ABSTRACT

PREPARATION AND CHARACTERIZATION OF TRANSITION METAL COMPLEXES OF SEVERAL 5-SUBSTITUTED TETRAZOLES

by Paul Labine

In this investigation, cobalt (II), copper (II), zinc (II) and chromium (III) ions were caused to react in aqueous solution with the sodium salts of 5-O-chlorophenyltetrazole, 5-p-chlorophenyltetrazole, 5-p-methoxyphenyltatrazole, 5-p-chlorobenzyltetrazole, and 5-phenyltetrazole. The divalent ions generally formed complexes of the type $MT_2 \cdot nH_2O$. However, nickel (II) ions formed $MT_{1.8} \cdot H_2O$ complexes. With copper (II) ions, two of the tetrazoles formed M(T)(OH) complexes. The chromium (III) ions formed $MT_2OH \cdot nH_2O$ complexes. No complexes could be obtained for iron (II), iron (III), or manganese (II).

The complexes were generally insoluble in acetone, nitromethane, 1,4 dioxane, methylenechloride, benzene, acetonitrile and methanol. A few of the complexes were insoluble in dimethylsulfoxide, N,N-dimethylformamide, and pyridine.

The complexes were usually decomposed by treating the solids with aqua regia. The copper (II) complexes could also be decomposed with concentrated ammonia but the complexes could be reformed by neutralizing the ammonia with hydrochloric acid.

A comparison of the infrared spectra of the complexes with the spectra of the tetrazoles and their respective sodium salts indicates that the tetrazoles coordinate as the anion. That is, the 1-nitrogen on the tetrazole ring is not protonated during complexation.

In most cases, the metal-nitrogen stretching bands arise, on complexation, from the splitting of ligand bands into two new bands. Very few of the bands in the 130-320 cm^{-1} region could be assigned to metal-nitrogen stretching bands due to the presence of broad bands which could not be resolved by using thicker mulls or by increasing the attenuation. It was therefore impossible to compare the tetrazoles in terms of the respective copper-nitrogen stretching frequencies might have been sufficient to list the tetrazoles in the order of increasing ligand strength.

The band positions in the electronic absorption spectra, could be utilized to list the ligands in the order of increasing ligand strength. The electronic absorption spectra of the solid nickel (II), cobalt (II), and chromium (III) complexes indicate octahedral symmetry. The spectra of the copper (II) complexes indicate tetragonal distortion.

The calculated magnetic moments indicate that most of the complexes are of the high-spin type. However, a few of the copper (II) complexes have subnormal magnetic moments which may indicate metal-metal bonding.

The esr spectra of the copper (II) complexes, diluted with zinc (II) ions, indicate tetragonal distortion due to differences of approximately 0.15 between $g_{||}$ and $g_{\perp}$ for several of the copper (II) complexes.

The esr parameters for the chromium (III) complexes were quite similar to those obtained for octahedral complexes of chromium (III).

The esr spectra of the nickel (II) and cobalt (II) complexes were generally quite complex and poorly resolved. Only bis (5-O-chlorophenyltetrazolato)cobalt(II) monohydrate gave an esr signal that could easily be interpreted. The g_{avg} value of this complex increased with a decrease in temperature. This unusual behavior may be due to changes in the structure of the complex with changes in temperature.

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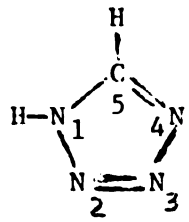
I. Historical

A. General

Tetrazoles are five membered ring compounds which contain four nitrogen atoms and one carbon atom. For the structure of the parent compound, tetrazole, refer to (I).



(I)

Thorough reviews (1,2) are available on the preparation and properties of 5-substituted, 1-substituted, and 1,5-disubstituted tetrazoles. In addition, Popov(3) has prepared an excellent review of the acidities and complexing abilities of various 1,5 disubstituted tetrazoles including pentamethylenetetrazole and substituted-pentamethylenetetrazoles.

B. Acid-Base Properties

The acid-base properties of substituted tetrazoles were investigated as early as 1914 by Olivera-Mandala (4). Tetrazole and 5-substituted tetrazoles usually have pKa values of 7 or less. Thus, these tetrazoles can be titrated with strong bases by using phenolphthalein as the indicator. The 5-substituted tetrazoles can also exhibit basic properties due to the presence of three other nitrogen atoms. The

basicities of these 5-substituted tetrazoles were calculated from the hydrolysis constant of the respective hydrochlorides and appear to be of the same order of magnitude as aniline (1). Herbst and Mihina (5) and Herbst and Wilson (6) determined potentiometrically the pKa values for 5-phenyl and 5-alkyl tetrazoles in water-methanol mixtures. In 1967, Caruso, Sears, and Popov (7) determined conductometrically the acidities of several 5-alkyl and 5-aryl tetrazoles in 1,1,3,3-tetramethylguanidine. Caruso et al., doubted the usefulness of the pKa values obtained previously in water-methanol mixtures because changes in liquid junction potential had not been considered in the previous calculations.

More recently, Charton (8) has calculated the macroscopic ionization constant K_M of several 5-substituted tetrazoles. These macroscopic constants were calculated from microconstants K_1 and K_2 which were themselves obtained from the extended Hammett equation. Since 5-substituted tetrazoles exist in two tautomeric forms, K_1 is the ionization constant for tautomer (I) and K_2 is the ionization constant K_M, is then calculated from $K_M = \frac{K_1 K_2}{K_1 + K_2}$.

Unlike 5-substituted tetrazoles, 1-substituted tetrazoles do not behave as acids. Stolle et al. (9) reported that they had removed the 5-carbon hydrogen from 1-phenyltetrazole with methyl magnesium iodide in ether. Gilbert (10), however, was

unable to remove the 5-carbon hydrogen from 1-phenyltetrazole by their method. In 1967, Garber (11) was successful in removing the 5-carbon hydrogen from 1-methyl and 1-cyclohexyltetrazoles by using n-butyl lithium in anhydrous tetrahydrofuran. The 1-methyltetrazole was converted to 1-methyl-5-tetrazolyl lithium $\cdot \frac{1}{2}$ tetrahydrofuran, which is insoluble in tetrahydrofuran and ether. Although the lithium salt of 1-cyclohexyltetrazole was not isolated as a solid, 1-cyclohexyltetrazole is probably converted to 1-cyclohexyl-5-tetrazolyl lithium. The lithium salts were then caused to react with dichlorobis(triethylphosphine)nickel(II) and gave bis(1-methyl-5-tetrazolyl)nickel(II) and bis(1-cyclohexyl-5-tetrazolyl)nickel(II).

In a recent publication, Erlich and Popov (12) investigated the acid-base properties of cyclopolymethylenetetrazoles in formic acid. The unsubstituted cyclopolymethylenetetrazoles act as fairly strong monoprotic bases in formic acid solution but show little proton affinity in aqueous solutions. The length of the hydrocarbon chain does not influence the basic strength of the tetrazole ring.

C. Characterization of Tetrazoles

Several tetrazoles and azoles have been characterized by nuclear magnetic resonance spectroscopy (13,14,15) and by mass spectroscopy (13). In addition, Guibe and Lucken (16)

reported the ^{14}N pure quadrupole resonance spectra of several azoles.

D. Coordination Compounds

Since 1892, a large number of metal complexes have been prepared with 5-substituted tetrazoles. Bladin (17) prepared the first silver complexes of tetrazole and 5-substituted tetrazoles by adding hot silver nitrate to aqueous solutions of the respective tetrazoles. Herbst and Garbrecht (18) and Herbst and Mihina (5) prepared silver complexes of other 5-substituted tetrazoles by a similar method.

In 1960, Brubaker (19) prepared two crystalline forms of bis(5-aminotetrazolato)copper(II). By using spectrophotometric and pH data, Brubaker calculated the formation constant for the copper(II) complex formed with 5-aminotetrazole in aqueous solution. His value of 10^{12} for the formation constant indicates that 5-aminotetrazole forms a very stable 2:1 complex with copper(II). Brubaker also found that there is very little interaction between the copper(II) ion and 1,5-dimethyltetrazole. This, in addition to the relatively small formation constant for the 2:1 complex (20) of silver(I) with pentamethylenetetrazole (hereafter abbreviated PMT), indicates that a replaceable hydrogen is required to form very stable complexes.

In 1961, Daugherty and Brubaker (21,22) prepared various bis(5-substituted tetrazolato)copper(II) and nickel(II) complexes. Methanol solutions of each tetrazole were added to methanol solutions of copper(II) or nickel(II) salts. Sulfate and chloride salts induced the rapid precipitation of solid complexes; whereas, the nitrate salts were ineffective in inducing precipitation.

The nickel(II) and copper(II) complexes displayed a few interesting properties. The complexes were insoluble in most solvents. As a result, they could not be purified by recrystallization. The complexes usually decomposed below their melting points. Hence, they could not be purified by sublimation. The insolubility of these complexes in both nonpolar and polar solvents suggests polymer formation.

Jonassen et al. (23,24,25) have prepared bis(5-trifluoromethyltetrazolato)iron(II), cobalt(II), nickel(II), and copper(II) complexes as well as bis(5-chlorotetrazolato)-iron(II) and bis(5-nitrotetrazolato)iron(II). The reflectance spectrum of bis(5-trifluoromethyltetrazolato)iron(II) indicates that the 5-trifluoromethyltetrazolate anion lies between 2,2'-bipyridine and 1,10-phenanthroline in the spectrochemical series. The low magnetic moment of 1.1 B.M. observed for bis(trifluoromethyltetrazolato)iron(II) indicates that "the paramagnetic state lies close to the spin-paired ground state." Pyrolysis (26) of the bis(5-trifluoromethyl-

tetrazolato)iron(II), cobalt(II), nickel(II), and copper(II) complexes yields the components H_2O, CF_3, CN, CN_2, N_2, $(CN)_2$ for each complex. The residues consisted of CoF_3, NiF_2, FeF_3. The enthalpy of decomposition was calculated from differential thermal analyses of the complexes.

In 1967, Beck and Fehlhammer (27) prepared bis(5-trifluoromethyltetrazolato)bis(triphenylphosphine)palladium(II) by reacting bis(triphenylphosphine)palladium(II) azide with trifluoroacetonitrile in dichloroethane at 0° C. Recently Beck et al. (28) have prepared several other trans-bis(5-substitutedtetrazolato)bis(triphenylphosphine) palladium(II) by a similar method. Addition of HCl or HN_3 in ethanol to the palladium complexes yields the respective 5-substituted tetrazoles.

A large number of complexes of 1-substituted tetrazoles are known. In 1910, Olivera-Mandala and Alagna (29) prepared tetrachlorobis(1-ethyltetrazolato)platinum(IV) by adding an alcoholic solution of platinum(IV) chloride to an alcoholic solution containing HCl and 1-ethyltetrazole.

In 1963, Brubaker and Gilbert (30) prepared various dichloro bis(1-substituted tetrazole)cobalt(II), nickel(II), platinum(II) and zinc(II) complexes. Like other tetrazole complexes, these 1-substituted tetrazole complexes cannot be recrystallized or sublimed. As mentioned previously,

Garber (11) prepared bis(1-methyl-5-tetrazolyl)nickel(II) and bis(1-cyclohexyl-5-tetrazolyl)nickel(II) by heating the respective lithium salts with dichlorobis(triethylphosphine) nickel(II). These nickel complexes are insoluble in all common solvents, will decompose when heated, and are senitive to the atmosphere. The reflectance spectra of these two complexes indicate octahedral symmetry. The magnetic moments of these nickel complexes indicate that the complexes are high spin.

In 1967, Beck and Fehlhammer (28) prepared tetraphenylarsonium tetrakis(1-cyclohexyl-5-tetrazolyl)gold(III) by reacting tetraphenylarsonium tetrazidogold(III) with cyclohexylisonitrile in dichloroethane at 0°C. The proton nmr spectrum in $DCCl_3$ showed three signals at τ=2.4,5.2,8.3 corresponding to the twenty phenyl protons, the four tertiary hydrogen atoms on the cyclohexylring, and the 40 methylene protons on the cyclohexyl ring.

Tetrazole itself forms metal complexes. Holm and Donnelly (31) prepared bis(tetrazolato)iron(II), cobalt(II), nickel(II) and cadmium(II) complexes by adding aqueous solutions of tetrazole to aqueous solutions of the respective metal ions. The iron(II) complex is very poorly defined and is easily oxidized by oxygen in the air. Mole ratio studies indicate that the tetrazolate anion forms

very weak complexes with nickel(II) ions in dimethylformamide.

In 1967, Garber (11) prepared bis(tetrazolato)copper(II) monohydrate by adding an aqueous tetrazole solution to an aqueous solution of copper(II) nitrate. The copper(II) complex decomposes upon heating and is insoluble in all common solvents. The reflectance spectrum of the complex indicates octahedral symmetry. The magnetic moment of the complex is 1.73 B.M. (1 electron value). The esr spectrum of the undiluted power showed no hyperfine splittings. Garber (11) was unsuccessful in diluting the copper complex by precipitating the copper complex as an impurity in bis(tetrazolato) zinc(II).

Garber et.al. (11,32) performed a vibrational analysis of sodium tetrazolate monohydrate. Vibrational assignments for bis(tetrazolato)copper(II) monohydrate and 1-methyltetrazole were made based on their normal coordinate analysis of sodium tetrazolate monohydrate.

Recently, Washburn and Peterson (33) prepared ferrocenyl tetrazole by reacting cyanoferrocene with trimethylazidosilane and aluminum(III)chloride in refluxing o-chlorobenzene.

1,5 disubstituted tetrazoles and substituted pentamethylenetrazoles form complexes with transition metal ions, interhalogens, and organic molecules. Interhalogen and molecular complexes of tetrazoles are reviewed by Popov (3).

Zwikker (34) Rheinboldt (35) and Dister (36) have prepared silver complexes of various substituted pentamethylenetetrazoles. Popov and Holm (20) studied the silver complexes of pentamethylenetetrazole, substituted pentamethylenetetrazole, and 1-cyclohexyl-5-methyltetrazole in acetonitrile. They determined potentiometrically that the formation constants for these complexes were approximately 10^2. By using polarographic techniques, they found that pentamethylenetetrazole forms extremely weak complexes with cobalt(II), thalium(I) and cadmium(II) in aqueous solution.

D'Itri and Popov (37,38) prepared anhydrous hexakis (PMT) manganese(II), iron(II), cobalt(II), nickel(II), copper(II), and zinc(II) complexes. Since the magnetic moments indicate that the complexes are high spin complexes, it is not surprising that the infrared spectra of the complexes were almost identical with the infrared spectrum of PMT.

Kuska, D'Itri and Popov (39) have obtained electron spin resonance spectra for $Mn(PMT)_6(ClO_4)_2$, $Cu(PMT)_6(ClO_4)_2$ and $Cu(PMT)_6(ClO_4)_2$. The esr spectrum of $Mn(PMT)_6(ClO_4)_2$ dispersed in $Zn(PMT)_6(ClO_4)_2$ indicated that the metal ligand bonds are 91 per cent ionic and that the complexes are essentially octahedral. Nuclear hyperfine splittings were resolved in the esr spectra of the undiluted copper(II) complexes. Both $Cu(PMT)_6(ClO_4)_2$ and $Cu(PMT)_4(ClO_4)_2$

exhibit tetragonal symmetry. The copper ligand bonds were found to be more covalent than the manganese ligand bonds.

Recently, Bowers and Ponov (40) prepared complexes of the type $M^{II}(PMT)_1X_2$ and $M^{II}(PMT)_2X_2$ by causing pentamethylenetetrazole to react with first row transition metal chlorides and bromides. These complexes were insoluble in polar and nonpolar solvents and have high melting or decomposition points. From magnetic and spectral evidence, it appears that the metal ions in $M^{II}(PMT)X_2$ complexes are in octanedral environments whereas the $M^{II}(PMT)_2X_2$ complexes may be tetrahedral. The $M^{II}(PMT)X_2$ complexes probably contain halogen bridges and are most likely polymeric. The $M(PMT)_2X_2$ complexes, on the other hand, are probably monomeric and seem to have a tetrahedral structure.

Pentamethylenetetrazole (41) was found to form 1:1 complexes with iodine monochloride, iodine monobromide, and iodine in carbon tetrachloride. The pentamethylenetetrazole-ICl complex could be obtained as a crystalline solid which could be purified by recrystallization from chloroform. Two independent structure determinations of the PMT-ICl complex (42) showed that PMT acts as a unidentate ligand and that ICl is bonded to the 4-nitrogen of the tetrazole ring. The linear ICl molecule is coplanar with the tetrazole ring. The seven membered ring of PMT is in a chair conformation. At present, it is uncertain whether the 4-nitrogen is the

donor site in all tetrazole complexes.

The crystal structure of dichlorobis(1-methyltetrazole) zinc(II) complex has also been determined (43). Crystals of this complex show that the zinc atom is in an approximately tetrahedral environment and that the zinc atom is coplanar with the two tetrazole rings with coordination through the four position of the tetrazole ring.

II. Experimental

A. Purity of Chemicals and Solvents

Reagent grade chemicals were used throughout this investigation.

B. Preparation of Tetrazoles and Related Chemicals

5-phenyltetrazole: This compound was prepared according to the method of Finnegan and Henry (44). In a 500ml.3-neck flask, 28.6g(0.44 mole) of sodium azide, 21.2g(0.40 mole) of ammonium chloride, 17.0g (0.40 mole) of lithium chloride and 41.2g (0.40 mole) of benzonitrile were suspended in 300ml of N,N-dimethylformamide. The mixture was stirred and heated at 100-110° for 17 hours. In accordance with Daugherty's observations (45), the color of the reaction mixture changed from colorless to orange-brown after a few hours. After 17 hours, the reaction mixture was allowed to cool to room temperature. The first batch of crude sodium salt was separated from the reaction mixture by filtration. The filtrate was distilled at reduced pressure until 50ml of filtrate remained in the distillation flask. The second batch of crude sodium salt, which precipitated during the distillation, was collected on a porcelain filter funnel. Both batches of crude sodium salt were combined and then dissolved in 200 ml of water. Insoluble materials were re-

moved by filtration. The filtrate was then acidified to pH=2 to precipitate the water-insoluble 5-phenyltetrazole. The crude product was collected on a porcelain filter funnel and thoroughly washed with ice water. The product was finally recrystallized twice according to the method of Caruso, Popov, and Sears (7). Crude 5-phenyltetrazole was added to 1,2-dichloroethane and the mixture was brought to boiling. Just enough methanol was then added to dissolve the tetrazole. As the solution cooled, needle-like crystals formed. These crystals were collected by filtration and were then dried to constant weight in a vacuum dessicator. The melting point of 215° agreed with that previously reported (7).

5-p-chlorobenzyltetrazole: The procedure for the preparation and recrystallization of 5-phenyltetrazole was used. 5-p-chloroacetonitrile Eastman Organic Chemicals was used in place of benzonitrile. The melting point of 162-163° for the recrystallized product agreed with that previously reported (7).

5-p-methoxyphenyltetrazole: The same procedure used for the preparation and recrystallization of 5-phenyltetrazole was employed. 5-anisonitrile was used in place of benzonitrile. The melting point of 239-240° for the recrystallized product agreed with that previously reported (4).

Anisonitrile was prepared according to the method of Van Es (46). 136g of p-anisaldehyde (1 mole), 80g of hydroxylamine hydrochloride (1 mole + 15%), 125g of sodium formate, and 1500ml of 98% formic acid were refluxed for one hour. A six fold dilution of the reaction mixture with water caused the anisonitrile to precipitate.

5-p-chlorophenyltetrazole: The procedure was the same as for the preparation and recrystallization of 5-phenyltetrazole. 5-o-chlorobenzonitrile was used in place of benzonitrile. The melting point of 179-180° agreed with that previously reported (6).

5-o-chlorobenzonitrile was prepared according to the method used in preparing anisonitrile. 5-o-chlorobenzaldehyde used in place of anisaldehyde.

5-p-chlorophenyltetrazole: The procedure was the same as for the preparation and recrystallization of 5-phenyltetrazole. 5-p-chlorobenzonitrile was used in place of benzonitrile. The melting point of 260-261°, agreed with that previously reported (7).

5-p-chlorobenzonitrile was prepared according to the method used in preparing anisonitrile. 5-p-chlorobenzaldehyde was used in place of anisaldehyde.

sodium salts of tetrazoles: Suspensions of the respective tetrazoles in water were titrated with 0.10M NaOH. The tetrazoles dissolved before the equivalence point was reached. The aqueous solutions of the sodium salts were evaporated nearly to dryness on a steam bath. The salts were then recrystallized from acetone and dried at 110° before use.

C. Preparation of Metal Complexes

Bis(5-phenyltetrazolato) cobalt(II)monohydrate: A complete description of the preparation of this compound will be given. This method applies to all cobalt(II), nickel(II), zinc(II), and copper(II) complexes. In all cases, precipitation occurred within a few minutes.

