should not exist (125). Peyronel (126) confirmed this with his X-ray studies of hexammine copper(II) bromide which showed the group symmetry to be cubic and indicated the configuration about the copper(II) ion to be a slightly distorted octahedron.

Since the tetragonal distortion splits the ^2Eg and $^2T_{2g}$ levels, three transitions from the dx^2-y^2 to dxy, dz^2 and degenerate (dxz, dyz) respectively are possible. The mole ratio study of copper(II) perchlorate hexahydrate, tetrakis- and hexakis(PMT)copper(II) perchlorate (Figures 7-9), visible (Figure 12), and reflectance spectra (Figure 15) of the tetrakis- and hexakis(PMT)copper(II) perchlorate all show a single unsymmetrical absorption band in the 15,000-12,500 cm^{-1} (680-800 mμ) region. This absorption consists of two and possibly all three of the above mentioned transitions.

The striking feature of these spectra in nitromethane is the steady shifting with an accompanying increase in molar absorptivity of the copper(II) perchlorate hexahydrate band on the addition of PMT (Figure 7) from 12,900 cm^{-1} (775 mμ, ϵ_{max} 15) to 14,900 cm^{-1} (670 mμ, apparent ϵ_{max} 82.5) where the stoichiometry of the tetrakis(PMT)-copper complex is reached. With the addition of the fifth molecule of PMT, this band continues to increase in absorbance but begins to shift to lower frequencies. When the sixth molecule of PMT is added, the absorption maximum has shifted to a limiting value of 14,200 cm^{-1} (705 mμ, apparent ϵ_{max} 129). Addition of still more PMT does not cause the maximum to shift further. However, the molar absorptivity continues to increase toward what appears to be a limiting value. When the tetrakis- or hexakis-(PMT)-copper(II) complexes (Figures 8,9) are dissolved in nitromethane, the absorption maxima are 14,900 cm^{-1} (670 mμ, apparent ϵ_{max} 80) and 14,700 cm^{-1} (680 mμ, apparent ϵ_{max} 102) respectively. As more PMT is added to each of these solutions, a hypsochromic shift is noted to a limiting value of 14,200 cm^{-1} (705 mμ), both having an apparent molar absorptivity of approximately 130. The reflectance spectra studies (Figure 15) show the same trend where the tetrakis- and hexakis-(PMT)-copper(II) complexes have respective absorption maxima at 16,000 and 13,500 cm^{-1} (625 and 740 mμ). The difference between the visible and reflectance spectra maxima is attributed to solvent effects.

Orgel (127) found in aqueous solution that the replacement of coordinated water molecules by ammonia causes a steady shift of the absorption maximum from 12,500 cm^{-1} (800 mμ, ϵ_{max} 11) to 16,950 cm^{-1} (590 mμ, ϵ_{max} 50) until four ammonia molecules are coordinated. The addition of a fifth ammonia molecule causes the absorption band to shift to 15,150 cm^{-1} (660 mμ), _i.e._, to lower energies. Orgel found no evidence for the addition of a sixth ammonia molecule even in liquid ammonia. Ethylenediammine complexes behave similarly while pyridine does not seem to form complexes with a pyridine/copper ratio greater than 4 to 1.

The magnetic moment of tetrakis- and hexakis(PMT)-copper(II) perchlorate was found to be 1.21 and 1.74 B.M. respectively, while the observed values of the magnetic moment for most copper(II) compounds having ionic or rather weak covalent bonds are 1.70-2.20 B.M. (88). The magnetic moment of hexakis(PMT)copper(II) perchlorate compares well with these values; however, no reason can be given (other than possible experimental error) for the low magnetic moment of tetrakis(PMT)copper(II) perchlorate.

From the above data it appears that these complexes are also of the outer-orbital type. The hexakis(PMT)-copper(II) complex has a distorted octahedral configuration utilizing sp^3d^2 orbitals for bonding, while the tetrakis-(PMT)copper(II) complex has a square coplanar configuration and can be interpreted most naturally in terms of sp^2d hybrid bonds (128).