Forty ml of an aqueous 0.10M solution of sodium 5-phenyltetrazolate were added dropwise to 200ml of a magnetically stirred aqueous 0.01M solution of cobalt(II) perchlorate hexahydrate. Since the complex was insoluble in most solvents, it could not be recrystallized.

The pink product was washed six times with distilled water, partially dried with anhydrous diethylether, and finally dried to constant weight in vacuo over P_2O_5. Digestion and prolonged washing of the precipitate were avoided because Daugherty (45) had reported that bis(5-phnyltetrazolato) copper(II) monohydrate was partially hydrolyzed to hydroxo(5-phenyltetrazolato)copper(II) by stirring the complex with water for twenty hours at room temperature.

Anal. Calcd. for $Co(C_7H_5N_4)_2 \cdot H_2O$: Co,16.0; C,45.78; H,3.29; N,31.45; Found: Co,16.1; C,44.24; H,2.89; N,30.86.

Bis(5-o-chlorophenyltetrazolato)cobalt(II)menohydrate: This pink product formed in a few minutes. Anal. Calcd. for $Co(C_7H_4N_4Cl)_2 \cdot H_2O$: Co,13.5; C,38.55; H,2.31; N,25.68; Found; Co,13.3; C,37.45; H,1.91; N,26.06.

Bis(5-p-chlorophenyltetrazolato)cobalt(II)monohydrate: This pink product formed in a few minutes. Anal.Calcd. for $Co(C_7H_4N_4Cl)_2 \cdot H_2O$: Co,13.5; C,38.55; H,2.31; N,25.68; Found: Co,13.4; C,37.85; H,1.95; N,25.95.

Bis(5-p-methoxyphenyltetrazolato)cobalt(II)monohydrate: This pink product formed immediately. The solid turned tan in color on drying to constant weight. Anal. Caled. for $Co(C_8H_7N_4O)_2 \cdot H_2O$: Co,13.5; C,44.03; H,3.90; N,25.68; Found: Co,13.9; C,42.78; H,3.23; N,25.85.

Bis(5-p-chlorobenzyltetrazolato)cobalt(II)monohydrate: This pink product formed immediately. The product turned brownish pink on drying to constant weight. Anal. Calcd. for $Co(C_8H_6N_4Cl)_2 \cdot H_2O$: Co,12.6; C,41.34; H,3.01; N,24.05. Found: Co,12.5; C,40.4; H,2.73; N,23.94.

Nickel complex of 5-p-chlorobenzyltetrazole: This blue-violet solid precipitates immediately. Anal. Calcd. for

$Ni(C_7H_4N_4Cl)_{1.8}\cdot H_2O$: Ni,14.7; C,37.70; H,2.29; N,25-20; Found: Ni,14.7; C,37.0; H,2.03; N,25.06;

Nickel complex of 5-p-methoxyphenyltetrazole: This metric blue violet solid precipitates immediately. Anal. Calcd. for $Ni(C_8H_7N_4O)_{1.8}\cdot H_2O$: Ni,13.16; C,44.95; H,4.10; N,26.2; Found: Ni,13.0; C,43.06; H,3.37: N,25.92:

Nickel complex of 5-phenyltetrazole: This blue violet solid precipitates immediately. Anal. Calcd. for $Ni(C_7H_5N_4)_{1.8}\cdot H_2O$ Ni,15.2; C,43.6; H,2.61; N,29.1; Found: Ni,15.5; C,44.6; H,2.82; N,30.13;

Bis(5-p-chlorobenzyltetrazolato)zinc(II): This white solid precipitates immediately. Anal. Calcd. for $Zn(C_8H_6N_4Cl)_2$: C,42.40; H,2.66; N,24.72; Found: C,42.33; H,2.33; N,25.05;

Bis(5-o-chlorophenyltetrazolato)zinc(II): This white solid precipitates immediately; Anal. Calcd. for $Zn(C_7H_4N_4Cl)_2$: C,39.55; H,1.89; N,26.35; Found: C,39.78; H,1.80; N,26.55;

Bis(5-p-chlorophenyltetrazolato)zinc(II) 3/2hydrate: This white solid precipitates immediately. Anal. Calcd. for $Zn(C_7H_4N_4Cl)_2\cdot 3/2H_2O$: C,37.10; H,2.44; N,24.80; Found: C,37.16; H,2.78; N,25.07;

Bis(5-p-methoxyphenyltetrazolato)Zinc(II): This white solid precipitates immediately. Anal. Calcd. for $Zn(C_8H_7N_4O)_2$: C,46.16; H,3.36; N,26.92; Found: C,45.86; H,3.31; N,27.00;

Bis(5-phenyltetrazolato)Zinc(II): This white solid precipitates immediately. Anal. Calcd. for $Zn(C_7H_5N_4)_2$: C,47.20; H,2.82; N,31.45; C,46.95; H,2.69; N,31.53;

Bis(5-p-chlorobenzyltetrazolato)copper(II)trihydrate: This blue-violet solid precipitates immediately. Anal. Calcd. for $Cu(C_8H_6N_4Cl)_2 \cdot 3H_2O$: Cu,12.57; C,39.02; H,3.58; N,22.16; Found: Cu,12.37; C,38.40; H,3.41; N,22.43;

Bis(5-o-chlorophenyltetrazolato)copper(II)monohydrate: This light green solid precipitates immediately. Anal. Calcd. for $Cu(C_7H_4N_4Cl)_2 \cdot H_2O$: Cu,14.39; C,38.10; H,2.28; N,25.39; Found: Cu,14.66; C,37.47; H,1.58; N,25.41;

Bis(5-p-chlorophenyltetrazolato)copper(II)monohydrate: This light blue solid precipitates immediately. Anal. Calcd. for $Cu(C_7H_4N_4Cl)_2 \cdot H_2O$: Cu,14.35; C,38.11; H,2.28; N,25.39; Found: Cu,14.37; C,37.01; H,1.98; N,25.32;

hydroxo(5-p-methoxyphenylterrazolato)copper(II): This light blue solid precipitates immediately. Anal. Calcd. for $Cu(C_8H_7N_4O)(OH)$ Cu,24.82; C,37.53; H,3.12; N,21.88; Found: Cu,25.01; C,37.68; H,2.93; N,22.20;

Hydroxo(5-phenyltetrazolato)copper(II): This dark blue solid precipitates immediately. Anal. Calcd. for $Cu(C_7H_5N_4)(OH)$: Cu,28.12; C.37.20; H,2.67; N,24.80; Found: Cu, 23.05; C,36.91; H,2.31; N,24.82;

Bis(5-phenyltetrazolato)copper(II)monohydrate: This complex could not be prepared from aqueous solution. It was finally prepared in methanol by a method previously reported by Daugherty (45). When methanol solutions of $CuSo_4 \cdot 5\ H_2O$ and 5-phenyltetrazole are mixed in any proportion, $Cu(C_7H_5N_4)_2 \cdot H_2O$ precipitates from solution after several hours. Anal. Calcd. for $Cu(C_7H_5N_4)_2 \cdot H_2O$: Cu,17.1; Found: Cu,17.3;

Attempted preparation of bis(5-p-methoxyphenyltetrazolato) copper(II):

Daugherty was unable to obtain this complex from methanol solution. Instead, he obtained a mixture which appeared to contain $Cu(C_8H_7N_4O)(OH)$ and $Cu_2(C_8H_7N_2O)_2SO_4 \cdot 2H_2O$. In the present investigation, $Cu(C_8H_7N_4O)(OH)$ was obtained instead of the desired product.

Hydroxo bis(5-p-chlorobenzyltetrazolato)chromium(III)tetrahydrate

The procedure for the preparation of this complex will be outlined in detail. The other chromium(III) complexes were prepared in the same manner. 60.0ml of aqueous 0.10M sodium 5-p-chlorobenzyltetrazolate was mixed with 200ml of

aqueous 0.01M chromium(III) perchlorate hexahydrate. Initially, the solution changed from dark green to yellow green as the reactants were mixed. After three minutes, 5-p-chlorobenzyltetrazole, a white solid, precipitated from the solution. The 5-p-chlorobenzyltetrazole was removed by filtration and the filtrate was retained. Another 60.0ml of aqueous 0.10M sodium 5-p-chlorobenzyltetrazolate was then mixed with the filtrate. After a few minutes a pinkish-violet solid precipitated from the solution. Anal. Calcd. for $Cr(C_8H_6N_4Cl)_2(OH)\cdot 4H_2O$: Cr,9.8; C,36.1; H,3.98; N,21.15; Found: Cr,9.4; C,35.5; H,3.42; N,21.13;

Hydroxo bis(5-o-chlorophenyltetrazolato)chromium(III)tetrahydrate

5-Orthochlorophenyltetrazole did not precipitate from solution. After an hour, the grey complex precipitated from solution. Anal. Calcd. for $Cr(C_7H_4N_4Cl)_2OH\cdot 4H_2O$: Cr,10.4; C,33.62; H,3.40; N,22.5; Found: Cr,10.0; C,33.16; H,2.31; N,21.92.

Hydroxo bis(5-p-chlorophenyltetrazolato)chromium(III)tetrahydrate:

This grey solid precipitated within four hours after the 5-p-chlorophenyltetrazole was removed by filtration. Anal. Calcd. for $Cr(C_7H_4N_4Cl)_2OH\cdot 4H_2O$: Cr,10.4; C,33.62; H,3.40; N,22.5; Found: Cr,10.0; C,33.54; H,2.64; N,21.91.

Hydroxo bis(5-p-methoxyphenyltetrazolato)chromium(III) hexahydrate:

p-Methoxyphenyltetrazole, a white solid, precipitated immediately. The grey complex precipitated from the filtrate within a few minutes after the addition of excess .10M sodium 5-p-methoxyphenyltetrazole. Anal. Calcd. $Cr(C_8H_7N_4O)_2OH \cdot 6H_2O$: Cr,9.9; C,36.3; H,5.22; N,21.21; Found: Cr,9.5; C,35.3; H,4.03; N,21.04.

Hydroxo bis(5-phenyltetrazolato)chromium(III)tetrahydrate:

5-Phenyltetrazole did not precipitate from solution. The pinkish violet complex precipitated from solution within four hours. The analytical data indicate that it contains impurities. Anal. Calcd. for $Cr(C_7H_5N_4)_2OH\ 4H_2O$: Cr,12.2; C,39.80; H,4.43; N,26.57; Found: Cr,11.5; C,39.13; H,3.68; N,25.99.

Attempted preparation of manganese(II)complexes: No color change or precipitation occurred when aqueous manganese(II) solutions were mixed with aqueous solutions of the sodium 5-substituted tetrazolates.

Attempted preparation of iron(II) or iron(III)complexes: In all cases, small quantities of an orange solid, probably ferric hydroxide, precipitated from solution.

D. Analytical Methods

Cobalt: weighed samples of the cobalt complexes were decomposed by heating the solids with aqua regia. The resulting blue-green solutions were evaporated to dryness on a hot plate. The residues were reheated with aqua regia and the solutions were evaporated to dryness. This process was continued until the residues were completely water soluble. The pink residues were then dissolved in water and the resulting solutions were made slightly acidic (pH 6). Murexide indicator was added and the pH of the solutions were adjusted with ammonia until the color of the indicator changed from orange to yellow. The solutions were then titrated with 0.0100IM ethylenediaminetetraacetic acid (EDTA) to a color change from yellow to violet (47).

Nickel: Only one of the nickel complexes could be titrated with EDTA. Evidently, the tetrazolate anion is incompletely destroyed by nitric acid and interfers with the color change of the indicator. Thus, the nickel samples were analyzed by the cyanide method. Weighed samples were treated with 20ml of 0.1068M KCN solutions, 5ml of concentrated aqueous ammonia, and 1ml of a KI solution containing 1.1g of KI per ml of solution.

The samples were allowed to stand overnight. The complexes dissolved to give pale yellow solutions. The excess cyanide in the sample solutions was titrated with

0.100M $AgNO_3$. Silver nitrate dried at 110° was used as a primary standard. The 0.1068M KCN solution was standardized with the 0.100M $AgNO_3$ solution. Daugherty (45) found that titrations of known nickel samples in the presence of tetrazole resulted in an error of less than 2%.

Copper: Only a few of the copper complexes could be analyzed by EDTA titration due to interferences in the color change of the indicator.

All of the complexes could be analyzed by atomic absorption spectroscopy. Samples for atomic absorption were dissolved in ammonia and were diluted to volumes such that the solutions contained less than 10 ppm of copper. All of the solutions were stored in plastic bottles to avoid contamination by impurities in glass or pyrex. Standard solutions containing 0 to 10 ppm of copper(II) ion were prepared from aqueous 0.009898M $Cu(ClO_4)_2 \cdot 6H_2O$ solution. The aqueous $Cu(ClO_4)_2 \cdot 6H_2O$ solution was standardized with 0.01001M EDTA. Analytical results obtained by the atomic absorption method agreed very closely with those that could be obtained by EDTA titrations.

Chromium: Samples for analysis were decomposed by heating the solids with aqua regia. The resulting green solutions were evaporated to dryness. The residues were treated several times with aqua regia. The excess chloride

ions, not used in complexing the metal ions, were precipitated with silver nitrate solution. The AgCl was removed by filtration. The Chromium(III) ions were then oxidized to dichromate ions by the use of 5.0 ml of a solution containing 0.10 M $(NH_4)_2S_2O_8$ and 0.10 M NH_4NO_3. A few milliliters of 0.10$AgNO_3$ were added to catalyze the oxidation. The oxidation was complete within five minutes. The oxidized samples were diluted to volume with enough water so that the absorbance values at 445 nm were less than 1.0 when 10.0 cm cells were used. The samples were compared against standard dichromate solutions which obeyed Beer's law at 445 nm.

The dichromate standard solution ranged in concentration between 0.0002 N and 0.0014 N and were prepared from a 0.009819 N $K_2Cr_2O_7$ solution. The 0.009819 N $K_2Cr_2O_7$ solution was prepared by using $K_2Cr_2O_7$ as a primary standard.

Carbon, Hydrogen, and Nitrogen Analyses: The carbon, hydrogen and nitrogen analyses were performed by the Micro-analytical Laboratory of the Institute of Water Research, Michigan State University, East Lansing, Michigan.

E. Magnetic Moment Measurements

Magnetic susceptibilities were measured by the Gouy method by use of methods similar to those described by Vander Vennen (48). However, the apparatus was modified in order to

allow a constant stream of helium to pass over the sample tube. Thus, water was prevented from condensing on the sample tube at low temperatures and the sample was protected from hydrolysis.

The calculation of the magnetic moment was made by the use of the equation: (49)

$$10^{6}\chi = F' \times \frac{\beta}{W_s} \qquad (1)$$

where χ is the gram-susceptibility of the sample: F' is the force exerted on the sample alone, i.e., the measured force corrected for the force experienced by the tube alone; W_s is the weight of the sample in grams; and β is the tube constant, for a given magnetic field and a given temperature.

In practice, each β value must be determined for a particular tube by use of a material of known susceptibility. F' values are obtained at several magnetic fields and at several temperatures. At a given temperature, the χ value of the calibrant will be constant and will be independent of the magnetic field. The F' values, however, are dependent on the magnetic field at a given temperature. Therefore, a β value can be calculated for each magnetic field at a given temperature. Since χ varies with temperature, other β values can be calculated from F' values at other temperatures.

In this work, $Hg[Co(SCN)_4]$ was used as a calibrant. Its susceptibility is 16.44×10^{6} cgs units at 293°K and it obeys

the Curie-Weiss Law, $\chi_g \alpha(T + 10)^{-1}$ where T is expressed in degrees absolute. Figgis and Nyholm (50) reported that $Hg[Co(SCN)_4]$ is a much better calibrant than $CuSO_4 \cdot 5H_2O$ or $Fe_2(NH_4)_2(SO_4)_2 \cdot 6H_2O$.

The molar susceptibility, χ_m' of the sample is obtained by multiplying the gram-susceptibility by the molecular weight. The susceptibility of the metal ion, χ_m' is obtained by correcting the molar susceptibility for any diamagnetic species present. Pascal's constants (51) were used to estimate the diamagnetism of the ligands and cations.

In normal paramagnetic substances, χ_m' related to the absolute temperature as

$$\chi_m' = \frac{C}{T} \qquad \text{Curie Law} \qquad (2)$$

or

$$\chi_m' = \frac{C}{(T + \theta)} \qquad \text{Curie-Weiss Law} \qquad (3)$$

For the latter case, a plot of $1/\chi_m'$ against T allows evaluation of θ from the intercept.

The magnetic moment μ of the sample may be calculated from the molar susceptibility by

$$\mu = 2.84 \ (T \times \chi_m')^{1/2} \qquad (4)$$

The low temperature studies were performed by using a specially constructed Dewar flask similar to that described by Vander Vennen (48). The magnetic moments were measured at

room temperature, 195°K, and 77°K.

F. Spectroscopic Measurements

The infrared spectra of the complexes were obtained by use of nujol and hexachlorobutadiene mulls, a Perkin Elmer Model 457 spectrophotometer (4000 cm^{-1} to 250 cm^{-1}) and a Perkin Elmer Model 301 spectrophotometer (680 cm^{-1} to 167cm^{-1}). Cesium iodide and polyethylene plates were used. The visible and ultraviolet solution spectra were obtained by use of a Cary Model 14 spectrophotometer.

The near infrared, visible and ultraviolet spectra of the solids were obtained on a Beckman Model DK-2 spectrophotometer (equipped with a reflectance attachment) at Dow Chemical Company, Midland, Michigan. The spectra were also obtained by the method of Cotton and Goodgame (52) by use of a Cary Model 14 spectrophotometer. In the Cotton and Goodgame (52) method, a nujol mull of the complex was painted onto a sheet of filter paper. The sheet of filter paper was then taped to the exit window of the sample compartment. Another sheet of filter paper was painted with nujol and this sheet was taped to the exit window in the reference compartment. The nujol mull method was generally quite satisfactory for bands in the ultraviolet and visible regions but gave rather poor results in the near infrared region. The major advantage of the nujol mull method lies in the accurate location of band maxima by use of the slowest scan rate on the Cary Model 14 spectrophotometer.

The electron spin resonance spectra of the powdered complexes were obtained at temperatures from -160° to 25° by use of a Varian E-4 EPR spectrometer equipped with a Varian E-257 variable temperature controller. Powdered samples were diluted by precipitating the zinc complex in the presence of copper(II), cobalt(II) or chromium(III) ions.

DISCUSSION OF RESULTS

From the analytical data, it appears that each cobalt(II), nickel(II), chromium(III), copper(II), and zinc(II) ions can only accommodate a maximum of two tetrazolate anions when the complexes are precipitated from aqueous solution. It is rather surprising that chromium(III) does not form a 3:1 complex. Apparently, the hydroxide and the tetrazolate anions compete in aqueous solution for the coordination sites on chromium(III). The 3:1 complex can possibly be prepared and precipitated from nonaqueous solutions by using tetralkylammonium salts in place of the sodium salt.

Copper(II) also forms hydroxo complexes. Daugherty (21) could only prepare bis(5-phenyltetrazolato) copper(II) from methanol solutions. Only impure bis(5-p-methoxyphenyltetrazolato) copper(II) could be obtained from methanol solutions (21).

As previously observed (22), nickel(II) forms complexes with a tetrazolate to nickel(II) ratio between one and two. Perhaps the complexes are 2:1 complexes with tetrazolate vacancies in the crystal structure.

The solubilities of these complexes are listed in Tables I to V. All of the complexes are insoluble in acetone, 1,4-dioxane, methylenechloride, benzene and acetonitrile. Only bis(5-p-chlorobenzyltetrazolato) copper(II) trihydrate is soluble in nitromethane. Some of the complexes are even insoluble in dimethylsulfoxide, methanol, N,N-dimethylformamide

and pyridine. Of these solvents, pyridine, dimethylsulfoxide, and N,N-dimethylformamide seem to be most suitable to dissolve the solids for measuring solution spectra.

Infrared Spectra

Comparisons of the infrared spectra of the tetrazoles and their respective sodium salts and complexes are shown in Tables VI to XV. Band assignments were based on the results of a normal coordinate analysis on sodium tetrazolate monohydrate (32) displayed in Table XVI. Table XVII shows the assignment of bands in sodium tetrazolate monohydrate (32).

Complexes containing water of hydration display bands in the 3350 to 3500cm^{-1} spectral region. Many of the sodium salts also contained an O-H stretch in their infrared spectra even though the salts had been dried at 110° for several hours.

The spectra of the tetrazoles and their respective sodium salts and complexes are quite similar with the exception of bands in the 2700-2850cm^{-1} spectral region. Bands in this region have been previously assigned as N-H stretches. (19) This assignment was further confirmed by Holm (31) who compared the spectra of 1-H-tetrazole and 1-D-tetrazole. No bands were found in the 2700-2850cm^{-1} spectral region for 1-D tetrazole. Due to the absence of the N-H stretch in the spectra of the complexes and the sodium salts, the tetrazoles appear to coordinate as the anion.

As a result of a normal coordinate analysis by Garber, et al., it appears that none of the infrared bands can be assigned to C-N and N-N stretching modes in contrast with previous assignments (23,31,53).

Despite the similarities in the spectra of the sodium salts and their respective complexes, the spectra of the sodium salts often contain additional bands. Jonassen (23) has postulated that fewer bands are found in the infrared spectra of the complexes than in the infrared spectra of their respective sodium salts because of the loss of resonance character in the complexes. Although all of the fundamental bands appear in both the sodium salts and their respective complexes, coordination of tetrazoles with metal ions often reduces the intensities of overtone and combination bands. Occasionally, more bands appear in the spectra of the complexes than in the spectra of the sodium salts or the tetrazoles. In these cases, coordination may cause a splitting of bands in the 4000 to 650cm^{-1} spectral region. This splitting of tetrazole bands also accounts for extra bands found in the far infrared spectra of PMT complexes in the metal-ligand deformation region (178-236 cm^{-1}) and the metal-nitrogen stretching region (250-450 cm^{-1}) (55).

The infrared spectra provide little information about the presence of perchlorate since the tetrazoles or sodium tetrazolates themselves have bands in the 620-630, 932, and 1090 cm^{-1} spectral regions which have been assigned as ionic perchlorate bands (54).

The far infrared spectra have been very useful in demonstrating metal-ligand interaction in tetrazolate (11) and PMT (55) complexes with copper(II). In most cases, the infrared bands of the tetrazoles in the 4000 to 650 cm^{-1} spectral region are unshifted on complexation (55). However, D'Itri (55) found that bands in the 180 to 360 cm^{-1} region are shifted to higher frequency on complexation. Furthermore, the frequency of a given band in the infrared spectrum of PMT was increased in frequency with a decrease in the ionic radius of the metal ion. Similar frequency shifts were observed in the present study as shown in Tables VI, VIII, X, XII, and XIV.

Sharp, et al. (56), Jungbauer and Curran (57), McWinnie (58), Goldstein, et al. (59), and Clark and Williams (60) have tentatively assigned bands in the 250 to 450 cm^{-1} region as the metal-nitrogen asymmetric stretches for transition metal complexes of substituted anilines, aniline, 2,2' bipyridylamine, heterocyclic bases, and pyridine respectively.

D'Itri and Popov (55) and Garber, et al. (32) also observed bands in the 250-320 cm^{-1} spectral region which they assigned to metal-nitrogen stretching frequencies.

In 1966, Frank and Rogers (61) compared themetal-nitrogen stretching frequencies for various copper(II) complexes of substituted-pyridines and listed these ligands in probably order of increasing donor strength. The ligand giving the largest metal-nitrogen stretching frequency was considered the strongest ligand.

A comparison of the far infrared spectra of the copper(II) complexes of the various 5- substituted tetrazoles and their respective sodium salts indicated that only a few of the bands could be tentatively assigned to metal-nitrogen stretching frequencies due to the presence of broad unresolvable bands. Clark and Williams (60) also found that the far infrared spectra of the polymeric octahedral complexes $MCl_2 \cdot 2$ pyridine (M = Mn, Fe, Co, and Ni) consisted of broad badly resolved bands in the 200 to 260 cm^{-1} spectral region. The far infrared spectra of the complexes are displayed in Figures 1-5.

Table I. Solubility of the Cobalt(II) Complexes in Various Solvents at 22°

	$5\text{-}C_6H_5CN_4$	$5\text{-}O\text{-}ClC_6H_4CN_4$	$5\text{-}p\text{-}ClC_6H_4CN_4$	$5\text{-}p\text{-}CH_3OC_6H_4CN_4$	$5\text{-}p\text{-}ClC_6H_4CH_2CN_4$
Acetone	i	i	i	i	i
Nitromethane	i	i	i	i	i
Dimethylsulfoxide	s	s	s	s	sl.s
1,4-Dioxane	i	i	i	i	i
N,N-Dimethylformamide	s	s	s	s	sl.s
Methanol	i	s	s	i	i
Pyridine	m.s	s	s	s	s
Methylenechloride	i	i	i	i	i
Benzene	i	i	i	i	i
Acetonitrile	i	i	i	i	i

i - insoluble
s - soluble
m.s - moderately soluble
sl.s - slightly soluble

Table II. Solubility of the Nickel (II) Complexes in Various Solvents at 22°

	$5\text{-}C_6H_5CN_4$	$5\text{-}o\text{-}ClC_6H_4CN_4$	$5\text{-}p\text{-}ClC_6H_4CN_4$	$5\text{-}p\text{-}CH_3OC_6H_4CN_4$	$5\text{-}p\text{-}ClC_6H_4CH_2CN_4$
Acetone	i	i	i	i	i
Nitromethane	i	i	i	i	i
Dimethylsulfoxide	s	s	m.s	m.s	m.s
1,4-Dioxane	i	i	i	i	i
N,N-Dimethylformamide	s	s	s	m.s	m.s
Methanol	i	i	i	i	i
Pyridine	s	s	s	m.s	m.s
Methylenechloride	i	i	i	i	i
Benzene	i	i	i	i	i
Acetonitrile	i	i	i	i	i

i - insoluble
s - soluble
sl.s - slightly soluble
m.s - moderately soluble

Table III. Solubility of the Copper (II) Complexes in Various Solvents at 22°

	5-$C_6H_5CN_4$	5-o-$ClC_6H_4CN_4$	5-p-$ClC_6H_4CN_4$	5-p-$CH_3OC_6H_4CN_4$	5-p-$ClC_6H_4CH_2CN_4$
Acetone	i	i	i	i	i
Nitromethane	i	i	i	i	sl.s
Dimethylsulfoxide	i	s	i	i	sl.s
1,4-Dioxane	i	i	i	i	i
N,N-Dimethylformamide	i	s	i	i	m.s
Methanol	i	i	i	i	i
Pyridine	i	s	i	i	s
Methylenechloride	i	i	i	i	i
Benzene	i	i	i	i	i
Acetonitrile	i	i	i	i	i

i - insoluble
s - soluble
sl.s - slightly soluble
m.s - moderately soluble

Table IV. Solubility of the Chromium (III) Complexes in Various Solvents at 22°

	$5\text{-}C_6H_5CN_4$	$5\text{-}o\text{-}ClC_6H_4CN_4$	$5\text{-}p\text{-}ClC_6H_4CN_4$	$5\text{-}p\text{-}CH_3OC_6H_4CN_4$	$5\text{-}p\text{-}ClC_6H_4CH_2CN_4$
Acetone	i	i	i	i	i
Nitromethane	i	i	i	i	i
Dimethylsulfoxide	s	m.s	s	m.s	s
1,4-Dioxane	i	i	i	i	i
N,N-Dimethylformamide	s	m.s	s	m.s	s
Methanol	s	sl.s	i	i	i
Pyridine	s	m.s	s	s	s
Methylenechloride	i	i	i	i	i
Benzene	i	i	i	i	i
Acetonitrile	i	i	i	i	i

i - insoluble
s - soluble
sl.s - slightly soluble
m.s - moderately soluble

Table V. Solubility of the Zinc (II) Complexes in Various Solvents at 22°

	$5\text{-}C_6H_5CN_4$	$5\text{-}o\text{-}ClC_6H_4CN_4$	$5\text{-}p\text{-}ClC_6H_4CN_4$	$5\text{-}p\text{-}CH_3OC_6H_4CN_4$	$5\text{-}p\text{-}ClC_6H_4CH_2CN_4$
Acetone	i	i	i	i	i
Nitromethane	i	i	i	i	i
Dimethylsulfoxide	i	i	s	s	s
1,4-Dioxane	i	i	i	i	i
N,N-Dimethylformamide	i	i	s	i	i
Methanol	i	i	s	i	i
Pyridine	i	s	s	s	s
Methylenechloride	i	i	i	i	i
Benzene	i	i	i	i	i
Acetonitrile	i	i	i	i	i

i - insoluble
s - soluble
Sl.s - Slightly soluble
m.s - moderately soluble

Table VI. Infrared Spectra[a] of 5-Phenyltetrazole, Sodium 5-Phenyltetrazolate and Various Complexes of 5-Phenyltetrazole in Nujol and Hexachlorobutadiene Mulls from 4000 to 167cm^{-1}

HT	NaT	$CoT_2 \cdot H_2O$	$NiT_{1.8} \cdot H_2O$	$CuT_2 \cdot H_2O$	$Zn(T)_2$	$CrT_2(OH) \cdot 4H_2O$
	3690(s)					
3560(m)	3570(s)					
	3500(s)			3480(s)		
	3370(s)[b]	3400(s)[b]	3400(s)[b]			3400(s)[b]
3210(m)						
3140(m)	3160(s)[b]	3120(m)	3130(m)	3120(m)	3125(m)	3125(m)
3050(m)	3050(s)	3060(s)	3060(s)	3060(w)	3060(m)	3030(m)
2980(m)	3000(s)[b]	1990(s)	3020(s)	3030(s)	3020(m)	3010(s)
2760(s)						
2660(s)[b]						

a Intensities in parenthesis (s = strong, m = medium, w = weak, vw = very weak, sh = shoulder). Breadth of peaks in brackets [b = broad]

Continued

Table VI. - Continued

HT	NaT	$CoT_2 \cdot H_2O$	$NiT_{1.8} \cdot H_2O$	$CuT_2 \cdot H_2O$	$Zn(T)_2$	$CrT_2(OH) \cdot 4H_2O$
2590(s)						
2530(s)[b]						
2460(s)[b]						
	2290(w)					
2000(m)						
1965(m)	1950(w)[b]	1950(w)[b]	1950(w)[b]	1960(w)[b]	1965(w)[b]	1970(w)[b]
1923(m)						
1850(m)[b]	1860(w)	1850(w)	1830(w)	1870(w)	1860(w)	1840(w)
1780(w)						
1760(w)[b]						
1730(w)	1680(m)	1700(m)			1710(w)[b]	1700(w)
1610(s)	1610(s)[b]	1600(s)	1610(m)	1620(m)	1610(m)	1620(w)[b]
1570(s)	1560(m)	1550(s)	1560(w)		1540(m)	1560(w)[b]

continued

Table VI. - Continued

HT	NaT	$CoT_2 \cdot H_2O$	$NiT_{1.8} \cdot H_2O$	$CuT_2 \cdot H_2O$	$Zn(T)_2$	$CrT_2(OH) \cdot 4H_2O$
1500(m)	1525(vw)	1520(w)	1520(w)	1530(m)	1520(w)	1520(w)
1470(s)	1460(s)	1460(s)	1470(s)			1470(s)
1430(w)	1450(s)	1450(s)	1450(s)	1460(s)	1460(s)	1450(s)
1400(s)	1380(m)	1390(s)		1390(s)	1380(m)	
	1360(m)	1340(w)	1360(m)	1360(m)	1340(w)	1360(m)
1290(m)	1290(m)	1280(m)	1280(m)	1280(m)	1280(s)	1280(m)
1260(m)	1260(w)	1245(m)	1245(m)	1260(w)	1240(m)	1230(w)
	1200(m)	1200(m)	1195(m)	1220(m)	1190(w)	121 (vw)
	1170(s)	1150(m)	1170(m)	1180(m)	1185(w)	1170(w)
	1130(m)	1150(m)	1155(m)		1165(w)	1160(w)
	1125(m)	1130(m)	1120(m)	1120(w)		1120(w)
1103(w)	1105(w)	1110(w)	1100(w)	1100(w)	1100(m)	1100(w)
1087(s)	1090(vw)	1080(s)	1080(s)	1081(m)	1080(s)	1080(m)

Continued

Table IV - continued

HT	NaT	$CoT_2 \cdot H_2O$	$NiT_{1.8} \cdot H_2O$	$CuT_2 \cdot H_2O$	$Zn(T)_2$	$CrT_2(OH) \cdot 4H_2O$
1057(m)	1070(m)	1070(m)	1060(m)			1070(w)
1036(m)	1025(m)	1035(w)	1028(w)	1036(w)	1040(w)	1028(w)
1015(m)	1010(m)	1010(m)	1010(m)	1010(w)	1015(m)	1010(m)
994(s)	990(w)[b]	980(w)[b]	975(w)[b]	960(w)[b]	980(w)[b]	960(w)[b]
924(w)	910(w)	920(w)	920(w)	920(w)	910(w)	910(w)
850(m)	860(m)	840(w)[b]	850(w)	850(w)[b]	850(w)[b]	850(w)[b]
790(m)	790(m)	790(m)	785(m)	790(m)	780(m)	780(m)
725(s)	725(s)	730(s)	730(s)	720(s)	730(s)	730(s)
700(s)	700(s)	705(s)				
685(s)	685(s)	690(s)	690(s)	680(s)	690(s)	680(s)
670(s)	675(s)					
660(m)	665(s)		650(w)			

Continued

Table VI. - Continued

HT	NaT	$CoT_2 \cdot H_2O$	$NiT_{1.8} \cdot H_2O$	$CuT_2 \cdot H_2O$	ZnT_2	$CrT_2(OH) \cdot 4H_2O$
		619(sh)	619(w)	∿619(sh)	∿590(sh)	
	540(sh)	540(m)		537(s)	525(m)	534(m)[b]
490(s)	503(s)	511(m)	511(w)	502(m)		
449(s)[b]	459(s)	455(m)		473(m)	453(m)	456(w)
407(sh)	420(sh)	420(w)		426(m)		418(w)
345(w)[b]	355(m)	376(s)	386(w)		400(w)	383(w)
					353(s)	
		328(m)[b]	341(w)	324(w)[b]	330(s)	323(w)
307(w)	308(w)		301(s)			299(w)
		284(s)[b]	270(w)[b]	286(w)	277(s)	284(w)
	250(sh)	250(sh)	several weak bands			251(w)
				238(m)		244(w)
			270 to 167cm^{-1}			
		224(s)[b]		216(m)	216(s)	220(w)
	207(sh)			207(m)	207(s)	199(w)
180(m)	170(m)[b]	180(m)[b]				190(w)

Table VII. Infrared Spectra[a] of 5-Phenyltetrazole and Sodium 5-Phenyltetrazolate with Band Assignments

HT	NaT	Genuine Vibrational Mode	Assignment
	3690(s)		
3560(m)	3570(s)		[$\nu_1 + \nu_{11}$)
	3500(s)		
	3370(s)[b]	ν_{13}	O-H stretch
3210(m)			
3140(m)	3160(s)[b]	ν_1	ring C-H
3050(m)	3050(s)		[ν_2 + 1600]
2980(m)	3000(s)[b]		
2760(s)		ν_{14}	[N-H stretch]
2660(s)[b]			
2590(s)			[2 ν_3]
2530(s)[b]			[$\nu_2 + \nu_5$]
2460(s)[b]			[$\nu_2 + \nu_8$]
	2290(w)		[$\nu_3 + \nu_8$]
2000(m)			[2 ν_{10}]
1965(m)	1950(w)[b]		[$\nu_7 + \nu_{10}$]
1923(m)			[$\nu_8 + \nu_{10}$]
1850(m)[b]	1860(w)		[$\nu_4 + \nu_9$]
1780(w)			
1760(w)[b]			[$\nu_5 + \nu_9$]

a Units are in cm^{-1}

b Brackets indicate possible assignments

Continued

Table VII. - Continued

HT	NaT	Genuine Vibrational Mode	Assignment
1730(w)[b]			
	1680(m)		O-H bend
1610	1610(m)		
1570(s)	1560(m)		[$\nu_9 + \nu_{10}$]
1500(m)	1525(vw)		[$\nu_7 + \nu_{11}$]
1470(s)	1460(s)	ν_2	ring deformation
1430(w)	1450(s)	ν_6	C-H in plane bend
1400(s)	1380(m)		[$\nu_{10} + \nu_{12}$]
	1360(m)		[$\nu_{10} + \nu_{11}$]
1290(m)	1290(m)	ν_3	ring vibration
1260(m)	1260(w)		$\nu_9 + \nu_{12}$
	1200(m)		$\nu_9 + \nu_{11}$
	1170(s)	ν_4	ring breathing
	1130(m)		[$\nu_{12} + 650$]
	1125(m)		[$\nu_{12} + 615$]
1103(w)	1105(w)		[$\nu_{11} + 650$]
1087(s)	1090(vw)		[$\nu_{11} + 615$]
1057(m)	1070(m)	ν_5	ring deformation
1036(m)	1025(m)	ν_7	ring deformation
1015(m)	1010(m)	ν_8	ring deformation
994(s)	980(w)[b]		[$\nu_{11} + \nu_{12}$]

Continued

Table VII. - Continued

HT	NaT	Genuine Vibrational Mode	Assignment
924(w)	910(w)	ν_{10}	C-H out of plane bend
850(m)	860(m)		[ν_{12} + 350]
796(m)	780(m)		
725(s)	725(s)	ν_9	ring deformation
700(s)	700(s)		[2(355)]
685(s)	685(s)		[ν_4 - ν_{11}]
670(s)	675(s)		
660(m)	665(s)		
	540(sh)		
490(s)	505(s)	ν_{12}	out-of-plane ring bend
449(w)[b]	459(s)	ν_{11}	out-of-plane ring bend
407(sh)	420(sh)		[ν_2 - ν_7]
345(w)[b]	355(m)		[ν_5 - ν_9]
307(w)	308(w)		[ν_7 - ν_9]
	250(sh)		[ν_9 - ν_{11}]
	207(sh)		[ν_{10} - ν_9]
108(s)	170(s)[b]		

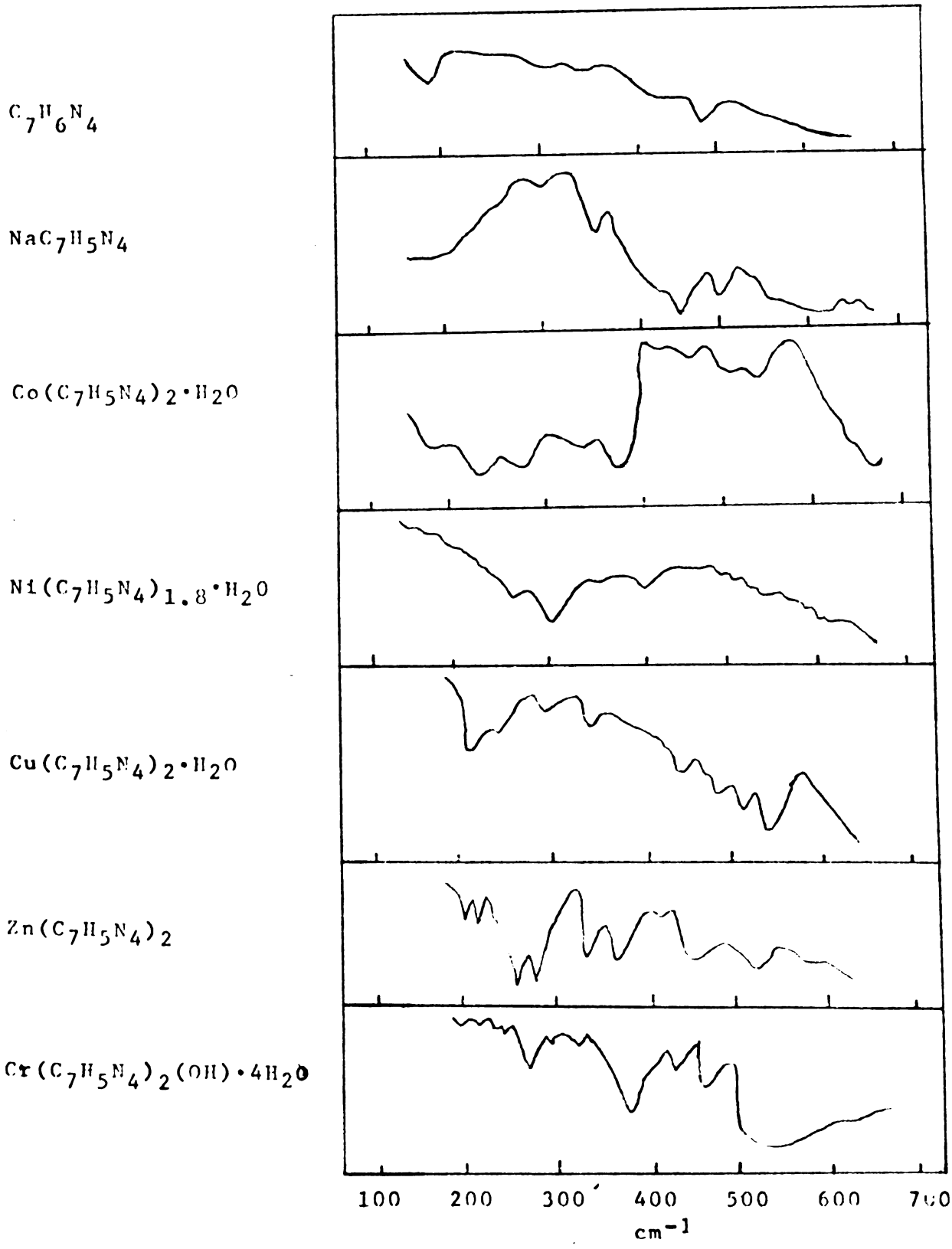


Figure 1 Far Infrared Spectra of 5-Phenyltetrazole, Sodium 5-Phenyltetrazolate and Various Complexes of Sodium 5-Phenyltetrazolate

Table VIII. Infrared Spectra[a] of 5-p-Methoxyphenyltetrazole, Sodium 5-p-Methoxyphenyltetrazole and Various Complexes of 5-p-Methoxyphenyltetrazole in Nujol and Hexachlorobutadiene Mulls from 4000 cm^{-1} to 167 cm^{-1}

HT	NaT	$CoT_2 \cdot H_2O$	$NiT_{1.8} \cdot H_2O$	Cu(T)(OH)	ZnT_2	$CrT_2(OH) \cdot 6H_2O$
3550(m)[b]	3570(s)	3500(sh)	3600(sh)	3570(m)		3600(s)
	3400(s)[b]	3400(m)[b]	3400(s)[b]			3400(s)[b]
3200(sh)	3200(sh)	3200(sh)	3200(sh)			3200(sh)
	3160(s)[b]					3160(s)
3100(sh)	3080(sh)	3080(s)[b]	3100(s)[b]		3090(s)	3080(s)[b]
	3040(sh)			3050(m)		
	3000(m)	3000(s)	3000(w)		3000(s)	3000(w)
2780(s)[b]						2780(s)[b]
						2740(s)[b]
2650(s)[b]						2640(s)[b]

a - see legend Table VI.