Hexakis(pentamethylenetetrazole)zinc(II) Perchlorate

Since there are no ligand field stabilization effects in zinc(II) compounds because of their completed d shells, the stereochemistry of these complexes is determined by the zinc(II) ion size, electrostatic and covalent bonding forces. While a coordination number of four, utilizing a tetrahedral configuration, is more common for zinc(II) compounds, a coordination number of six and octahedral configuration are observed with the hexammine (129), hexaquo, and tris(ethylenediammine)zinc(II) complexes (130). Pauling (131) states that a square coplanar configuration is theoretically not possible for metal ions having filled shells; and, accordingly, only four tetrahedral or six octahedral bonds are to be expected.

Pentamethylenetetrazole is a weak electron donor and under anhydrous conditions can form stable complexes with most of the first row transition metal ions. A maximum coordination number of six is possible for each of the metal ions used in this study because partially filled d-orbitals are energetically available for all except zinc(II), referred to above.

Hexakis(PMT)cobalt(II) and nickel(II) perchlorate have been shown to have an octahedral configuration based on their physical properties. The configuration of hexakis(PMT)copper(II) perchlorate and the remainder of the hexakis(PMT) transition metal perchlorates are postulated to be octahedral since the X-ray powder diffraction data showed that all of these six coordinated complexes are isomorphous.

Since the complexes dissolve readily in polar solvents and PMT molecules are satisfying all six coordination sites of the particular transition metal involved, an ionic complex is expected. This is seen experimentally in the infrared spectra of the complexes since the ν_1 and ν_3 bands of the perchlorate anion are unaffected.

The electron spin resonance data indicate that the complexes are in a distorted octahedral or tetragonal configuration, and the metal ligand bond is about 91% ionic. These findings are in good agreement with Pauling's (132) proposed criterion for distinguishing between essentially ionic and essentially covalent bonding between the metal ion and its ligands, where the number of unpaired electrons in a complex as deduced from the measured susceptibility is the same as that expected for the free (gaseous) metal ion. The bonding with ligands is considered to be ionic and due to either coulombic attraction as in $(FeF_6)^{3-}$ or electrostatic polarization of neutral ligands such as PMT by the central metal ion.

A complete and satisfying explanation for the formation of the hexacoordinated copper(II)-PMT complex cannot be given at the present time, however, there are factors other than ligand field energies of the copper(II) ion to be considered. The actual geometry and coordination structure which define the ligand field in a given complex are determined largely by the bonding interaction between the metal ion and the ligand (133). It appears that certain configurations may be obtainable only with the assistance of certain anions such as the perchlorate ion.

Since the perchlorate ion is the least polarizable anion known, it has a very slight tendency to serve as a ligand in complexes which allow for more complete electrostatic polarization type bonding of the PMT molecules to the respective central metal ion.

Since all 1-5 dialkyl substituted tetrazoles, i.e., PMT, are incapable of simple salt formation, the PMT ligand can coordinate through any one of the tetrazole ring nitrogen lone pairs as a σ bond or by interactions of the π electrons associated with the ring. It appears from the physical data evaluated that the lone pair of electrons on the apex nitrogen (the number 3 nitrogen) of the tetrazole ring forms a σ bond with the central metal ion.

The following distorted octahedral configuration (Figure 37) having four equidistant and two longer bond distances is postulated for the hexakis-(PMT)-transition metal ion perchlorates. The tetrakis-(PMT)-copper(II) perchlorate, in all probability, has a square coplanar configuration and could be depicted by extending the two vertical PMT molecules (Figure 37) until they are no longer coordinated.

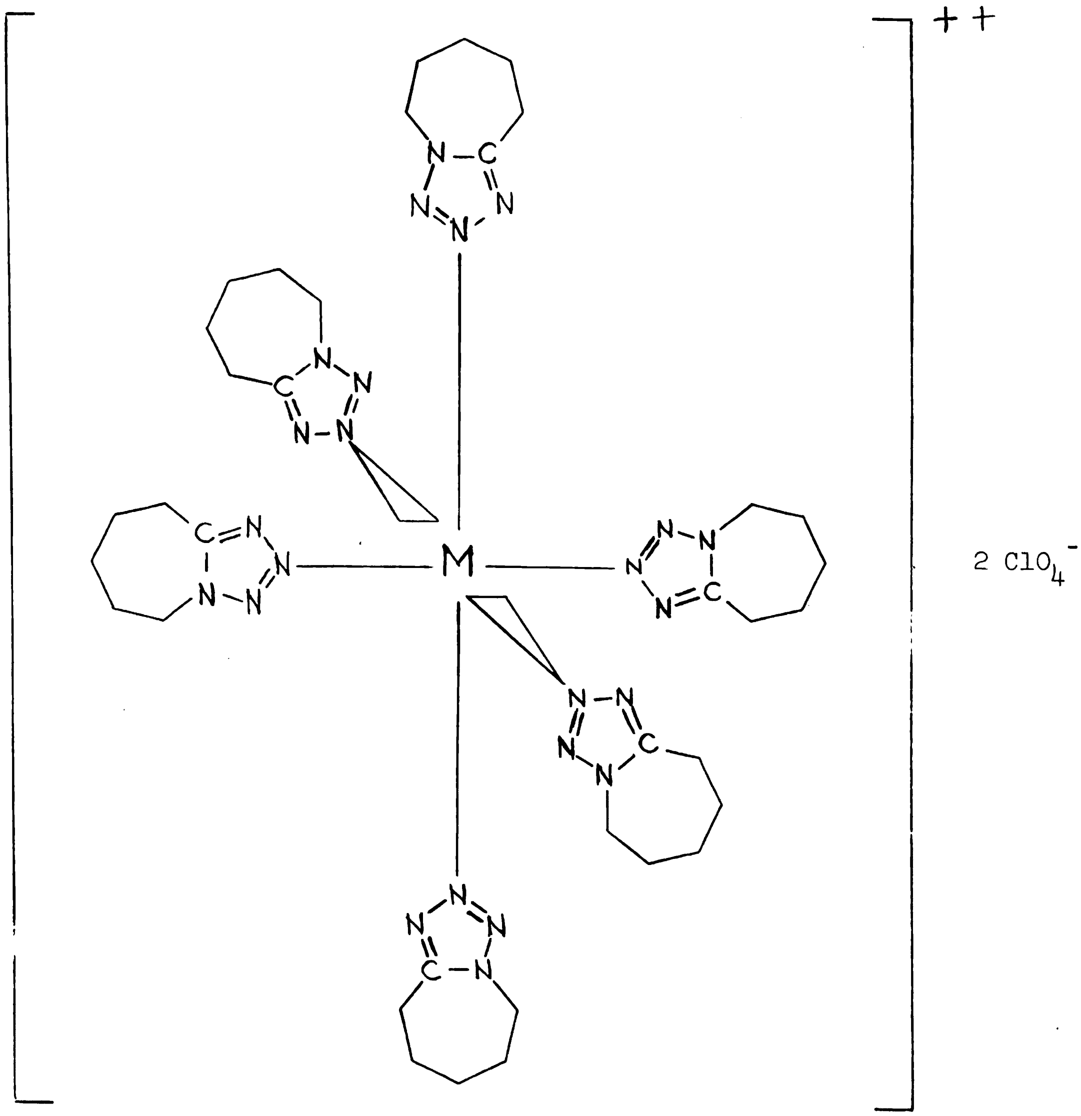

Figure 37. The proposed structural configuration of the hexakis-(pentamethylenetetrazole)-transition metal perchlorate complexes.