Continued

Table VIII. - Continued

HT	NaT	$CoT_2 \cdot H_2O$	$NiT_{1.8} \cdot H_2O$	CuT(OH)	ZnT_2	$CrT_2(OH) \cdot 6H_2O$
2600(s)[b]					2550(w)	2550(s)
2500(s)[b]						2480(s)
	2280(w)					
2080(w)				2040(w)[b]	2040(w)[b]	
1950(w)[b]		1970(w)[b]				
1910(w)[b]	1920(w)	1900(w)[b]		1930(w)		
1878(w)	1880(w)					
1800(w)[b]		1800(w)[b]				
1770(w)						
1730(w)						
1710(w)						
1700(w)	1690(m)					
1620(s)	1620(m)	1615(m)	1620(m)	1620(m)	1620(s)	1620(s)

Continued

Table VIII. - Continued

HT	NaT	$CoT_2 \cdot H_2O$	$NiT_{1.8} \cdot H_2O$	CuT(OH)	ZnT_2	$CrT_2(OH) \cdot 6H_2O$
1590(s)	1585(s)	1580(w)	1580(m)	1585(w)	1580(m)	1580(s)
1520(s)	1535(m)	1540(s)	1540(s)	1545(w)	1540(m)	1540(m)
		1510(m)	1500(m)	1510(m)[b]	1510(m)	1500(s)
1480(m)					1475(s)	
1460(s)	1450(s)	1455(s)	1460(s)	1460(s)	1465(s)	1455(s)
1450(s)	1440(s)	1440(s)	1440(s)	1440(s)	1445(s)	1440(s)
1420(s)				1405(w)	1425(sh)	1410(s)
1380(m)	1370(s)	1380(s)	1380(m)[b]	1380(m)	1395(s)	1370(m)
1360(s)sh		1360(s)	1360(m)[b]	1360(m)[b]	1360(s)	
1320(m)	1310(s)			1320(m)	1320(s)	
	1300(m)	1310(s)	1300(s)	1300(s)	1310(s)	1300(s)
1300(s)	1290(s)	1285(s)	1290(s)	1280(s)	1290(s)	1290(s)

Continued

Table VIII. - Continued

HT	NaT	$CoT_2 \cdot H_2O$	$NiT_{1.8} \cdot H_2O$	CuT(OH)	ZnT_2	$CrT_2(OH) \cdot 6H_2O$
1270(s)	1250(s)	1250(s)	1250(s)	1250(s)	1250(s)	1260(s)
		1230(s)				1230(s)
1190(w)	1205(m)		1210(s)	1205(m)	1200(m)	1205(w)
	1175(s)			1180(m)	1180(s)	1180(s)
1170(s)	1170(sh)	1170(s)	1170(s)	1160(m)		1160(s)
1150(m)	1140(m)	1140(s)	1140(s)	1140(w)	1140(s)	1140(s)
1140(s)		1130(m)	1130(m)	1130(vw)	1130(m)	1130(s)
1130(m)	1120(m)	1110(m)	1110(s)		1110(m)	1110(s)
1090(m)	1100(m)	1105(m)	1100(m)	1100(m)	1100(m)	1080(s)
1070(m)	1080(vw)	1060(m)	1060(m)	1060(m)	1070(m)	1070(s)
1050(m)	1030(m)	1030(m)	1030(m)	1030(m)	1040(m)	1030(m)
1020(m)	1025(s)	1020(s)	1020(s)	1015(m)	1015(s)	1015(s)

Continued

Table VIII - Continued

HT	NaT	$CoT_2 \cdot H_2O$	$NiT_{1.8} \cdot H_2O$	CuT(OH)	ZnT_2	$CrT_2(OH) \cdot 6H_2O$
1000(m)	1000(s)	1000(m)	1000(s)	1000(m)	1000(m)	1000(m)
			980(s)	980(s)	990(w)[b]	990(s)
950(m)			940(s)	950(s)[b]	960(w)[b]	940(m)
880(w)	890(vw)		890(m)	890(vw)[b]	890(m)	890(s)
860(s)			850(s)	850(s)	850(s)	850(s)
820(m)	830(s)	835(m)	830(s)	825(m)	830(s)	830(s)
810(m)	790(w)	790(w)	790(s)	790(m)	780(m)	790(m)
750(s)	760(s)	750(m)	760(s)	760(m)	760(s)	760(s)
						750(s)
720(w)	720(w)	720(m)	720(s)	720(m)	725(m)	720(s)
700(m)					715(m)	700(m)
					705(m)	690(m)
660(w)	660(m)	650(m)	650(m)	650(m)	650(w)	670(s)

Continued

Table VIII. - Continued

HT	NaT	$CoT_2 \cdot H_2O$	$NiT_{1.8} \cdot H_2O$	Cu(T)(OH)	ZnT_2	$CrT_2(OH) \cdot 6H_2O$
631(w)	638(w)					631(s)
608(s)	611(s)	619(s)	621(s)	619(s)	625(s)	621(s)
				550(w)		
522(s)	520(s)	534(m)	534(m)	528(s)	540(s)	534(m)[b]
499(w)	497(s)	499(w)	501(sh)		501(s)	
447(s)	447(s)	455(w)[b]	495(w)	476(s)	466(s)	457(sh)
		436(w)[b]		438(w)		
387(m)	419(sh)			390(m)	407(w)	390(w)
312(m)	319(m)	345(w)	352(m)[b]	350(sh)		345(w)
			307(m)	329(m)	331(s)	312(w)
			292(w)			
			284(w)	286(w)[b]	286(s)[b]	286(w)
249(s)	261(m)[b]	266(w)[b]	268(w)		276(sh)	268(w)
			260(w)	260(w)	256(s)[b]	
			238(w)[b]		243(s)[b]	

Continued

Table VIII. - Continued

HT	NaT	$CoT_2 \cdot H_2O$	$NiT_{1.8} \cdot H_2O$	Cu(T)(OH)	ZnT_2	$CrT_2(OH) \cdot 6H_2O$
	213(m)		213(w)[b]			215(vw)
200(w)	205(m)					
	191(s)			195(s)	195(w)	
169(s)				184(s)	180(w)	127(vw)

Table IX. Infrared Spectra[a] of 5-p-Methoxyphenyltetrazole and Sodium 5-p-Methoxyphenyltetrazolate

HT	NaT	Genuine Vibrational Mode	Assignment
3500(m)[b]	3570(s)		[ν_1 + ν_{11}]
	3400(s)[b]	ν_{13}	O-H stretch
3200(sh)	3200(sh)		1620 + 1585
	3160(s)[b]	ν_1	ring C-H stretch
3100(sh)	3080(sh)		[ν_2 + 1600]
	3040(sh)		
	3000(m)		[2(1 ν_2)]
2780(s)[b]		ν_{14}	[N-H stretch]
2650(s)[b]			
2600(s)[b]			[2(ν_3)]
2500(s)[b]			[ν_2 + ν_5]
	2280(w)		[ν_3 + ν_8]
2080(w)			[2(ν_7)]
1950(w)[b]			[ν_5 + ν_{10}]
1910(w)[b]	1920(w)		[ν_8 + ν_{10}]
1870(w)	1880(w)		[ν_4 + ν_9]
1800(w)[b]			[2 ν_{10}]
1170(w)			[ν_5 + ν_9]
1730(w)			[ν_7 + ν_9]
1710(w)			[ν_8 + ν_9]

a Units are in cm^{-1}
b Brackets indicate possible assignments

Continued

Table IX. - Continued

HT	NaT	Genuine Vibrational Mode	Assignment
1700(w)	1690(m)		[$\nu_1 - \nu_2$]
1620(s)	1620(m)		
1590(s)	1585(s)		[$\nu_9 + \nu_{10}$]
1520(s)	1535(m)		[$\nu_5 + \nu_{11}$]
1480(m)			[$\nu_7 + \nu_{11}$]
1460(s)	1450(s)	ν_2	ring deformation
1450(s)	1440(s)	ν_6	C-H in-plane bend
1420(s)			[2(700)]
1380(m)	1370(s)		[$\nu_{10} + \nu_{12}$]
1360(s)sh			[$\nu_{10} + \nu_{11}$]
1320(m)	1310(s)		
1300(s)	1300(m)	ν_3	ring vibration
	1290(s)		
1270(s)	1250(s)		[$\nu_9 + \nu_{12}$]
1190(w)	1205(m)		[$\nu_9 + \nu_{11}$]
	1175(s)		
1170(s)	1170(sh)	ν_4	ring breathing
1150(m)	1140(m)		[$\nu_{12} + 650$]
1140(s)			[$\nu_{12} + 615$]
1130(m)	1120(m)		[$\nu_{11} + 650$]
1090(m)	1100(m)		[$\nu_{11} + 615$]

Continued

Table IX. - Continued

HT	NaT	Genuine Vibrational Mode	Assignment
1070(m)	1080(vw)	ν_5	ring deformation
1050(m)	1030(m)	ν_7	ring deformation
1020(m)	1025(s)	ν_8	ring deformation
1000(m)	1000(s)		(1454-454) or 2(500)
950(m)			
880(w)	890(vw)	ν_{10}	C-H out-of-plane bend
860(s)			[ν_{12} + 350)
820(m)	830(s)		
810(m)	790(w)		
750(s)	760(s)		
720(w)	720(w)	ν_6	ring deformation
700(m)			
660(w)	660(w)		
631(w)	638(w)		
608(s)	611(s)		[$\nu_5 - \nu_{11}$]
522(s)	520(s)	ν_{12}	out-of-plane ring bend
499(w)	497(s)		
447(s)	447(s)	ν_{11}	out-of-plane ring bend
	409(sh)		[$\nu_2 - \nu_7$]
387(m)	387(sh)		[$\nu_3 - \nu_{10}$]
312(m)	319(m)		[$\nu_7 - \nu_9$]

Continued

Table IX. - Continued

HT	NaT	Genuine Vibrational Mode	Assignment
249(s)	261(m)[b]		[$\nu_9 - \nu_{11}$]
	213(m)		
200(w)	205(m)		[$\nu_{10} - \nu_9$]
169(s)	191(s)		

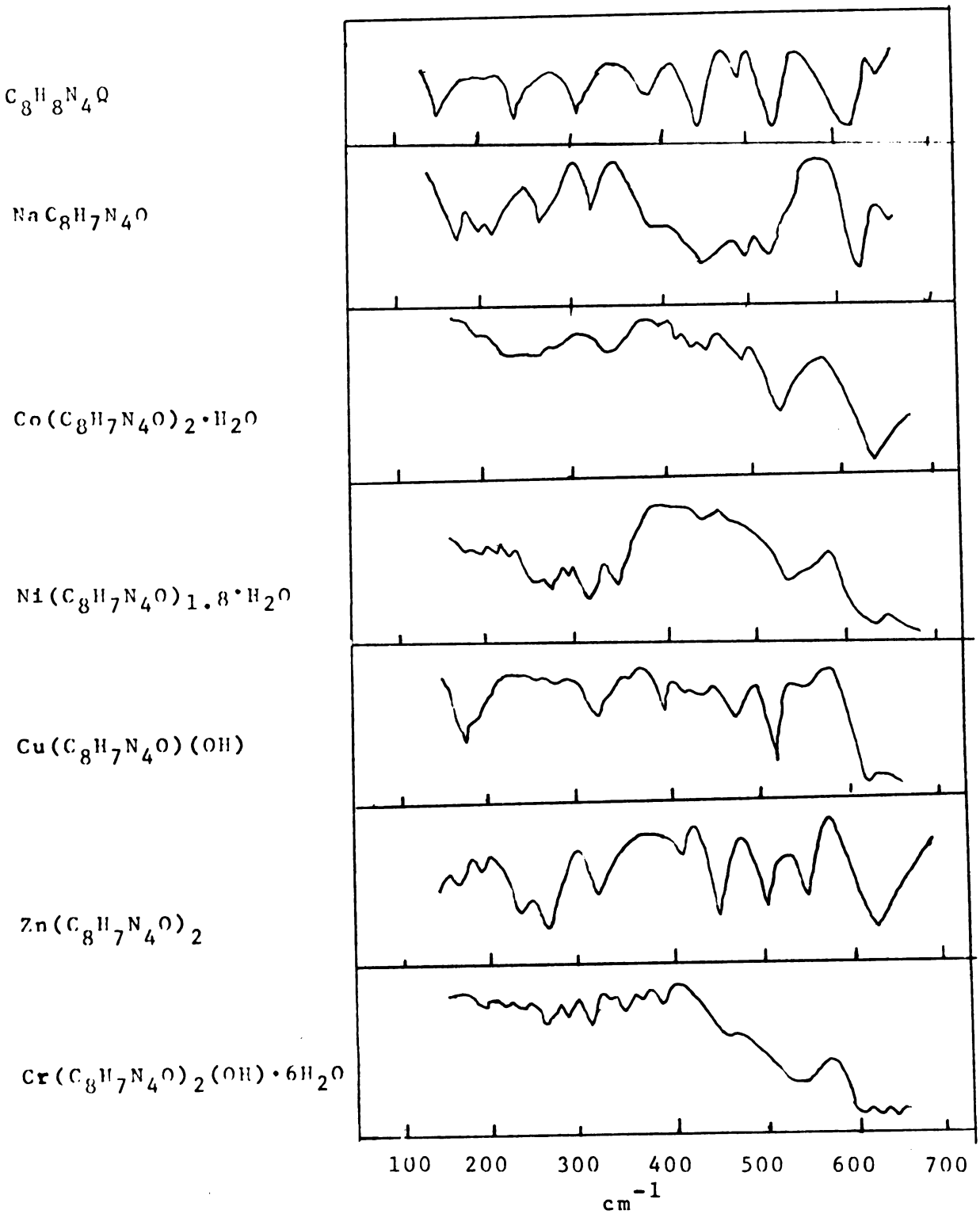


Figure 2 Far Infrared Spectra of 5-p-Methoxyphenyltetrazole, Sodium 5-p-Methoxyphenyltetrazolate, and Various Complexes of 5-p-Methoxyphenyltetrazole

Table X Infrared Spectra[a] of 5-p-Chlorophenyltetrazole, Sodium 5-p-Chlorophenyltetrazolate and Various Complexes of 5-p-Chlorophenyltetrazole in Nujol and Hexachlorobutadiene Mulls from 4000 to 167cm^{-1}

HT	NaT	$CoT_2 \cdot H_2O$	$NiT_{1.8} \cdot H_2O$	$CuT_2 \cdot H_2O$	$ZnT_2 \cdot \frac{3}{2}H_2O$	$CrT_2(OH) \cdot 4H_2O$
	3570(s)			3550(s)		
	3420(s)					
	3340(m)[b]	3360(s)[b]	3350(m)[b]	3330(s)[b]	3350(s)[b]	3350(m)[b]
3090(m)	3150(s)[b]	3150(s)[b]	3150(s)[b]	3100(m)	3100(s)	3100(s)
3060(m)	3060(s)			3070(m)		3080(s)
2800(m)						
1750(m)[b]						
2720(m)[b]						
2630(m)[b]						
2540(m)[b]						
2270(m)[b]	1170(w)[b]					
1915(w)[b]	1930(w)[b]					

a - see legend Table VI

Continued

Table X - continued

HT	NaT	$CoT_2 \cdot H_2O$	$NiT_{1.8} \cdot H_2O$	$CuT_2 \cdot H_2O$	$ZnT_2 \cdot \frac{3}{2}H_2O$	$CrT_2(OH) \cdot 4H_2O$
	1920(m)					
	1900(w)					
1600(s)	1610(s)	1610(m)	1620(s)	1600(s)	1610(s)	1600(s)
1550(s)	1565(m)	1565(w)	1570(s)	1560(m)	1550(s)	1560(m)
1525(w)	1520(w)	1515(w)	1520(w)	1510(w)	1500(w)	1510(w)
1495(s)	1490(w)[b]	1480(w)	1480(w)	1490(w)	1480(w)	1470(w)
1480(s)	1460(m)	1440(s)	1450(s)	1460(s)	1450(s)	1460(s)
1435(s)	1420(s)	1415(s)	1400(s)	1425(s)	1420(s)	1420(s)
1405(s)						
1370(s)	1350(m)	1350(m)[b]	1370(m)	1350(m)	1370(m)	1360(m)
1300(w)	1310(m)	1300(w)[b]	1300(s)[b]			
1275(w)	1275(m)	1270(w)	1280(s)	1280(m)	1290(m)	1280(m)
1260(w)						
1250(s)	1205(m)		1210(m)	1215(m)		

Continued

Table X - continued

HT	NaT	$CoT_2 \cdot H_2O$	$NiT_{1.8} \cdot H_2O$	$CuT_2 \cdot H_2O$	$ZnT_2 \cdot \frac{3}{2}H_2O$	$CrT_2(OH) \cdot 4H_2O$
	1180(w)					
1160(s)	1150(w)	1160(m)[b]	1180(m)	1175(s)	1170(s)	1160(m)
1140(m)						
1120(m)	1125(s)	1120(m)	1135(m)	1150(s)	1130(m)	1150(w)
1090(s)	1100(s)	1090(s)	1100(s)	1100(s)	1100(s)	1090(s)
1085(s)						
1065(s)						
1050(s)	1050(m)		1070(m)	1050(m)	1070(m)	1050(w)
1020(s)	1020(m)			1030(m)		
1015(s)						
1000(s)	1000(s)	1010(s)	1030(s)	1020(s)	1020(m)	1010(s)
980(s)	980(m)	980(m)	980(s)		980(m)	980(m)
960(m)	960(s)	940(w)[b]	950(m)	960(s)	960(s)	940(m)[b]

Continued

Table X - Continued

HT	NaT	$CoT_2 \cdot H_2O$	$NiT_{1.8} \cdot H_2O$	$CuT_2 \cdot H_2O$	$ZnT_2 \cdot \frac{3}{2}H_2O$	$CrT_2(OH) \cdot 4H_2O$
875(s)[b]	900(w)			900(w)	900(w)	880(w)[b]
850(s)	850(s)	850(m)	870(s)	860(m)	850(s)	850(s)
840(s)	840(s)	830(m)	850(s)	830(s)	840(s)	830(s)
790(w)	760(s)	790(w)	800(m)	800(w)		790(w)
740(s)	750(s)	760(m)	775(s)	750(s)	760(s)	770(m)
						750(m)
						740(s)
730(s)	720(s)	720(m)	725(s)	725(s)	720(m)	720(s)
680(s)	650(m)	650(w)	660(m)	650(m)	640(m)	650(m)

Continued

Table X. - Continued

HT	NaT	$CoT_2 \cdot H_2O$	$NiT_{1.8} \cdot H_2O$	$CuT_2 \cdot H_2O$	$ZnT_2 \cdot \frac{3}{2}H_2O$	$CrT_2(OH) \cdot 4H_2O$
615(sh)		625(sh)	625(m)	623(m)[b]		600(sh)
				532(s)		
505(s)	507(s)	517(s)	517(s)	509(m)	513(s)	507(s)
459(s)	467(s)	476(m)	475(m)	474(s)	474(m)	467(m)
366(w)	368(m)	379(w)		376(m)	387(m)	376(w)
					370(m)	
321(w)		327(m)[b]	334(s)[b]	337(m)	325(m)	330(m)
296(w)[b]	294(m)	293(m)	286(m)[b]	290(s)	293(m)	291(m)
258(sh)	256(m)[b]	275(m)		275(s)	275(m)	280(s)
			265(m)[b]			267(w)
		244(m)		241(s)	243(m)[b]	246(m)
215(w)	221(s)[b]					225(m)
186(w)	196(s)			194(s)[b]	195(s)[b]	200(m)
170(s)	180(s)			184(s)[b]	180(s)[b]	