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APPENDICES

APPENDIX I

Attempted Determination of the Stepwise Formation Constants of Hexakis-(Pentamethylenetetrazole)-Copper(II) Perchlorate in Nitromethane

As part of this investigation, several attempts were made to determine formation constants for the hexakis-(PMT)-copper(II) perchlorate system which would give an estimate of the electron donor strength of PMT. A knowledge of the formation constant would also lead to a better understanding of the nature of the complex.

From the method of continuous variations (see p. 39) it can be concluded that more than one species is present in solution containing PMT and copper(II) perchlorate. Therefore, the method of Newman and Hume (85) was applied in an attempt to calculate the successive formation constants. The limiting absorbance of a solution where the concentration of PMT was much greater than the total metal concentration was first determined in order to calculate the molar absorptivity at the limiting concentration. Next, the absorbance of solutions containing varying amounts of PMT with constant or varying amounts of metal ion was determined at various wavelengths. When the ratio of PMT to water is large (water being introduced in the form of hydrated salt and as a solvent impurity) the following equation is applicable at the selected wavelengths.

$$\log \left\{ \frac{\epsilon_o M_t - A}{A} \right\} = - \left\{ \log X_t^m / Y_t^s \right\} - \log kn \qquad (1)$$

where:

ϵ_o = The molar absorptivity of the solution which is assumed to be entirely due to the highest complex - MXm,

M_t = The total analytical concentration of the central metal ion,

X_t^m = Total analytical concentration of PMT,

Y_t^s = Total concentration of water,

k_n = Highest stepwise formation constant,

A = Absorbance of the solution,

m = moles of PMT,

s = moles of water.

If the proper values of m and s are assumed, a plot of equation 1 yields a straight line with a slope of negative unity. From the intercept k_n is obtained.

If, on the other hand, there are two species in solution and both are absorbing, the following equation can be applied at those wavelengths where only the highest species is absorbing:

$$A = k_n \left\{ (\epsilon_o M_t - A) X_t^m / Y_t^s \right\} + (\epsilon_{n-m}) M_t \qquad (2)$$

where:

$_{n-m}$ = The molar absorptivity of the next to the highest complex.

In applying equation 2, it is assumed that only one of the two species present is absorbing at the selected wavelength. This is only true if the same value of k_n is obtained from equation 2 as that obtained from equation 1.

The presence of three species is indicated when deviations from straight lines are observed in the plots of equations 1 and 2. The authors point out that other more inclusive equations become applicable when these deviations are observed. Newman and Hume's method depends on reaching a limiting absorbance from which a limiting molar absorptivity can be calculated, and on finding a wavelength where only one of the species in solution is absorbing.

In this study an accurate limiting molar absorptivity could not be determined. Also, upon plotting the first and second equations at various wavelengths, curved lines were obtained which indicated that more than one species was present, and it was not possible to interpret the experimental data which was obtained.

APPENDIX II

Electron Spin Resonance of Hexakis-(Pentamethylenetetrazole)-Manganese(II) and Copper(II) Perchlorates

This work was accomplished by Dr. Henry A. Kuska in this laboratory and is cited here for the sake of completeness. A Varian V-4500 spectrometer equipped with 100 Kc/sec. modulation was used for the measurements. The magnetic field was measured with a proton nuclear magnetic resonance gaussmeter.

Hexakis-(Pentamethylenetetrazole)-Manganese(II) Perchlorate

The ESR data are given in Table XIV and Figure 38 along with some literature data for comparison. The value of the ionicity, $N^2 = 0.91$ for $Mn(PMT)_6(ClO_4)_2$, indicates that the PMT ligand is a weak electron donor in this system. Although for other transition metal complexes the interpretation of ESR metal hyperfine splittings in terms of ionicity of the metal-ligand bonds is presently too complex to have a quantitative significance (134), for Mn(II) a plot of the percent ionicity of the host lattice as determined by Pauling's equation (135,136) for the ionic character of a bond

$$I = 1 - \exp \frac{-(X_A - X_B)^2}{4}$$

(where X_A and X_B refer to the values of the electro-

TABLE XIV

Electron Spin Resonance Data for Some Mn(II) Complexes

	$A(10^{-4}cm^{-1})$	g	$D(10^{-4}cm^{-1})$	N^2	Reference
$Mn(PMT)_6(ClO_4)_2$ in $Zn(PMT)_6(ClO_4)_2$	84.4	2.001	750	0.91	*
$Mn(PMT)_6(ClO_4)_2$ in $Fe(PMT)_6(ClO_4)_2$	84	2.00	750	0.91	*
$Mn(PMT)_6(ClO_4)_2$ in CH_3NO_2	87.1	2.001	0	0.94	*
$Mn(H_2O)_6^{2+}$	89.0				138
$Mn(CN)_6^{3-}$	78.3				139

*This investigation.

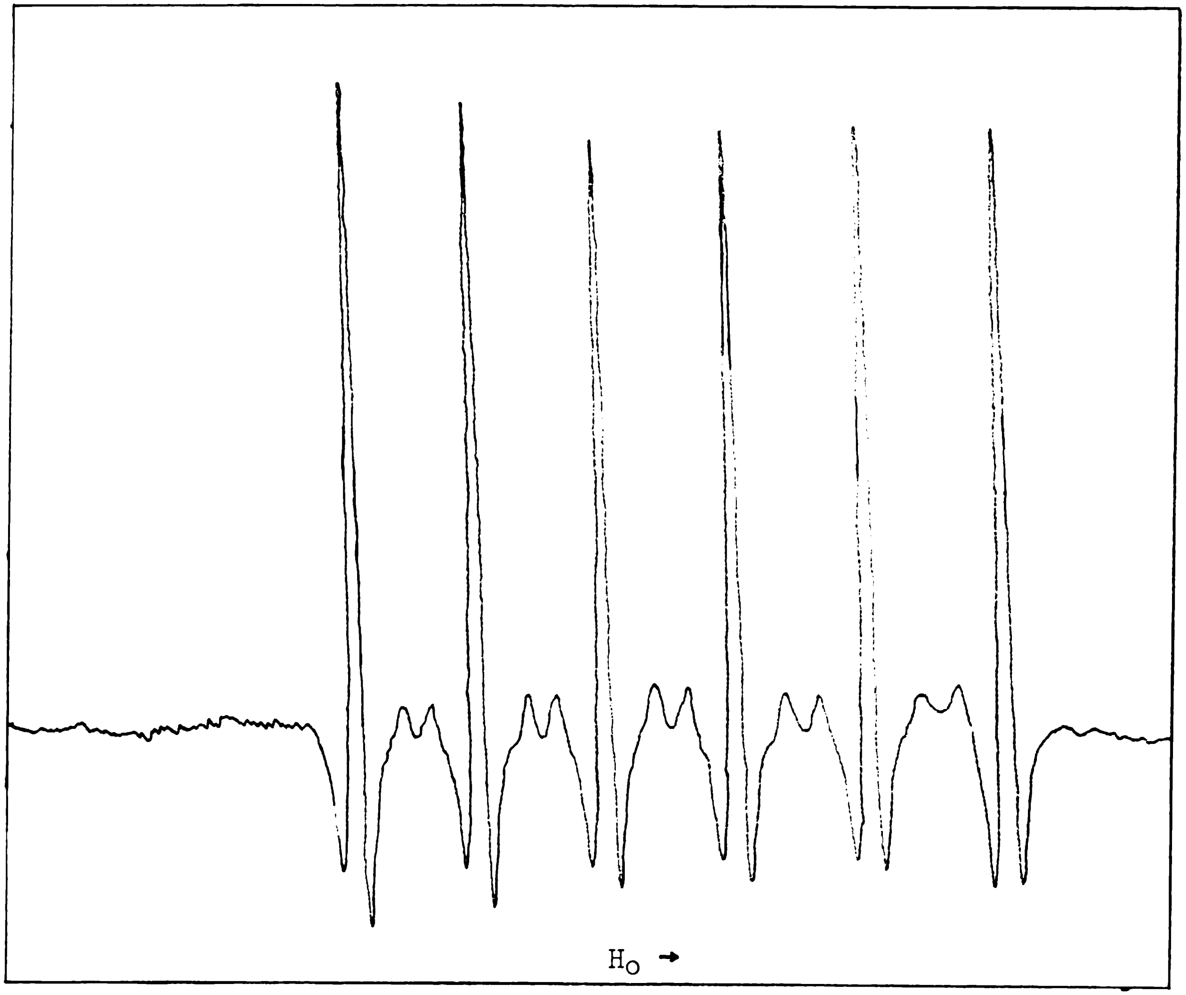

Figure 38. The ESR Spectrum of 1% $Mn(PMT)_6(ClO_4)_2$ in $Zn(PMT)_6(ClO_4)_2$ (second derivative plot).

negativity of the two atoms in the bond) gives an extrapolated value at 100% ionicity in good agreement with the theoretical value (137).

Forbidden Mn(II) transitions were observed in the spectra of $Zn(PMT)_6(ClO_4)_2$. The transitions consisted of a pair of lines separated by 23.1 gauss from each other between each pair of allowed lines. The relative intensity compared to the allowed lines was 1 to 18. The transitions were not observed in either the room temperature or the frozen spectra of $Mn(PMT)_6(ClO_4)_2$ in the solvents CH_3NO_2, CH_3CN, and dimethylsulfoxide (DMSO). From the intensity ratio 1/18, an approximate value of the measure of departure from octahedral symmetry D, (assuming that the distortion gives an effective axial symmetry[a], D can be obtained by the following equation (140,141):

$$\text{I.R. (intensity ratio)} = \frac{8}{15}\left[\frac{3}{4}\frac{D}{gBH}\right]^2 \left[\frac{1+S(S+1)}{3M(M-1)}\right]\left[I(I+1)-m^2+m\right]$$

[a]This assumption that the distortion is axial is made purely for convenience so that an approximation of the D value can be obtained.