Table XI. Infrared Spectra[a] of 5-p-Chlorophenyltetrazole and Sodium 5-p-Chlorophenyltetrazolate with Band Assignments

HT	NaT	Genuine Vibrational Mode	Assignment
	3570(s)		[$\nu_1 + \nu_{11}$]
	3420(s)	ν_{13}	O-H stretch
	3340(m)[b]		
3090(m)	3150(s)[b]	ν_1	ring C-H stretch
3060(m)	3060(s)		[$\nu_2 + 1600$]
2800(m)			[N-H stretch]
2750(m)[b]			[$\nu_2 + \nu_3$]
2720(m)[b]			[$\nu_3 + \nu_6$]
2630(m)[b]			[$\nu_2 + \nu_4$]
2540(m)[b]			[$\nu_2 + \nu_5$]
2270(m)[b]	2270(w)[b]		[$\nu_3 + \nu_8$]
1915(w)[b]	1930(w)[b]		[$\nu_7 + \nu_{10}$]
	1920(m)		[$\nu_8 + \nu_{10}$]
	1900(w)		[$\nu_4 + \nu_9$]
1600(s)	1610(s)		[$\nu_9 + \nu_{10}$]
1550(s)	1565(m)		
1525(w)	1520(w)		[$\nu_7 + \nu_{12}$]
1495(s)	1490(w)[b]		[$\nu_8 + \nu_{12}$]

a Units are in cm^{-1}
b Brackets indicate possible assignments

Continued

Table XI. - Continued

HT	NaT	Genuine Vibrational Mode	Assignment
1480(s)	1460(m)	ν_2	ring deformation
1435(s)	1420(s)	ν_6	C-H in-plane bend
1405(s)			[ν_{10} + ν_{12}]
1370(s)	1350(m)		[ν_{10} + ν_{11}]
1300(w)	1310(m)	ν_3	ring vibration
1275(w)	1275(m)		
1260(w)			
1250(s)	1255(m)		[ν_9 + ν_{12}]
	1180(w)		[ν_9 + ν_{11}]
1160(s)	1150(w)	ν_4	ring vibration
1140(m)			[ν_{12} + 650]
1120(m)	1125(s)		[ν_{12} + 615]
1090(s)	1100(s)		[ν_{11} + 650]
1085(s)			[ν_{11} + 615]
1065(s)			[ν_9 + ν_{366}]
1050(s)	1050(m)	ν_5	ring deformation
1020(s)	1020(m)	ν_7	ring deformation
1015(s)			[2 ν_{12}]
1000(s)	1000(s)	ν_8	ring deformation
980(s)	980(m)		[ν_{11} + ν_{12}]
960(m)	900(m)		[ν_2 - ν_{12}]
875(s)[b]	900(w)	ν_{10}	C-H out-of-plane

Continued

Table XI. - Continued

HT	NaT	Genuine Vibrational Mode	Assignment
850(s)	850(s)		[ν_{12} + 368]
840(s)	840(s)		[ν_{12} + 321]
790(w)	760(s)		[ν_2 - ν_9]
740(s)	750(s)		[ν_6 - ν_9]
730(s)	720(s)	ν_9	ring deformation
680(s)	650(m)		[ν_4 - ν_{11}]
615(sh)			[ν_5 - ν_{11}]
505(s)	507(s)	ν_{12}	(out of plane ring bends)
459(s)	467(s)	ν_{11}	(out of plane ring bend)
366(w)	368(m)		[ν_5 -ν_9]
321(w)			[ν_7 -ν_9]
296(w)[b]	294(m)		[ν_8 -ν_9]
258(sh)	256(m)[b]		[ν_9 - ν_{11}]
215(w)	221(s)[b]		[ν_9 - ν_{12}]
186(w)	186(s)		[ν_{10} - ν_9]
170(s)	180(s)		[680 - ν_{12}]

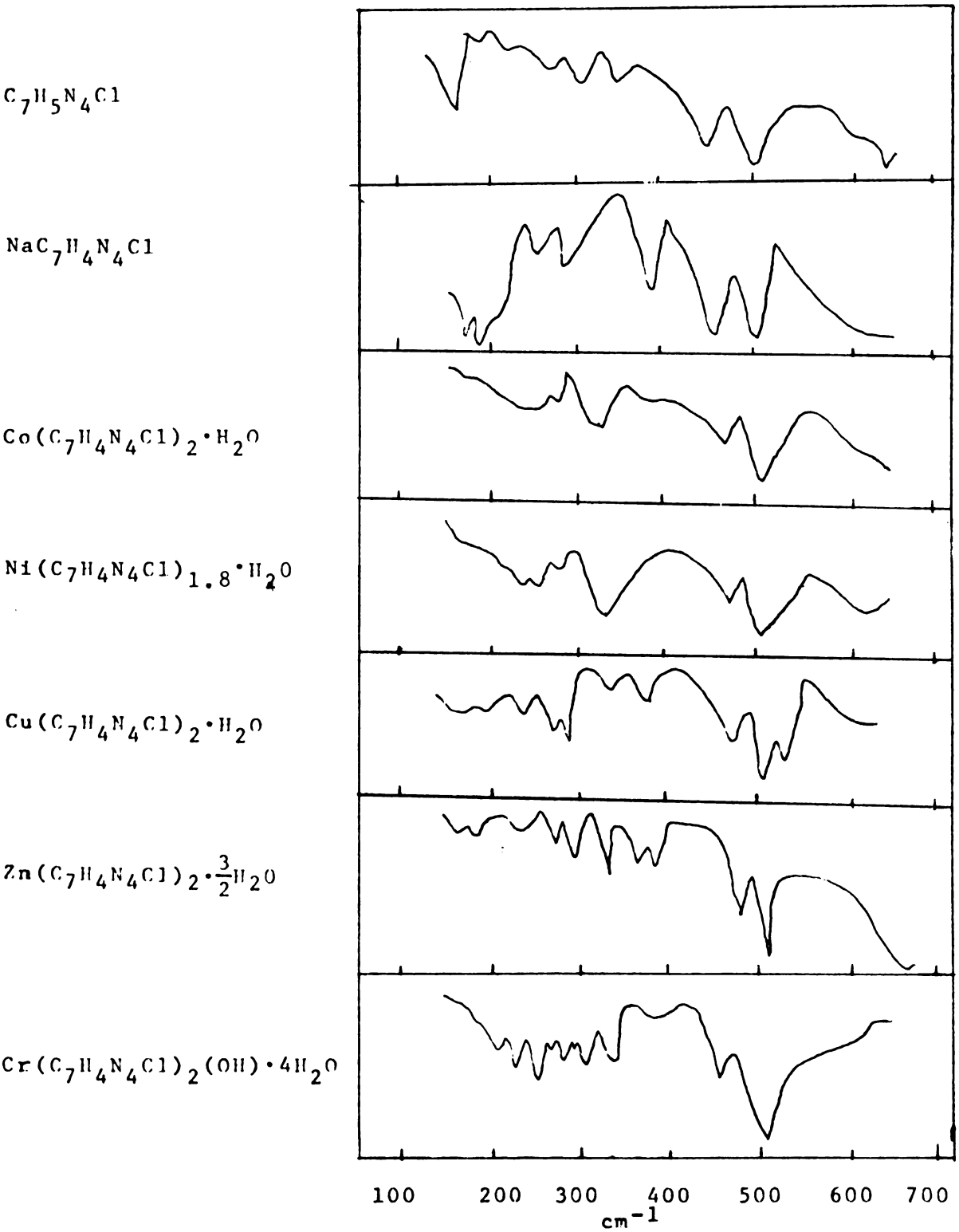


Figure 3 Far Infrared Spectra of 5-p-Chlorophenyltetrazole, Sodium 5-p-chlorophenyltetrazolate and various complexes of 5-p-chlorophenyltetrazole

Table XII Infrared Spectra[a] of 5-p-Chlorobenzyltetrazole, Sodium 5-p-Chlorobenzyltetrazolate, and Various Complexes of 5-p-Chlorobenzyltetrazole in Nujol and Hexachlorobutadiene Mulls from 4000 to 167cm^{-1}

HT	NaT	$CoT_2 \cdot H_2O$	$NiT_{1.8} \cdot H_2O$	$CuT_2 \cdot 3H_2O$	ZnT_2	$CrT_2OH \cdot 4H_2O$
	3660(sh)	3600(sh)	3650(sh)	3600(sh)		3600(sh)
	3540(sh					
	3340(m)	3350(m)[b]	3350(m)[b]	3400(s)[b]		3300(s)[b]
	3300(s)[b]					
				3200(sh)		3200(sh)
3120(w)	3100(s)[b]	3100(m)[b]	3100(sh)		3110(m)	3100(sh)
3080(w)					3090(m)	
					3060(m)	
				3040(m)	3040(m)	
2700(s)						
2600(s)						
2540(s)[b]						
2500(s)						

a - see legend Table XI

Continued

Table XII - Continued

HT	NaT	$CoT_2 \cdot H_2O$	$NiT_{1.8} \cdot H_2O$	$CuT_2 \cdot 3H_2O$	ZnT_2	$CrT_2OH \cdot 4H_2O$
2480(s)						
2440(s)						
2060(m)[b]	2140(w)					
					1940(w)	
					1930(w)	
1910(s)	1920(w)	1920(w)	1920(w)[b]	1920(w)[b]	1920(w)	1920(w)[b]
	1890(w)	1880(w)			1900(w)	
1820(s)[b]	1800(w)				1800(w)	
	1770(w)	1780(w)			1780(w)	
	1640(s)				1750(w)	
	1630(s)	1630(w)[b]		1630(w)[b]	1640(w)[b]	1640(m)[b]
1580(m)	1590(m)	1590(m)	1610(m)[b]		1600(m)	1600(m)
1575(m)	1570(m)				1580(m)	1550(m)
1530(w)						

Continued

Table XII - Continued

HT	NaT	$CoT_2 \cdot H_2O$	$NiT_{1.8} \cdot H_2O$	$CuT_2 \cdot 3H_2O$	ZnT_2	$CrT_2(OH) \cdot 4H_2O$
1495(s)	1495(s)	1490(s)	1495(s)	1500(s)	1490(s)	1490(s)
	1470(s)	1470(m)[b]	1480(s)	1470(w)	1480(s)	1470(m)[b]
				1470(s)		
1440(s)	1430(s)	1425(s)	1430(s)	1440(w)[b]	1445(s)	1430(m)[b]
1410(s)	1420(s)	1410(s)	1410(s)	1410(s)	1420(s)	1410(m)
1405(s)	1400(s)	1390(m)		1390(sh)	1400(s)	1390(m)
					1370(sh)	
1355(m)	1320(w)	1320(w)[b]		1330(w)[b]	1335(w)	
1330(w)						
1310(m)	1310(w)	1310(m)	1310(w)[b]		1310(m)	1320(m)[b]
1290(m)	1280(m)	1290(m)	1290(w)	1290(m)	1295(m)	1290(w)[b]
1266(m)					1285(s)	
1245(m)	1240(w)	1240(m)[b]	1245(w)[b]	1240(m)	1250(s)	1245(w)[b]
1205(s)	1210(s)	1200(m)[b]	1200(m)	1200(w)	1200(s)	1200(w)

Continued

Table XII - Continued

HT	NaT	$CoT_2 \cdot H_2O$	$NiT_{1.8} \cdot H_2O$	$CuT_2 \cdot 3H_2O$	ZnT_2	$CrT_2(OH) \cdot 4H_2O$
				1185(m)	1185(s)	
1100(w)	1170(s)				1170(m)	1170(m)[b]
	1150(m)	1150(m)		1160(m)[b]	1150(s)	1150(s)
	1135(s)	1140(s)	1140(m)	1140(s)	1140(s)	
	1130(s)				1115(sh)	
1110(s)	1125(s)				1010(s)	1110(sh)
1085(s)	1090(s)	1090(s)	1090(s)	1090(s)	1085(s)	1090(s)
1050(s)	1070(s)	1040(w)	1050(w)		1065(s)	1050(m)[b]
1015(s)	1020(m)				1020(s)	
990(s)	1015(s)	1015(s)	1010(s)	1010(s)	1015(s)	1015(s)
975(m)	980(w)		970(m)	980(m)	970(w)[b]	980(m)[b]
960(m)						
940(s)	950(m)	950(w)[b]	940(m)	940(w)[b]	940(w)[b]	940(m)[b]
	935(w)					

Continued

Table XII - Continued

HT	NaT	$CoT_2 \cdot H_2O$	$NiT_{1.8} \cdot H_2O$	$CuT_2 \cdot 3H_2O$	ZnT_2	$CrT_2(OH) \cdot 4H_2O$
915(s)	905(m)	900(m)[b]	915(m)		915(s)	915(m)[b]
			890(w)	890(w)[b]	890(w)[b]	880(w)[b]
850(m)	850(s)	845(m)[b]	850(m)	850(m)	850(m)	840(m)
835(s)				840(w)	830(s)	
820(s)		820(m)[b]			815(s)	815(m)[b]
805(s)	810(s)	805(sh)		805(s)	800(s)	
	795(s)	790(s)	790(s)	790(s)	790(s)	785(s)
770(s)	780(s)		780(w)	765(sh)	780(s)	780(m)[sh]
720(m)	740(m)(sh)	720(s)		725(m)	715(s)	720(s)
690(m)	710(s)	705(m)(sh)	715(s)	705(w)	705(s)	690(m)
680(m)	690(s)	695(m)	690(m)		695(m)	690(m)
650(m)	640(m)	650(w)	650(w)	650(w)[b]	650(m)	650(w)

Continued

Table XII. - Continued

HT	NaT	$CoT_2 \cdot H_2O$	$NiT_{1.8} \cdot H_2O$	$CuT_2 \cdot 3H_2O$	ZnT_2	$CrT_2OH \cdot 4H_2O$
618(sh)						
521(vw)	521(s)[b]		555(m)[b]			
486(s)	497(s)	499(s)[b]	495(s)	495(m)	501(w)	492(sh)
		486(s)[b]		480(s)	484(s)	
437(s)	424(s)	447(s)	447(m)	447(m)	435(m)	443(s)
					399(s)	
347(w)	367(m)[b]	376(w)[b]		380(w)	372(m)	370(w)
		347(m)		350(w)	350(w)	350(w)
	319(m)	325(w)	325(w)	325(s)	322(w)	327(s)
307(w)	307(w)			302(m)	310(m)	301(w)
285(w)	282(w)		292(w)[b]			
		270(s)[b]	279(w)[b]		277(s)	278(w)
233(w)	242(s)			240(w)	231(m)	232(s)[b]
	217(s)[b]		213(w)	223(w)	211(w)	203(w)
196(m)						
	174(s)[b]	176(sh)	177(w)	187(w)[b]	177(m)	
157(w)			167(w)			

Table XIII. Infrared Spectra[a] of 5-p-Chlorobenzyltetrazolate and Sodium 5-p-Chlorobenzyltetrazolate

HT	NaT	Genuine Vibrational Mode	Assignment
	3660(sh)		
	3540(sh)		[$\nu_1 + \nu_{11}$][b]
	3340(m)	ν_{13}	O-H stretch
	3300(s)[b]		
3120(w)	3100(s)[b]	ν_1	ring C-H stretch
3080(w)			[$\nu_2 + 1600$]
2700(s)		ν_{14}	[N-H stretch]
2600(s)			[$\nu_2 + \nu_4$]
2540(s)[b]			[$\nu_2 + \nu_5$]
2500(s)			
2480(s)			[$\nu_3 + \nu_4$]
2440(s)			
2160(m)[b]	2140(w)		[$2\nu_5$]
1910(s)	1920(w)		[$\nu_7 + \nu_{10}$]
	1890(w)		[$\nu_4 + \nu_9$]
1820(s)[b]	1800(w)		[$2\ \nu_{10}$]
	1770(w)		[$\nu_5 + \nu_9$]
	1640(s)		O-H bend

a Units are in cm^{-1}
b Brackets indicate possible assignments

Continued

Table XIII. - Continued

HT	NaT	Genuine Vibrational Mode	Assignment
	1630(s)		$[\nu_4 + \nu_{11}]$
1580(m)	1590(m)		$[\nu_9 + \nu_{10}]$
1575(m)	1570(m)		$[850 + \nu_9]$
1530(w)			$[\nu_5 + \nu_{11}]$
1495(s)	1495(s)		$[\nu_7 + \nu_{11}]$
	1470(s)		$[\nu_8 + \nu_{11}]$
1440(s)	1430(s)	ν_2	ring deformation
1410(s)	1420(s)	ν_6	C-H in plane bend
1405(s)	1400(s)		$[2\ \nu_9]$
1355	1320(w)		$[\nu_{10} + \nu_{11}]$
1330(w)			
1310(w)	1310(w)		
1290(m)	1280(m)	ν_3	ring deformation
1260(m)			
1245(m)	1240(w)		$[\nu_9 + \nu_{12}]$
1205(s)	1210(s)		$[\nu_9 + \nu_{11}]$
1180(w)	1170(s)	ν_4	ring breathing
	1150(m)		$[\nu_{12} + 650]$
	1135(s)		$[\nu_{12} + 615]$
	1130(s)		
1110(s)	1125(s)		$[\nu_{11} + 650]$

Continued

Table XIII - Continued

HT	NaT	Genuine Vibrational Mode	Assignment
1085(s)	1090(s)		[ν_{11} + 615]
1050(s)	1070(s)	ν_5	ring deformation
1015(s)	1020(m)	ν_7	ring deformation
990(s)	1015(s)	ν_8	ring deformation
975(m)	980(w)		[ν_{11} + ν_{12}]
960(m)			
940(s)	950(m)		[ν_2 - ν_{12}]
	935(w)		
915(s)	965(m)	ν_{10}	C-H out of plane bend
850(s)	850(s)		
835(s)			
820(s)			
805(s)	810(s)		
	795(s)		
770(s)	780(s)		[ν_2 - ν_9]
720(m)	740(sh)		[ν_6 - ν_9]
690	710(s)	ν_9	ring deformation
680(m)	690(s)		[ν_4 + ν_{11}]
650(m)	640(m)		
618(sh)			[ν_5 - ν_{11}]
	521(s)[b]	ν_{12}	out-of-plane ring bend

Continued

Table XIII. - Continued

HT	NaT	Genuine Vibrational Mode	Assignment
486(s)	497(s)		
437(s)	424(s)	ν_{11}	out-of-plane ring bend
	367(w)[b]		$[\nu_5 - \nu_9]$
	319(m)		$[\nu_7 - \nu_9]$
307(m)	307(w)		$[\nu_8 - \nu_9]$
285(m)	282(m)		
233(w)	242(s)		$[\nu_9 - \nu_{11}]$
	217(s)[b]		
196			
	174(s)[b]		$[\nu_{10} - \nu_9]$
157			

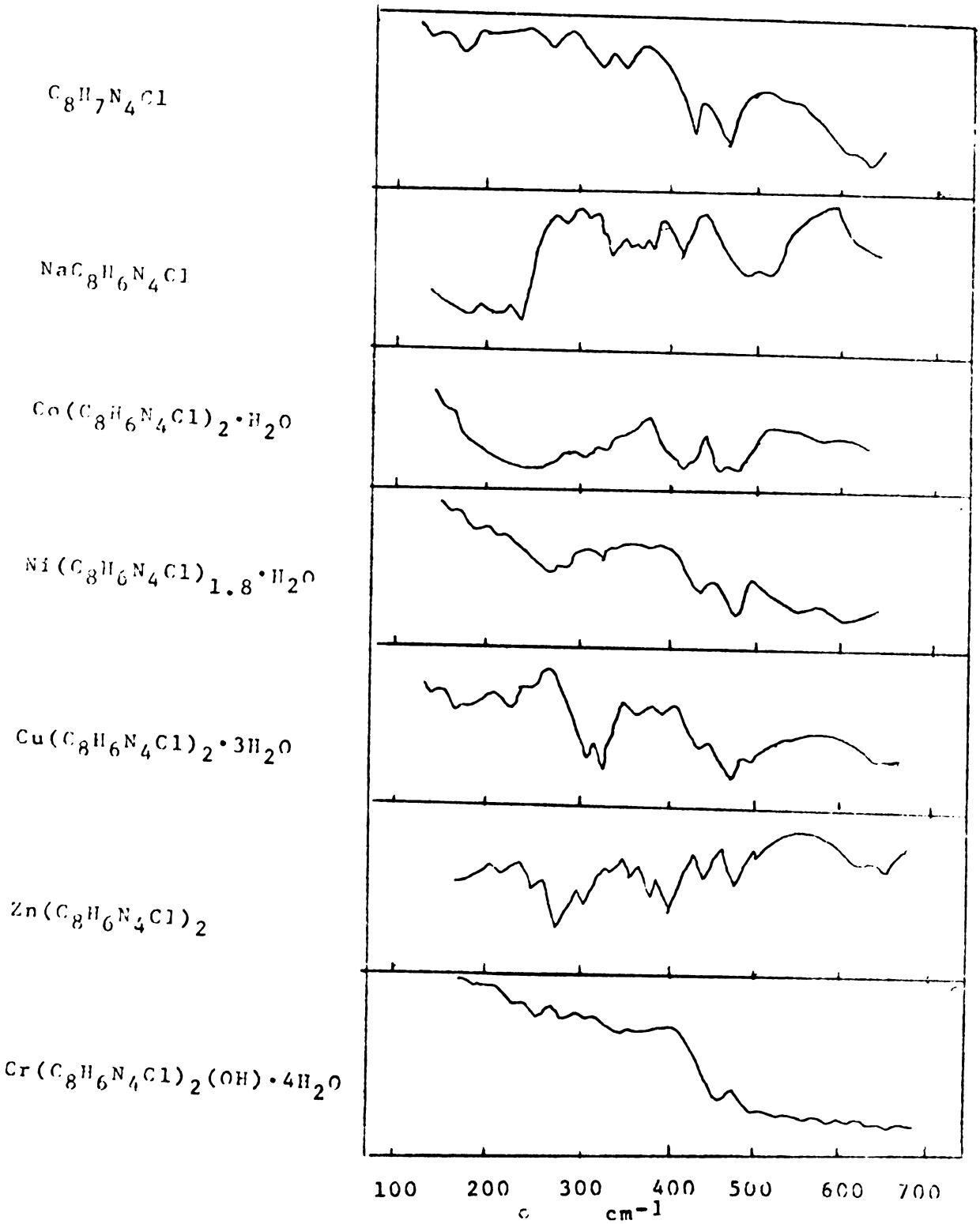


Figure 4 Far Infrared Spectra of 5-p-Chlorobenzyltetrazole, Sodium 5-p-Chlorobenzyltetrazolate and Several Complexes of 5-p-Chlorobenzyltetrazole