where $S = \frac{5}{2}$ (total electron spin), $I = \frac{5}{2}$ (total nuclear spin), $m = \frac{1}{2}$ (component of electron spin), and $M = \frac{1}{2}$ (component of nuclear spin). From this equation D is determined to be approximately 750×10^{-4} cm^{-1}. This value indicates that there is a large distortion from octahedral symmetry in the solids since Mn(II) complexes with small distortions have D values in the range of 0 to 200×10^{-4} cm^{-1}.

The line width (peak to peak width on the derivative curve) is approximately 10 gauss in $Zn(PMT)_6(ClO_4)_2$ and $Fe(PMT)_6(ClO_4)_2$. This puts an upper limit on the nitrogen splitting of approximately two gauss assuming that there are six equivalent nitrogens bonded to the Mn(II). A two gauss nitrogen splitting would give a value of N^2 equal to 0.94 calculated from the equations of Helmholz (142) assuming an sp^3 hybrid nitrogen orbital.

Part of the explanation for the high ionic character of the metal-ligand bonds may be that it is due to a steric effect. This explanation draws support from the ESR spectra of $Mn(PMT)_6(ClO_4)_2$ in organic solvents. The absence of the forbidden transitions indicates that the symmetry is octahedral while the ESR Mn(II) hyperfine splitting value indicates that the bonds are more ionic, A = 87.1 in the solution, than in the solid, A = 84.4.

This increase in ionicity is consistent with a model in which, after the distortion introduced by crystal packing is removed by dissolving the complex in a solution, the six now equivalent ligands are sterically forced to form more ionic bonds to the Mn(II) than the original inequivalent ligands.

Tetrakis- and Hexakis-(Pentamethylenetetrazole)Copper(II) Perchlorate.

The ESR data are given in Table XV along with some literature data for comparison. A surprising result of this investigation is that it was possible to resolve the copper nuclear hyperfine splittings in the undiluted samples (see Figure 39). As discussed by Assour and Harrison (143), interactions between neighboring ions are expected to broaden the hyperfine lines so that at best only a resolution of the parallel ($g_{||}$) and perpendicular ($g_{\perp}$) absorptions are expected. The present work appears to be the first reported case of high resolution of this type. The corresponding Mn(II) complexes did not show this resolution,presumably due to the greater dipolar interaction of five unpaired electrons in Mn(II) compared to the one unpaired electron in Cu(II).

The ESR data indicate that the environment of $Cu(PMT)_4(ClO_4)_2$ in nitrobenzene is similar to the environment in

TABLE XV

ESR Data for Cu(II) Complexes with Nitrogen Bonding Ligands

	$g_{\|\|}$	$A_{\|\|}^{Cu}(10^4 cm^{-1})$	$g_{\perp}$	$A_{\|\|}^{N}(10^4 cm^{-1})$	$A_{\perp}^{N}(10^4 cm^{-1})$	Reference
$Cu(pyridine)_4^{2+}$ in P+$(pyridine)_4(NO_3)_2$	2.236	192	2.050	16	12.6	144
in undiluted $Cu(pyridine)_4(ClO_4)_2$	2.265	190	2.06			145
in $Cd(pyridine)_4(Ts)_2$	2.290	162	2.050	13	11.2	144
$Cu(4\text{-}CNC_5H_4N)_6(ClO_4)_2$ in $Cd(4\text{-}CNC_5H_4N)_6(ClO_4)_2$	2.274	173	2.065	14	11.2	144
$Cu(4\text{-}CH_3C_5H_4N)_3(Ts)_2$ in $Cd(4\text{-}CH_3C_5H_4N)_4(Ts)_2$	2.283	171	2.055	14	12.5	144
$Cu(4\text{-}(CH_3)_2NC_5H_4N)_4(Ts)_2$ in $Cd(4\text{-}(CH_3)_2NC_5H_4N)_3(Ts)_2$	2.283	166	2.055	15	12.5	144

TABLE XV (continued)	$g_{\parallel}$	$A_{\parallel}^{Cu}$ ($10^4 cm^{-1}$)	$g_{\perp}$	$A_{\parallel}^{N}$ ($10^4 cm^{-1}$)	$A_{\perp}^{N}$ ($10^4 cm^{-1}$)	Reference
$Cu(PMT)_4(ClO_4)_2$ undiluted powder	2.283	180	2.07			*
$Cu(PMT)_4(ClO_4)_2$ in nitrobenzene	2.285	177	2.08			*
$Cu(PMT)_6(ClO_4)_2$ undiluted powder	2.328	118	2.12			*
$Cu(PMT)_6(ClO_4)_2$ in nitromethane	2.305	164	2.06			*
$Cu(NH_3)_4SO_4$		172				146
$Cu(NO_3)_2$ in ethyl acetate	2.34	121				147

*This investigation.