Table XIV Infrared Spectra[a] of 5-o-Chlorophenyltetrazole, Sodium 5-p-Chlorophenyltetrazolate and Various Complexes of 5-p-Chlorophenyltetrazole in Nujol and Hexachlorobutadiene Mulls from 4000 to 167cm^{-1}

HT	NaT	$CoT_2 \cdot H_2O$	$NiT_{1.8} \cdot H_2O$	$CuT_2 \cdot H2O$	ZnT_2	$CrT_2OH \cdot 4H_2O$
	3550(s)[b]	3550(s)	3550(s)[b]	3500(s)[b]	3550(w)[b]	3550(s)[b]
3450(w)	3450(s)[b]	3350(s)[b]	3315(s)[b]	3400(s)[b]		3300(s)[b]
	3250(m)[b]		3100(s)[b]			3150(s)[b]
3190(m)						
2110(m)						
3050(s)	3050(m)	3060(m)	3060(m)	3060(w)	3050(s)	3050(s)[b]
2990(s)					3000(w)	
2820(s)						
2800(s)						
2700(s)[b]						
2600(s)[b]						
2400(s)[b]						
2390(m)						

a - see legend Table VI

Continued

Table XIV - continued

HT	NaT	$CoT_2 \cdot H_2O$	$NiT_{1.8} \cdot H_2O$	$CuT_2 \cdot H_2O$	ZnT_2	$CrT_2OH \cdot 4H_2O$
2050(m)						
2000(m)						
1950(m)					1950(m)	
1920(w)[b]	1920(w)[b]	1920(w)[b]	1910(w)[b]	1910(w)[b]	1910(m)	1920(w)[b]
1850(m)[b]					1820(m)	
1800(m)[b]	1800(w)				1800(m)	
1750(m)						
1700(m)					1700(m)	1700(m)
1650(m)	1650(m)	1640(m)				1640(m)
						1625(m)
1590(s)	1590(m)[b]	1600(m)	1590(m)	1590(m)	1600(m)	1600(m)
1560(s)	1560(m)	1560(m)	1565(m)	1560(m)	1565(m)	1560(m)
1550(s)						
1540(s)						

Continued

Table XIV - continued

HT	NaT	$CoT_2 \cdot H_2O$	$NiT_{1.8} \cdot H_2O$	$CuT_2 \cdot H_2O$	ZnT_2	$CrT_2OH \cdot 4H_2O$
1490(s)	1500(m)	1520(w)	1525(m)	1510(w)	1510(m)	1525(m)
1455(s)	1450(s)	1450(s)	1460(s)	1440(s)	1460(s)	1460(s)
	1435(s)				1440(s)	
1400(s)	1420(s)	1420(s)	1420(s)	1410(s)	1400(s)	1425(s)
1370(s)	1360(s)					
1360(s)	1350(s)	1350(m)	1360(m)	1360(m)	1350(s)	1350(s)
1290(m)	1310(m)[b]	1300(w)[b]	1300(vw)	1305(m)[b]	1280(m)	1300(m)[b]
1280(w)						
1270(m)					1260(m)	
1245(s)	1220(m)				1250(s)	
	1210(m)		1210(w)	1200(w)	1220(w)	1220(m)
1170(s)	1170(m)	1170(m)[b]	1170(m)[b]	1170(m)[b]	1180(m)	1170(m)[b]
1160(s)	1160(s)	1160(m)[b]		1150(m)[b]	1160(m)	
1150(s)	1150(m)				1150(m)	

Continued

Table XIV - continued

HT	NaT	$CoT_2 \cdot H_2O$	$NiT_{1.8} \cdot H_2O$	$CuT_2 \cdot H_2O$	ZnT_2	$CrT_2OH \cdot 4H_2O$
1120(s)	1135(s)	1135(m)	1130(m)	1130(m)	1140(m)	1125(m)
	1120(w)					
1100(m)	1100(s)			1095(m)	1110(s)	
1095(m)	1090(w)	1090(m)	1080(m)	1085(m)	1090(s)	
1070(s)	1070(s)	1055(m)	1065(m)	1070(m)	1065(m)	1070(m)
1060(s)						
1040(s)	1040(s)	1030(s)	1040(m)	1035(m)	1050(s)	1040(m)
1030(s)						
1010(s)	1010(s)	1010(m)	1020(m)	1020(m)	1025(s)	1025(m)
990(s)						
980(s)	970(m)	975(m)	980(w)	980(s)	980(m)	980(s)
950(s)	950(m)	940(m)	950(w)[b]	940(m)	950(m)	945(m)
940(s)						
	910(vw)[b]	910(w)[b]	910(vw)[b]	910(w)	900(w)	900(w)

Continued

Table XIV - continued

HT	NaT	$CoT_2 \cdot H_2O$	$NiT_{1.8} \cdot H_2O$	$CuT_2 \cdot H_2O$	ZnT_2	$CrT_2OH \cdot 4H_2O$
880(s)	890(w)	885(vw)	880(vw)	890(w)	890(w)	
	850(m)	850(m)	850(m)	850(s)	850(m)	850(s)
	785(m)	790(w)	800(w)	800(m)	800(w)	820(w)
780(s)	780(s)	780(m)[b]	780(m)[b]	780(m)	780(m)	770(m)
750(s)	750(s)	745(s)	750(s)	750(s)	750(s)	750(s)
740(s)						
730(s)		730(s)	730(m)	730(s)	740(s)	730(s)
710(s)	720(s)	720(s)	720(m)	720(s)	730(s)	720(s)
700(m)						
650(s)	650(s)	650(m)	650(m)	650(s)	650(s)	650(s)

Continued

Table XIV.- Continued

HT	NaT	$CoT_2 \cdot H_2O$	$NiT_{1.8} \cdot H_2O$	$CuT_2 \cdot H_2O$	ZnT_2	$CrT_2OH \cdot 4H_2O$
650(s)	650(s)	650(m)	650(m)	650(m)	650(s)	650(s)
				570(vw)	580(sh)	
		532(w)[b]	542(w)[b]	542(w)	550(w)	531(w)
521(m)	494(s)	496(s)	490(w)[b]	490(w)[b]		
475(w)	478(s)				472(m)	
440(w)	453(s)	457(s)	459(s)	457(s)	453(m)	455(s)
430(w)	435(s)	438(s)	442(s)	442(s)	432(m)	
		354(s)	364(s)	370(s)	368(s)	383(w)
332(s)	333(s)[b]		330(sh)		334(m)	332(s)
			311(s)[b]			302(w)
259(m)	270(s)[b]	297(s)[b]	283(w)[b]	298(s)[b]	275(s)	278(w)[b]
252(m)	vw Band	250(vw)	254(w)[b]		254(s)	246(w)[b]
223(w)		231(vw)		225(w)	227(sh)	230(w)[b]
	212(w)	219(vw)		210(w)	213(w)	

Continued

Table XIV. - Continued

HT	NaT	$CoT_2 \cdot H_2O$	$NiT_{1.8} \cdot H_2O$	$CuT_2 \cdot H_2O$	ZnT_2	$CrT_2OH \cdot 4H_2O$
206(w)	208(w)	210(vw)	203(w)[b]	202(w)	203(w)	203(w)[b]
	193(w)[b]					
169(s)	177(s)	175(s)		184(m)	180(m)	

Table XV. Infrared Spectra[a] of 5-o-Chlorophenyltetrazole Sodium 5-o-Chlorophenyltetrazolate with Assignments

HT	NaT	Genuine Vibrational Mode	Assignment
	3550(s)[b]		[$\nu_1 + \nu_{11}$][b]
3450(w)			
	3450(s)[b]	ν_{13}	O-H stretch
	3250(m)[b]		
3190(m)			
3120(m)		ν_1	ring C-H stretch
3050(s)	3050(m)		[1600 + ν_2]
2990(s)			[2(1500)]
1820(s)			
2800(s)		ν_{14}	[N-H stretch]
2700(s)[b]			[$\nu_3 + \nu_6$]
2600(s)[b]			[2 ν_3]
2400(s)[b]			
2390(m)			
2050(m)			[$\nu_7 + \nu_8$]
2000(m)			[2 ν_{10}]
1950(m)			[$\nu_7 + \nu_{10}$]

a Units are in cm^{-1}
b Brackets indicate possible assignments

Continued

Table XV. - Continued

HT	NaT	Genuine Vibrational Mode	Assignment
1920(w)[b]	1920(w)[b]		[$\nu_8 + \nu_{10}$]
1850(m)[b]			[$\nu_4 + \nu_9$]
1800(m)[b]	1800(w)		[2 ν_{10}]
1750(m)			[$\nu_5 + \nu_9$]
1700(m)			[$\nu_8 + \nu_9$]
1650(m)	1650(m)		[$\nu_4 + \nu_{11}$]
1590(s)	1590(m)[b]		[$\nu_9 + \nu_{10}$]
1560(s)	1560(m)		
1550(s)			[850 + ν_9]
1540(s)			[$\nu_5 + \nu_{11}$]
1490(s)	1500(m)		[$\nu_7 + \nu_{11}$]
1455(s)	1450(s)	ν_2	ring deformation
	1435(s)	ν_6	C-H in-plane bend
1400(s)	1420(s)		[2(700)]
1370(s)	1360(s)		[$\nu_{10} + \nu_{11}$]
1360(s)	1350(s)		
1290(m)	1310(m)[b]	ν_3	ring vibration
1280(w)			
1270(m)			[$\nu_9 + \nu_{12}$]

Continued

Table XV. - Continued

HT	NaT	Genuine Vibrational Mode	Assignment
1245(s)	1220(m)		[$\nu_9 + \nu_{11}$]
	1210(m)		
1170(s)	1170(m)	ν_4	ring breathing
1160(s)	1160(s)		(702 + 454)
1150(s)	1150(m)		[$\nu_{12} + 650$]
1120(s)	1135(s)		[$\nu_{12} + 615$]
	1120(w)		
1100(m)	1100(s)		[$\nu_{11} + 650$]
1075(m)	1090(w)		[$\nu_{11} + 615$]
1070(s)	1070(s)	ν_5	ring deformation
1060(s)			
1040(s)	1040(s)	ν_7	ring deformation
1030(s)			
1010(s)	1010(s)	ν_8	ring deformation
990(s)			
980(s)	970(m)		[$\nu_{11} + \nu_{12}$]
950(s)	950(m)		[$\nu_2 - \nu_{12}$]
940(s)			
	910(vw)[b]		

Continued

Table XV. - Continued

HT	NaT	Genuine Vibrational Mode	Assignment
880(s)	890(w)	ν_{10}	C-H out of plane band
	850(m)		
	785(m)		
780(s)	780(s)		[ν_2 - ν_9]
750(s)	750(s)		[ν_6 - ν_9]
740(s)			
730(s)			
710(s)	720(s)	ν_9	ring deformation
700(m)			
650(s)	650(s)		[ν_4 - ν_{11}]
521(m)	494(s)	ν_{12}	out-of-plane ring bend
475(w)	478(s)		
440(w)	453(s)	ν_{11}	out-of-plane ring bend
435(w)	435(s)		[ν_2 - ν_7]
332(s)	333(s)[b]		[ν_7 - ν_9]
259(m)	270(s)[b]		[ν_9 - ν_{11}]
252(m)			
223(w)			[9 - 12]
	212(w)		

Continued

Table XV. - Continued

HT	NaT	Genuine Vibrational Mode	Assignment
206(w)	208(w)		[ν_{10} - ν_9]
	193(w)[b]		
169(s)	177(s)		[630 - ν_{12}]

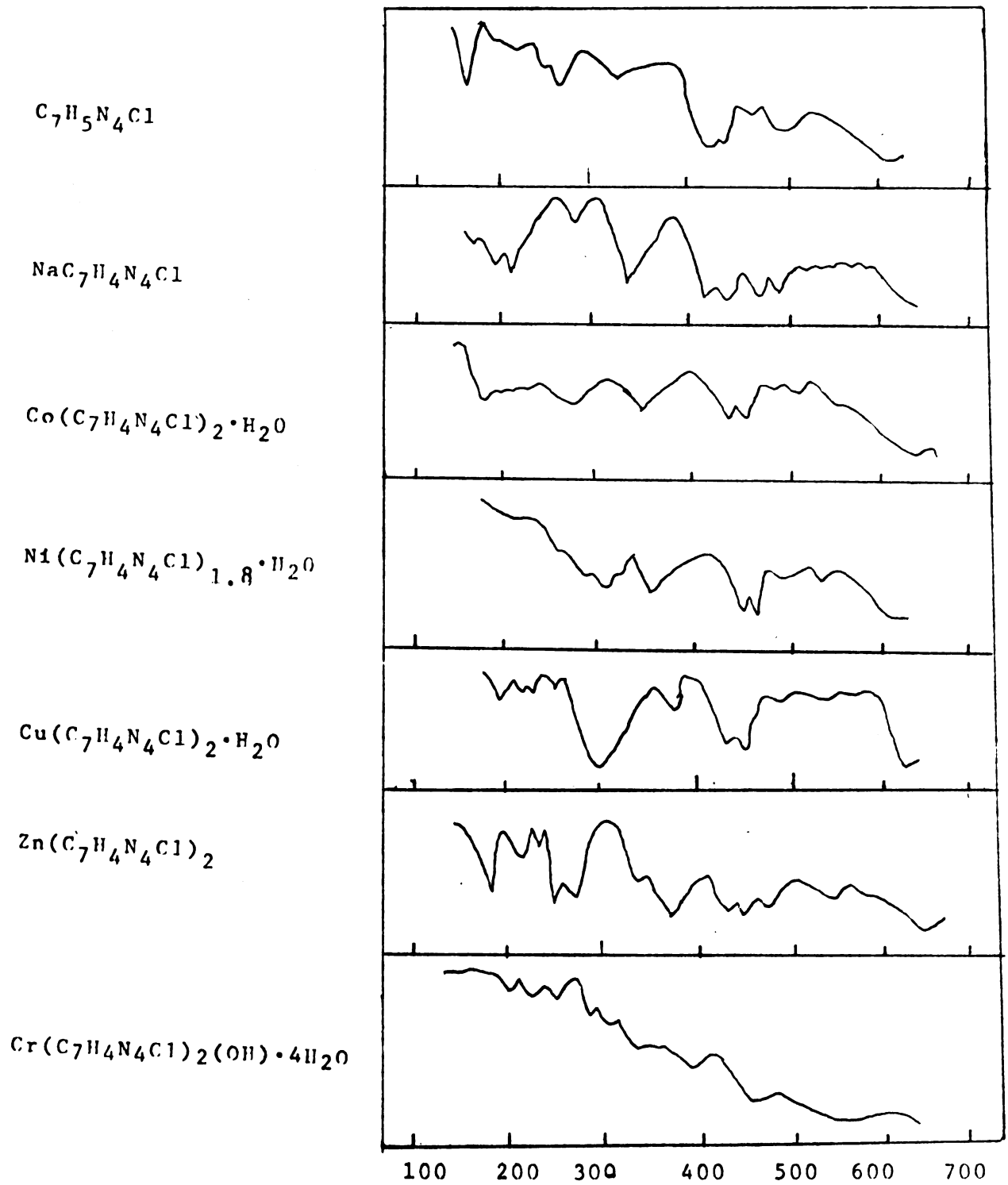


Figure5 Far Infrared Spectra of 5-o-Chlorophenyltetrazole, Sodium 5-oChlorophenyltetrazolate and Various Complexes of 5-o-Chlorophenyltetrazole

Table XVI. Results of the Normal Coordinate Analysis[32] Calculation for Sodium Tetrazolate.

Species	Vibrational Modes	Observed Frequency	Calculated Frequency
A_1	ν_1	3120	3125
	ν_2	1455	1461
	ν_3	1290	1243
	ν_4	1161	1138
	ν_5	1065	962
B_1	ν_6	1445	1453
	ν_7	1023	1063
	ν_8	1015	1013
	ν_9	702	730
B_2	ν_{10}	910	910
	ν_{11}	454	456
A_2	ν_{12}	---	537

[a]Units are in cm^{-1}

Table XVII. Infrared Spectrum for Sodium Tetrazolate Monohydrate[32] with Assignments[a].

Vibrational	Observed Frequency, cm^{-1}	Assignment
	3300	O-H stretch
ν_1	3120	C-H stretch
	2930	$[\nu_2 + \nu_{61}$
	2370	$[\nu_2 + \nu_{10}]$
	1785	$\nu_5 + \nu_9$
	1685	$\nu_8 + \nu_9$
	1640	O-H bend
ν_2	1455	sym. ring deformation
ν_6	1445	C-H in-plane bend
ν_3	1290	sym. ring deformation
	1210	$\nu_9 + \nu_{12}$(a)
ν_4	1161	sym. ring breathing
	1132	$\nu_6 + \nu_{11}$
ν_5	1065	sym. ring deformation
ν_7	1023	asym. ring deformation
ν_8	1015	asym. ring deformation
ν_{10}	910	C-H out-of-plane bend
ν_9	702	asym. ring deformation
	660	$1640-\nu_8$
ν_{11}	454	out-of-plane ring bend asym. with respect to C_2 axis

[a] ν_{12} is taken as the calculated value.

Electronic Absorption Spectra

The band maxima for the complexes are displayed in Tables XVIII to XXV. In most cases, additional bands were found in the near infrared region (4000-10000 cm^{-1}). These bands are possibly overtone or combination bands of infrared bands found in the 650-4000 cm^{-1} region.

The data in Table XVIII indicated that substituted 5-phenyltetrazoles and 5-benzyltetrazoles are similar in ligand strength to 5-trifluoromethyltetrazole (25), tetrazole (32), and other strong nitrogen donors (64,65).

Unlike hexaaquocopper(II) and copper(ii) perchlorate hexahydrate which may have a slightly distorted octahedral structure, the appearance of the $^2B_{1g} \rightarrow {}^2A_{1g}$ band (64,65) seems to suggest Jahn Teller distortion.

Jonassen et al. (25) have suggested the utility of the ratio of the energy of the $^3A_{2g} \rightarrow {}^3T_{2g}$ (F) transition in the nickel complex to that of the $^2B_{1g} \rightarrow {}^2A_{1g}$ transition in the corresponding copper(II) complex. Jonassen et al. (25) reported that their energy ratio of 1.3 is intermediate between that for complexes containing six ligands ($\tilde{\sim}$1.4) and that for complexes displaying weak tetragonal distortion ($\tilde{\sim}$1.1). This ratio is also smaller than that for complexes displaying strong tetragonal distortion ($\tilde{\sim}$1.6). The value for the energy ratio of approximately 1.1 in this study indicates that the copper(II) complexes only experience

weak tetragonal distortion. This value of 1.1 is very similar to that obtained for diaquo bis(dipyridyl)copper(II), and tris (dipyridyl)copper(II) (64).

In Table XVIII, the band positions in the complexes for the $^2B_{1g} \rightarrow {}^2B_{1g}$ transition are listed in order of increasing energy. It is expected that the maximum error in these bands is 100 cm^{-1} at the slowest scan rate on the Cary Model 14 spectrophotometer. Therefore it seems reasonable to suggest the following order of ligand strengths:

$$5\text{-p-ClC}_6\text{H}_4\text{CH}_2\text{CN}_4 > 5\text{-p-CH}_3\text{OC}_6\text{H}_4\text{CN}_4 =$$

$$5\text{-C}_6\text{H}_5\text{CN}_4 > 5\text{-p-ClC}_6\text{H}_4\text{CN}_4 > 5\text{-o-ClC}_6\text{H}_4\text{CN}_4$$

Although the copper(II) complexes with 5-p-methoxyphenyl-tetrazole is a hydroxo complex there is apparently little difference between the spectra of hydroxo(5-substituted tetrazolato) copper(II) and that of bis-(5-substituted tetrazolato)copper(II). For example, the spectrum of bis(5-phenyltetrazolato)copper(II) monohydrate and hydroxo(5-phenyltetrazolato)copper(II) are quite similar as shown in Table XVIII.