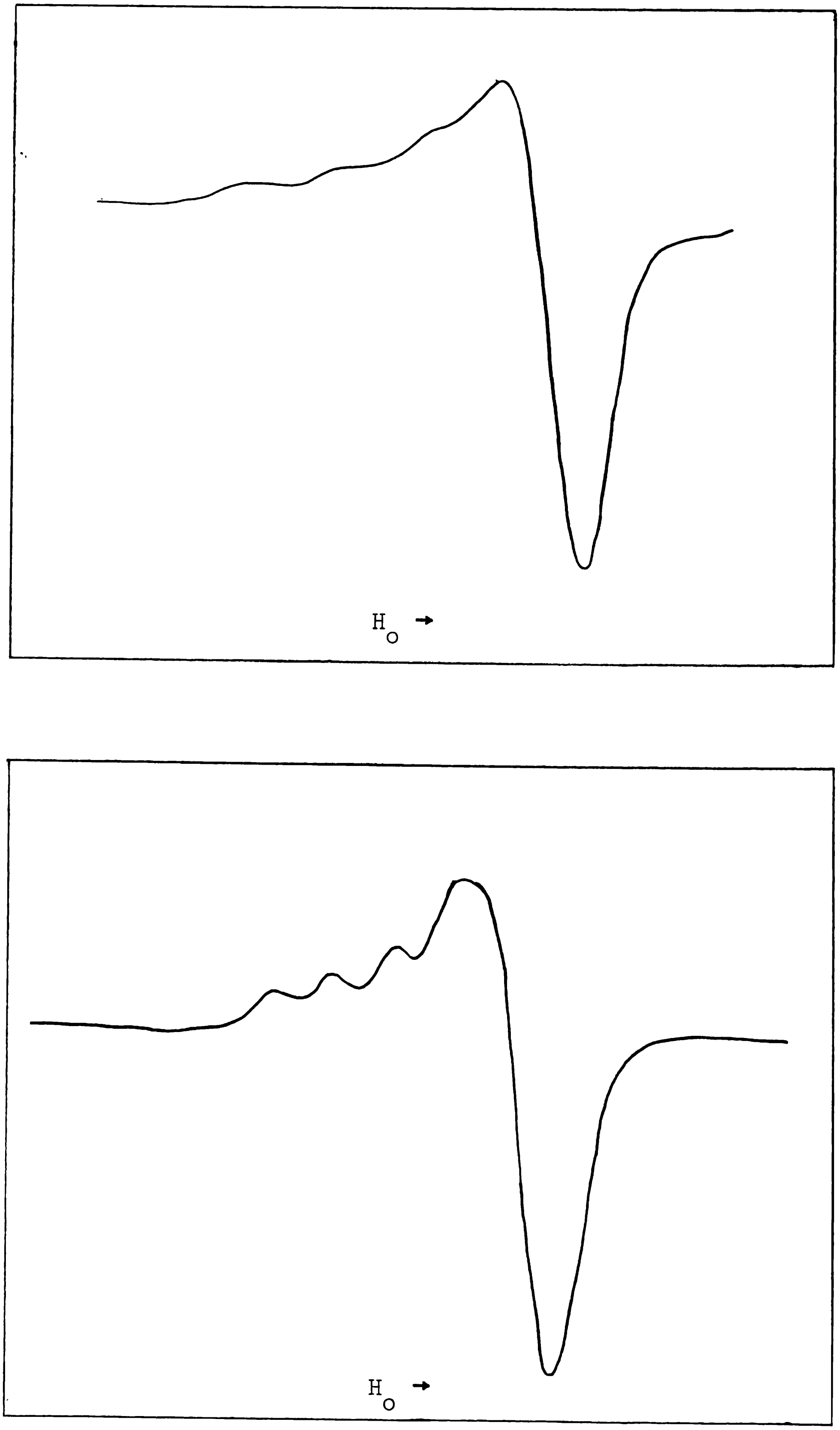

Figure 39. The ESR Spectra of Undiluted $Cu(PMT)_4(ClO_4)_2$ (top) and $Cu(PMT)_6(ClO_4)_2$ powder (bottom).

the pure powder with the complexes having definite tetragonal symmetry, as expected, since Cu(II) normally prefers a tetragonal crystal field stabilization.

A quantitative calculation of the molecular orbital coefficients cannot be made since the d-d electronic transitions could not be assigned from the visible reflectance and solution spectra which gave only one broad band which probably contains the three expected transitions. However, a comparison of the ESR $A_{||}$ data for the PMT complexes with the other nitrogen bonding complexes listed in Table XV indicates that for $Cu(PMT)_4(ClO_4)_2$ the PMT is a less basic ligand than the pyridine in $Cu(pyridine)_4(ClO_4)_2$ complex. The difference in the ESR data between $Cu(pyridine)_4(NO_3)_2$ and $Cu(pyridine)_4(Ts)_2$[b], shows that the ligands in the axial positions can have a large effect on the experimental $A_{||}$ values so that a further comparison with the other complexes would be of uncertain validity.

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[b]Ts = p-toluenesulfonate anion.