It should be stressed that the $^2B_{1g} \rightarrow {}^2E_g$ was not observed in this work nor in that by Garber *et al.* (32).

An examination of Table XIX reveals that 5-o-chlorophenyl-tetrazole is a stronger ligand than dimethylsulfoxide and dimethyl-formamide, but it is slightly weaker than pyridine as evidenced by a comparison of the band positions in the complex with those

in the copper perchlorate hexahydrate in the same solvent. Because of experimental difficulties in obtaining spectra that are free of solvent peaks in the near infrared region (4000-10000 cm^{-1}), one cannot be certain wether the complexes are tetragonal in solution. The reflectance spectra, however, do suggest tetragonal symmetry.

The data in Table XX seem to indicate that the solid cobalt complexes are octahedral because of similarities in the spectra of the complexes with those of high spin 6-coordinate cobalt(II) complexes and $Co(ClO_4)_2 \cdot 6H_2O$. The band position of the shoulder at approximately 19000 cm^{-1} was very difficult to determine in this study.

The band positions in the solution spectra listed in Table XXI and associated molar absorptivities indicate octahedral symmetry in solution. Based on the band positions in solution, it appears that dimethylformamide, dimethylsulfoxide, and pyridine are slightly stronger ligands than the tetrazoles.

In the case of the nickel(II) complexes, it appears that these complexes are octahedral as shown in Tables XXII and XXIII by a comparison of the band positions and molar absorptivities of these complexes with those of known octahedral complexes. A comparison of the $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) band positions for all of the nickel(II) complexes indicates that the 5-p-chlorobenzyltetrazole is the strongest ligand in the series and that 5-o-chlorophenyl-tetrazole is again one of the weakest ligands. A ratio of 1.8

for the band positions of the $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) transition to the band position for the $^3A_{2g} \rightarrow {}^3T_{2g}$ (F) transition indicates octahedral symmetry as well (64).

The chromium(III) complexes also appear to be octahedral as shown in Tables XXV and XXVI by comparing the band positions and molar absorptivities in the spectra of the complexes with those of known octahedral complexes. From Table XXIV, it again appears that 5-p-chlorobenzyltetrazole is the strongest ligand in the series due to the relative magnitudes of the band positions of the $^4A_{2g} \rightarrow {}^4T_{2g}$ (F) band. Chromium(III) also appears to have octahedral symmetry in solution as shown in Table XXV.

Table XVIII. Reflectance and Nujol Mull Spectra[a] of Copper(II) Perchlorate Hexahydrate and the Copper(II) Complexes[b] of Various 5-Substituted Tetrazoles.

Compound	$^2T_{2g} \rightarrow {}^2E_g$	$^2B_{1g} \rightarrow {}^2A_{1g}$	$^2B_{1g} \rightarrow {}^2B_{2g}$	$^2B_{1g} \rightarrow {}^2E_g$	Charge transfer
$Cu(H_2O)_6^{+2}$	12,600[60]				
$Cu(ClO_4)_2 \cdot 6H_2O$(Solid)	12500[c]				
$Cu(5\text{-}F_3CCN_4)_2 \cdot H_2O$(Solid)[25]		9000	14700	17900	
$Cu(CN_4H)_2 \cdot H_2O$(Solid)[32]			14900		37500
$Cu(5\text{-}o\text{-}ClC_6H_4CN_4)_2 \cdot H_2O$(Solid)		11100(sh)	[16130]		27800
$Cu(5\text{-}p\text{-}ClC_6H_4CN_4)_2 \cdot H_2O$(Solid)		10400	[17020]		27800
$Cu(5\text{-}C_6H_5CN_4)(OH)$(Solid)		10400	[17350]		28600
$Cu(5\text{-}C_6H_5CN_4)_2 \cdot H_2O$(Solid)		10400(sh)	[17300]		28600
$Cu(5\text{-}p\text{-}CH_3OC_6H_4)N_4)(OH)$(Solid)		10400(sh)	[17470]		28600
$Cu(5\text{-}p\text{-}ClC_6H_4CH_2CN_4)_2 \cdot 3H_2O$(Solid)		10400	[17780]		28600

[a]Band positions are expressed in wave numbers, cm^{-1}. DMSO represents dimethylsulfoxide, DMF represents N,N-dimethylformamide, and C_5H_5N represents pyridine. (number)-the number represents the molar absorptivity of the absorption band. (-) indicates that the molar absorptivity

Continued

cannot be calculated since the chemical system does not obey the Beer-Lambert Law. [number] indicates that the band position in brackets was found by both the nujol mull method and the reflectance method. The number in brackets is the band position which was determined very accurately ($\pm$25A°) on the Cary Model 14 spectrophotometer.

[b] Additional bands were found at 4460, 5160, 5920, 6390cm^{-1}

[c] An additional band was found at 6890cm^{-1}

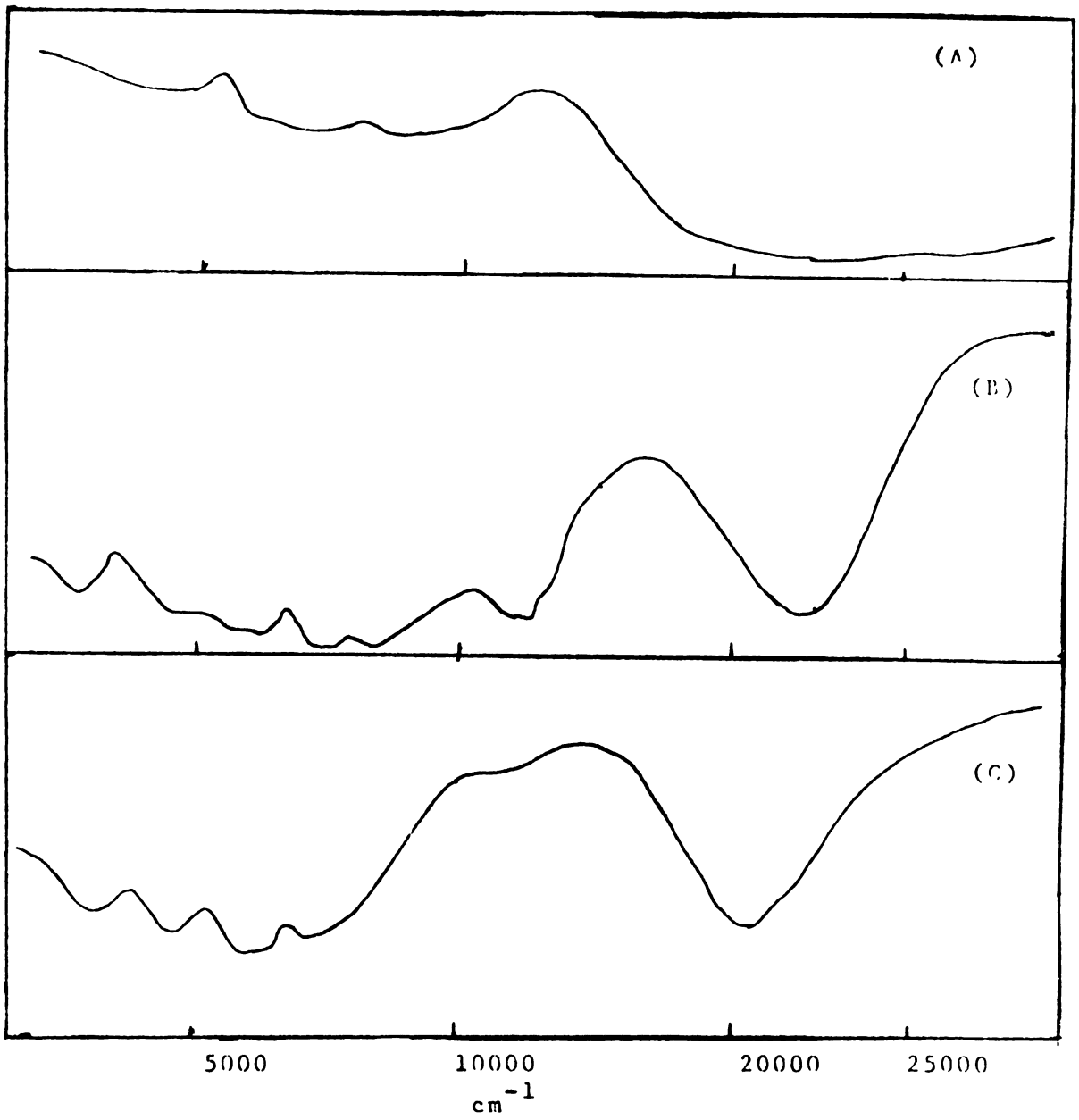


Figure 6. Reflectance Spectra of (A) Copper(II) Perchlorate Hexahydrate (B) Bis(5-p-Chlorophenyltetrazolato) Copper(II) Monohydrate and (C) Bis(5-o-Chlorophenyltetrazolato) Copper(II) Monohydrate

Table XIX. A Comparison of the Reflectance, Nujol Mull, and Solution Spectra of Copper(II) Perchlorate Hexahydrate[b] and the Copper(II) Complexes of Various 5-substituted tetrazoles[a]

Compound	$^2T_{2g} \rightarrow {}^2E_g$	$^2B_{1g} \rightarrow {}^2A_{1g}$	$^2B_{1g} \rightarrow {}^2B_{2g}$	$^2B_{1g} \rightarrow {}^2E_g$	Charge transfer
$Cu(ClO_4)_2 \cdot 6H_2O$(Solid)[c]	12500				
$Cu(ClO_4)_2 \cdot 6H_2O(H_2O)$	12900				
$Cu(ClO_4)_2 \cdot 6H_2O$(DMSO)	12500(64)				33000
$Cu(ClO_4)_2 \cdot 6H_2O$(DMF)			13500(33)		33000
$Cu(ClO_4)_2 \cdot 6H_2O(C_5H_5N)$			16200(20)		31000
$Cu(5\text{-}o\text{-}ClC_6H_4CN_4)_2 \cdot H_2O$(Solid)[c]		1100(sh)	[16130]		27800
$Cu(5\text{-}o\text{-}ClC_6H_4CN_4)_2 \cdot H_2O$(DMSO)			13500(66)		33000
$Cu(5\text{-}o\text{-}ClC_6H_4CN_4)_2 \cdot H_2O$(DMF)			15200(80)		33000
$Cu(5\text{-}o\text{-}ClC_6H_4CN_4)_2 \cdot H_2O(C_5H_5N)$			15700(140)		32300
$Cu(5\text{-}p\text{-}ClC_6H_4CH_2CN_4)_2 \cdot H_2O$(Solid)[c]		10400	[17780]		28600
$Cu(5\text{-}p\text{-}ClC_6H_4CH_2CN_4)_2 \cdot H_2O(C_5H_5N)$			15400(33)		33000

a see footnote a Table XVIII

Continued

b No solution spectra are reported for $Cu(5\text{-}C_6H_5CN_4)(OH)$, $Cu(5\text{-}C_6H_5CN_4)_2 \cdot H_2O$, $Cu(5\text{-}p\text{-}ClC_6H_4CN_4)_2 \cdot H_2O$, and $Cu(5\text{-}p\text{-}CH_3OC_6H_4CN_4)OH$ due to their insolubility in ten common solvents.

c Additional bands were found at 5150, 5800, and 6980cm^{-1}

Table XX. Reflectance and Nujol Mull Spectra[a] of Cobalt(II) Perchlorate Hexahydrate and the Cobalt(II) Complexes[b] of Various 5-Substituted Tetrazoles.

Compound	$^4T_{1g} \xrightarrow{(F)} {}^4T_{2g}(F)$	$^4T_{1g} \xrightarrow{(F)} {}^2F_g$	$^4T_{1g} \xrightarrow{(F)} {}^4A_{2g}(F)$	$^4T_{1g} \xrightarrow{(F)} {}^4T_{1g}(P)$
$Co(ClO_4)_2 \cdot 6H_2O$(Solid)	8330		19801	21505
$Co(L)_6^{+2}$ (high spin)	∿8-9000	∿11000[d]	∿16-18000	∿20-21000
$Co(F_3CCN_4)_2 \cdot 6H_2O$(Solid)	10400			21300
$Co(5\text{-}p\text{-}ClC_6H_4CN_4)_2 \cdot H_2O$(Solid)	8970		19000(sh)	20400
$Co(5\text{-}C_6H_5CN_4)_2 \cdot H_2O$(Solid)	9090			21050
$Co(5\text{-}p\text{-}CH_3OC_6H_4CN_4)_2 \cdot H_2O$(Solid)	9480	11030[c]	19000(sh)	21100
$Co(5\text{-}o\text{-}ClC_6H_4CN_4)_2 \cdot H_2O$(Solid)	9520		19000(sh)	20600
$Co(5\text{-}p\text{-}ClC_6H_4CH_2CN_4)_2 \cdot H_2O$(Solid)	10000	11450[c]	19000(sh)	22160[c]

a See footnote a Table XVIII

b Additional bands were found at 4550, 5150, 5970 and 6900cm^{-1}.

c This band is only found by the nujol mull method.

d Not often observed.

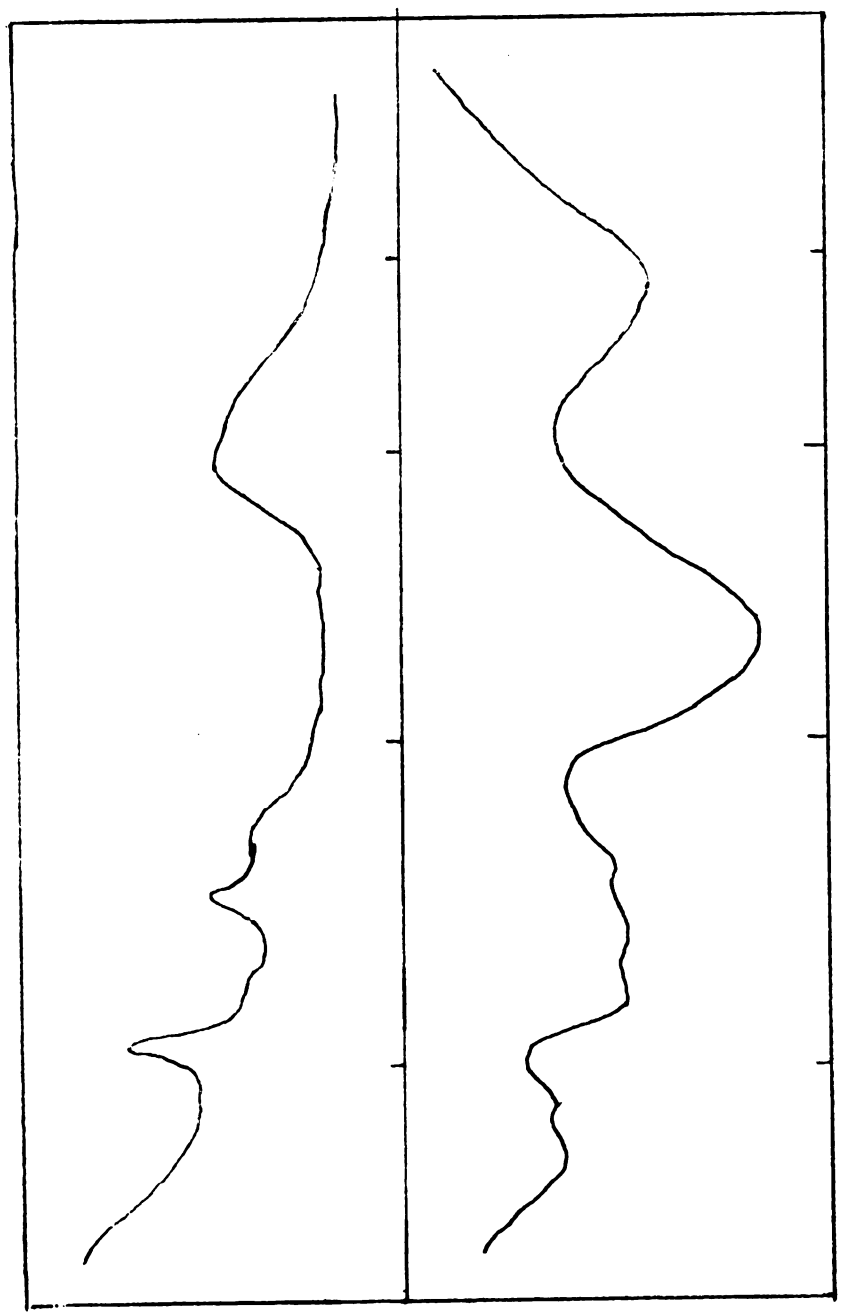


Figure 7. Reflectance Spectra of (A) Cobalt(II) Perchlorate Hexahydrate and (B) Bis (5-p-chlorophenyltetrazolato) Cobalt(II) Monohydrate

Table XXI. A Comparison of the Reflectance[a] Nujol Mull and Solution[a] Spectra of Cobalt(II) perchloratehexahydrate and the Cobalt(II) Complexes[b] of Various 5-Substituted Tetrazoles.

Compound	$^4T_{1g} \rightarrow {}^4T_{2g}(F)$	$^4T_{1g} \rightarrow {}^2E_g$	$^4T_{1g} \rightarrow {}^4A_{2g}(F)$	$^4T_{1g} \rightarrow {}^4T_{1g}(P)$
CoL_6^{+2} (high spin)	~8-9000	~100000		
$Co(ClO_4)_2 \cdot 6H_2O$(Solid)	8330(sh)		19800	21505
$Co(ClO_4)_2 \cdot 6H_2O(C_5H_5N)$			20700(11)	
$Co(ClO_4)_2 \cdot 6H_2O$(DMF)			19300(32)	21500
$Co(ClO_4)_2 \cdot 6H_2O$(DMSO)			18900(20)	21500
$Co(5\text{-}CF_3CN_4)_2 \cdot 6H_2O$(Solid)[24]	10400			21300
$Co(PMT)_6(ClO_4)_2$(Solid)[38]	8500			20400
$Co(5\text{-}o\text{-}ClC_6H_4CN_4)_2 \cdot H_2O$(Solid)	9523		19000(sh)	20600
$Co(5\text{-}o\text{-}ClC_6H_4CN_4)_2 \cdot H_2O(C_5H_5N)$			19000(sh)	21700(11)
$Co(5\text{-}o\text{-}ClC_6H_4CN_4)_2 \cdot H_2O$(DMF)			19100(sh)	20500(27)
$Co(5\text{-}o\text{-}ClC_6H_4CN_4)_2 \cdot H_2O$(DMSO)				19600(23)

Continued

Table XXI. - Continued

Compound	$^4T_{1g} \rightarrow {}^4T_{2g}(F)$	$^4T_{1g} \rightarrow {}^2E_g$	$^4T_{1g} \rightarrow {}^4A_{2g}(F)$	$^4T_{1g} \rightarrow {}^4T_{1g}(P)$
$Co(5\text{-}p\text{-}ClC_6H_4CN_4)_2 \cdot H_2O$(Solid)	8970		19000(sh)	25400
$Co(5\text{-}p\text{-}ClC_6H_4CN_4)_2 \cdot H_2O(C_5H_5N)$			19000(sh)	21100(34)
$Co(5\text{-}p\text{-}ClC_6H_4CN_4)_2 \cdot H_2O$(DMF)			19100(sh)	20400(27)
$Co(5\text{-}p\text{-}ClC_6H_4CH_2CN_4)_2 \cdot H_2O$(Solid)	10000	11450[c]	1900(sh)	22160[c]
$Co(5\text{-}p\text{-}ClC_6H_4CH_2CN_4)_2 \cdot H_2O(C_5H_5N)$			19000(sh)	21500(39)
$Co(5\text{-}p\text{-}ClC_6H_4CH_2CN_4)_2 \cdot H_2O$(DMF)			19000(sh)	21800(-)
$Co(5\text{-}p\text{-}CH_3OC_6H_4CN_4)_2 \cdot H_2O$(Solid)	9480	11030[c]	19000(sh)	21100
$Co(5\text{-}p\text{-}CH_3OC_6H_4CN_4)_2 \cdot H_2O(C_5H_5N)$				21700(85)
$Co(5\text{-}p\text{-}CH_3OC_6H_4CN_4)_2 \cdot H_2O$(DMF)			19100(sh)	20800(4)
$Co(5\text{-}C_6H_5CN_4)_2 \cdot H_2O$(Solid)	9090			21050
$Co(5\text{-}C_6H_5CN_4)_2 \cdot H_2O(C_5H_5N)$				21400(46)
$Co(5\text{-}C_6H_5CN_4)_2 \cdot H_2O$(DMF)			19200(sh)	21100(17)

Continued

Table XXI. - Continued

a See footnote a Table XVIII

b Bands are also found at 4550, 5150, 5970 and 6900cm^{-1}

c Bands only found by the nujol mull method

d Not often observed

e A charge transfer band was found from 32000 to 35000cm^{-1} for each complex

Table XXII. Reflectance and Nujol Mull Spectra [a] of Nickel(II) Perchlorate Hexahydrate and the Nickel(II) Complexes [b] of Various 5-Substituted Tetrazoles.

Compound	$^3A_{2g} \rightarrow {}^3T_{2g}(F)$	$^3A_{2g} \rightarrow {}^1E_g$	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$
$Ni(ClO_4)_2 \cdot 6H_2O$(Solid)	8500	13890	15150(sh)	25000
$Ni(PMT)_6ClO_4$(Solid)[38]	9760		16000	
$Ni(F_3C\text{-}CN_4)_2 \cdot 4H_2O$(Solid)[25]	11400	(13200)[c]	18500	28500
$Ni(5\text{-}C_6H_5CN_4)_{1.8} \cdot H_2O$	10400		[17800][b]	28500
$Ni(5\text{-}o\text{-}ClC_6H_4CN_4)_{1.8} \cdot H_2O$	10400		[17800]	28500
$Ni(5\text{-}p\text{-}ClC_6H_4CN_4)_{1.8} \cdot H_2O$	10400		[18400]	28500
$Ni(5\text{-}p\text{-}CH_3OC_6H_4CN_4)_{1.8} \cdot H_2O$	10400		[18400]	28500
$Ni(5\text{-}p\text{-}ClC_6H_4CH_2CN_4)_{1.8} \cdot H_2O$	10400		[18700]	25600

a See footnote a Table XVIII

b Additional bands were found at 4650, 5140, 5970, 6900cm^{-1}

c Although this shoulder is assigned to the $^3A_{2g} \rightarrow {}^1E_g$, the assignment was challenged because of the intensity of the peak.

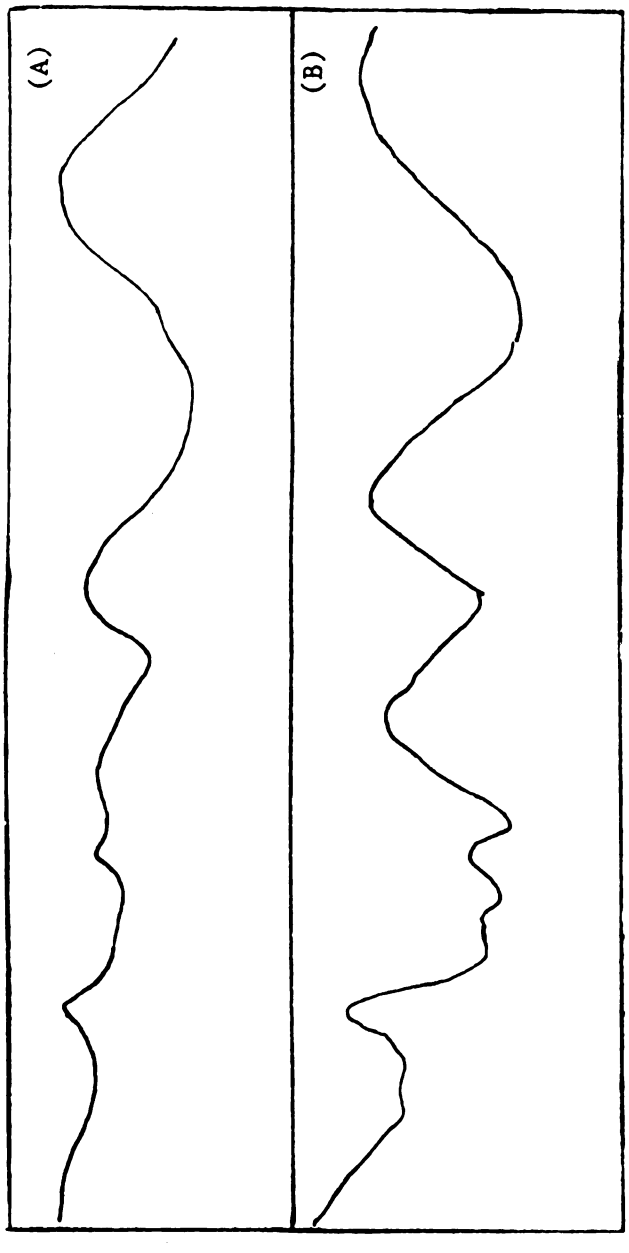


Figure 3. Reflectance Spectra of (A) Nickel(II) Perchlorate Hexahydrate and (B) Nickel(II) Complex of 5-o-Chlorophenyltetrazole

Table XXIII. A Comparison of the Reflectance[a,d], Nujol Mull and Solution Spectra of Nickel(II) Perchlorate Hexahydrate and the Nickel(II) Complexes[b] of Various 5-Substituted Tetrazoles.

Compound	$^3A_{2g} \rightarrow {}^3T_{2g}(F)$	$^3A_{2g} \rightarrow {}^1E_g$	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$
$Ni(ClO_4)_2 \cdot 6H_2O$(Solid)	[8333]	[3890]	[15150(sh)]	[25640]
$Ni(ClO_4)_2 \cdot 6H_2O$(DMSO)		13400(5)[c]	14900(3)	24500(20)
$Ni(ClO_4)_2 \cdot 6H_2O$(DMF)		13700(7)	14900(8)	25300(26
$Ni(ClO_4)_2 \cdot 6H_2O(C_5H_5N)$			16700(5)	27000(~9)
$Ni(5\text{-}p\text{-}ClC_6H_4CN_4)_{1.8} \cdot H_2O$(Solid)	10400		[18400]	]8500
$Ni(5\text{-}p\text{-}ClC_6H_4CN_4)_{1.8} \cdot H_2O$(DMSO)			16700(6)	27000(12)
$Ni(5\text{-}p\text{-}ClC_6H_4CN_4)_{1.8} \cdot H_2O$(DMF)			17500(11)	
$Ni(5\text{-}p\text{-}ClC_6H_4CN_4)_{1.8} \cdot H_2O(C_5H_5N)$			17700(6)	
$Ni(5\text{-}p\text{-}ClC_6H_4CH_2CN_4)_{1.8} \cdot H_2O$(Solid)	10400		[18700]	25600
$Ni(5\text{-}p\text{-}ClC_6H_4CH_2CN_4)_{1.8} \cdot H_2O$(DMSO)			13200(-)	
$Ni(5\text{-}p\text{-}ClC_6H_4CH_2CN_4)_{1.8} \cdot H_2O$(DMF)			18200(6)	27800(12)
$Ni(5\text{-}p\text{-}ClC_6H_4CH_2CN_4)_{1.8} \cdot H_2O(C_5H_5N)$			18200(7)	

Continued

Table XXIII. - Continued

Compound	$^3A_{2g} \rightarrow {}^3T_{2g}(F)$	$^3A_{2g} \rightarrow {}^1E_g$	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$	Charge Transfer
$Ni(5\text{-}p\text{-}CH_3OC_6H_4CN_4)_{1.8}\cdot H_2O$(Solid)	10400		[18400]	28500	
$Ni(5\text{-}p\text{-}CH_3OC_6H_4CN_4)_{1.8}\cdot H_2O$(DMF)			17200(8)	27500(15)	
$Ni(5\text{-}p\text{-}CH_3OC_6H_4CN_4)_{1.8}\cdot H_2O(C_5H_5N)$			17900(8)		32700
$Ni(5\text{-}o\text{-}Cl\text{-}C_6H_4CN_4)_{1.8}\cdot H_2O$(Solid)	10400		[17800]	28500	
$Ni(5\text{-}o\text{-}Cl\text{-}C_6H_4CN_4)_{1.8}\cdot H_2O$(DMF)			17300(23)	27900(30)	
$Ni(5\text{-}o\text{-}Cl\text{-}C_6H_4CN_4)_{1.8}\cdot H_2O(C_5H_5N)$			17900(12)		32300
$Ni(5\text{-}C_6H_5CN_4)_{1.8}\cdot H_2O$(Solid)	10400		[17800]	28500	
$Ni(5\text{-}C_6H_5CN_4)_{1.8}\cdot H_2O$(DMF)			17300(3)	27800(8)	
$Ni(5\text{-}C_6H_5CN_4)_{1.8}\cdot H_2O(C_5H_5N)$			18200(-)	24500(-) (SHOULDER)	

a See footnote a Table XVIII

b Additional bands were also found at 4650, 5140, 5970, 6900cm^{-1}

c A band at 13700cm^{-1} (sh) was also observed

Table XXIV. Reflectance and Nujol Mull Spectra[a] of Chromium(III) Perchlorate Hexahydrate and the Chromium(III) Complexes[b] of Various 5-Substituted Tetrazoles

Compound	$^4A_{2g} \rightarrow {}^4T_{2g}(F)$	$^4A_{2g} \rightarrow {}^4T_{1g}(F)$	$^4A_{2g} \rightarrow {}^4T_{1g}(P)$
$Cr(ClO_4)_3 \cdot 6H_2O$(Solid)	17400[e]	24400	
$Cr(H_2O)_6^{+2}$ (c)	17400	24700	37000
$Cr(NH_3)_6^{+3}$ (d)	21500	28500	
$Cr(en)_3^{+3}$ (d)	21800	28500	
$Cr(5\text{-}p\text{-}CH_3OC_6H_4CN_4)_2(OH) \cdot 6H_2O$(Solid)	[17400]		
$Cr(5\text{-}p\text{-}ClC_6H_4CN_4)_2OH \cdot 4H_2O$(Solid)	[17700]	24700	
$Cr(5\text{-}C_6H_4CN_4)_2OH \cdot 4H_2O$(Solid)	[17900]	24400	
$Cr(5\text{-}o\text{-}ClC_6H_4CN_4)_2OH \cdot 4H_2O$(Solid)	[18200]	25000	
$Cr(5\text{-}p\text{-}ClC_6H_4CH_2CN_4)_2OH \cdot 4H_2O$ (Solid)	[18200]	24500	

a see footnote a Table XVIII

b Additional bands were found at 4550, 5130, 5900, 6900 and 10200 cm^{-1}

c reference 62

d reference 63

e An additional band was found at 8330cm^{-1}

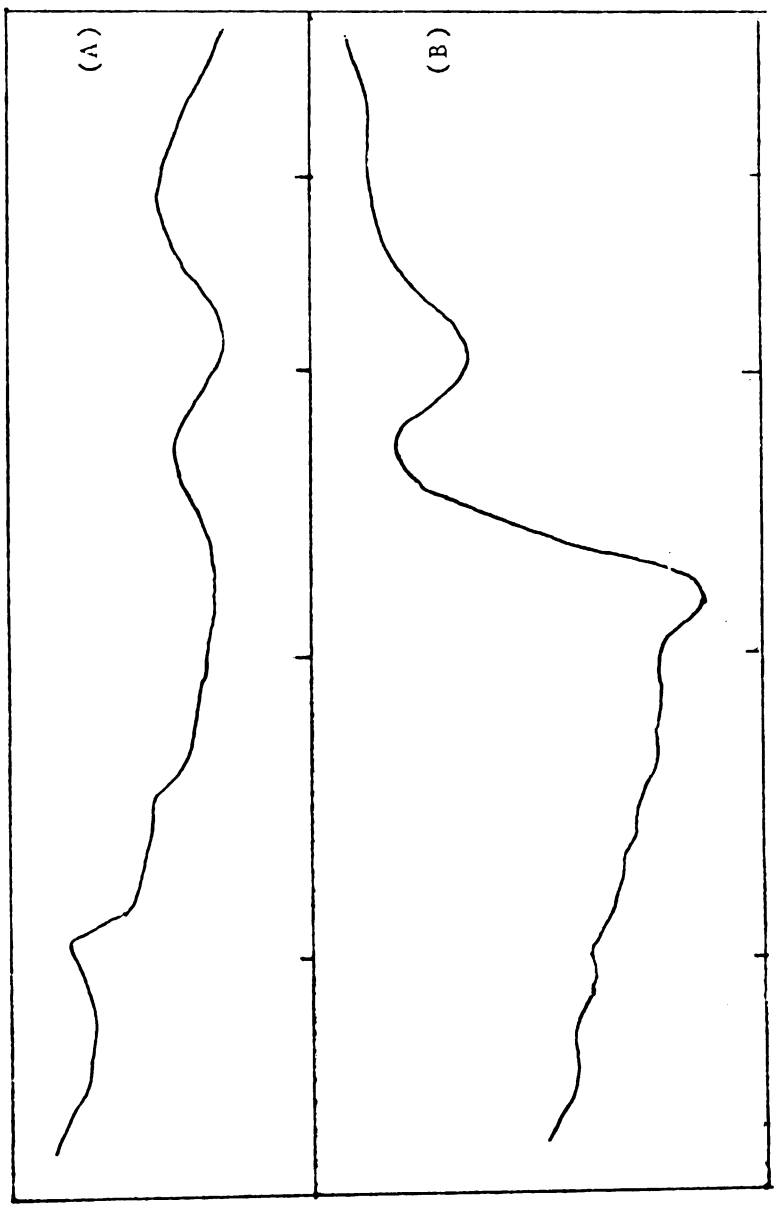


Figure 9. Reflectance Spectra of (A) Chromium(III) Perchlorate Hexahydrate and (B) Hydroxo bis(5-phenyltetrazolato) Chromium(III) Tetrahydrate

Table XXV. A Comparison of the Reflectance,[a] Nujol Mull, and Solution Spectra of Chromium(III) perchlorate Hexahydrate and the Chromium(III) Complexes[b] of Various 5-Substituted Tetrazoles

Compound	$^4A_{2g} \rightarrow {}^4T_{2g}(F)$	$^4A_{2g} \rightarrow {}^4T_{1g}(F)$	$^4A_{2g} \rightarrow {}^4T_{1g}(P)$
$Cr(ClO_4)_3 \cdot 6H_2O$(Solid)	17400	24400	
$Cr(ClO_4)_3 \cdot 6H_2O$(DMSO)	16600(30)	23800(36)	33000(30)
$Cr(ClO_4)_3 \cdot 6H_2O$(DMF)	17400(26)	24500(39)	34500(-)
$Cr(ClO_4)_3 \cdot 6H_2O(C_5H_5N)$	18800(16)	25000(13)	32300(41)
$Cr(5\text{-}p\text{-}ClC_6H_4CN_4)_2OH \cdot 4H_2O$(Solid)	[17700]	24700	
$Cr(5\text{-}p\text{-}ClC_6H_4CN_4)_2OH \cdot 4H_2O$(DMSO)	17900(27)	24200(30)	33800(-)
$Cr(5\text{-}p\text{-}ClC_6H_4CN_4)_2OH \cdot 4H_2O$(DMF)	18200(61)	25000(88)	34000(-)
$Cr(5\text{-}p\text{-}ClC_6H_4CN_4)_2OH \cdot 4H_2O(C_5H_5N)$	18200(28)	25000(32)	32400(870)
$Cr(5\text{-}o\text{-}ClC_6H_4CN_4)_2OH \cdot 4H_2O$(Solid)	[18200]	25000	
$Cr(5\text{-}o\text{-}ClC_6H_4CN_4)_2OH \cdot 4H_2O(C_5H_5N)$	18600(45)	25400(58)	32800(-)
$Cr(5\text{-}p\text{-}CH_3OC_6H_4CN_4)_2OH \cdot 6H_2O$(Solid)	[17400]		
$Cr(5\text{-}p\text{-}CH_3OC_6H_4CN_4)_2OH \cdot 6H_2O(C_5H_5N)$	18200(42)		32800(610)

a see footnote a Table XVIII

b additional bands were found at 5120, 6900, 8330 and 10200 cm^{-1} Continued

Table XXV. - Continued

Compound	$^4A_{2g} \rightarrow {}^4T_{2g}(F)$	$^4A_{2g} \rightarrow {}^4T_{1g}(F)$	$^4A_{2g} \rightarrow {}^4T_{1g}(P)$
$Cr(5\text{-}p\text{-}ClC_6H_4CH_2CN_4)_2OH \cdot 4H_2O$(Solid)	[18200]	24500	
$Cr(5\text{-}p\text{-}ClC_6H_4CH_2CN_4)_2OH \cdot 4H_2O(C_5H_5N)$	18200(3)	24800(40)	32800(163)
$Cr(5\text{-}C_6H_5CN_4)_2OH \cdot 4H_2O$(Solid)	[17900]	24400	
$Cr(5\text{-}C_6H_5CN_4)_2OH \cdot 4H_2O(C_5H_5N)$	18200(41)	25000(54)	32800(127)

Magnetic Moments

The magnetic moments of the various complexes are listed in Table XXVI.

According to Barefield and Busch (69), high spin 6-coordinate, 5-coordinate and 4-coordinate cobalt(II) complexes have magnetic moment values of 4.7-5.2, 4.2-4.6, and 4.2-4.8 respectively. Thus, only the pseudo-octahedral 6-coordinate complexes can usually be identified by use of magnetic moment data. The cobalt(II) complexes of 5-p-chlorophenyltetrazole, 5-o-chlorophenyltetrazole, and 5-p-chlorobenzyltetrazole appear to be octahedral or pseudo-octahedral complexes. On the other hand, the cobalt(II) complexes of 5-phenyltetrazole and 5-p-methoxyphenyltetrazole may be either 5-coordinate or 4-coordinate and their magnetic moments are very close to the spin only value. Magnetic moments of these cobalt(II) complexes are very temperature dependent.

Most of the cobalt(II) complexes have large values for θ, the Weiss constant. Figgis and Lewis (51) state that large values of θ indicate that the excited states lie far enough from the ground state that they may be "thermally occupied" at the temperature in question. In addition, Cotton and Wilkinson (70) state that large values of θ can possibly be explained in terms of strong "interionic or

intermolecular interactions".

According to Barefield and Busch (69), high spin 6-coordinate, 5-coordinate, and 4-coordinate nickel(II) complexes have magnetic moments of 3.0-3.3, 3.0-3.45, and 3.45-4.0 respectively.

The nickel(II) complexes of 5-phenyltetrazole, 5-o-chlorophenyltetrazole and 5-p-chlorophenyltetrazole may be 6-coordinate.

However, the nickel(II) complexes of 5-p-methoxyphenyltetrazole and 5-p-chlorobenzyltetrazole may be 4-coordinate.

The magnetic moments of the nickel(II) complexes are very temperature dependent and the Weiss constanst are quite large for these complexes.

The magnetic moments at 295^{o} of 1.35 B.M. and 1.06 B.M. for the copper(II) complexes of 5-phenyltetrazole and 5-p-methoxyphenyltetrazole are unusually low and may be due to copper-copper interactions. Kato *et al.* (71) have classified copper-to-copper magnetic interactions as either direct interactions or super-exchange interactions. Direct interactions involve metal-metal bonding similar to that found in copper(II) acetate monohydrate. Super exchange interactions are more common when a ligand acts as a bridge between the metal ions of 1.96 and 1.75. The magnetic moments of copper(II) complexes of 5-o-chlorophenyltetrazole and 5-p-chlorophenyltetrazole are within the expected range of 1.7-2.2 for

copper(II) complexes. The magnetic moments of the copper(II) complexes are very temperature dependent and the Weiss constants are very large.

The magnetic moments of the chromium(III) complexes agree with the expected value (51) of 3.87-5.29. The chromium(III) complex of 5-p-methoxyphenyltetrazole has a magnetic moment of 3.06 at 295°. This observed moment is lower than expected and may be due to direct metal-metal bonding or super exchange interaction by analogy with the copper(II) complexes.

Table XXVI. Magnetic Moments [a] of the Cobalt(II) Nickel(II), Chromium(III), and Copper(II) Complexes of Various 5-Substituted Tetrazoles

Compound	295°K	195°K	77°K	Θ (°K)
$Co(5\text{-}p\text{-}ClC_6H_4CN_4)_2 \cdot H_2O$	5.36	4.98	3.94	105
$Co(5\text{-}C_6H_5CN_4)_2 \cdot H_2O$	4.09	3.91	3.01	115
$Co(5\text{-}p\text{-}CH_3OC_6H_4CN_4)_2 \cdot H_2O$	3.89	3.83	3.43	25
$Co(5\text{-}o\text{-}ClC_6H_4CN_4)_2 \cdot H_2O$	4.99	4.57	3.89	130
$Co(5\text{-}p\text{-}ClC_6H_4CH_2CN_4)_2 \cdot H_2O$	4.82	4.45	3.69	100
$Ni(5\text{-}C_6H_5CN_4)_{1.8} \cdot H_2O$	3.07	2.90	2.43	80
$Ni(5\text{-}o\text{-}ClC_6H_4CN_4)_{1.8} \cdot H_2O$	3.12	3.12	2.44	85
$Ni(5\text{-}p\text{-}ClC_6H_4CN_4)_{1.8} \cdot H_2O$	3.35	3.12	2.54	100
$Ni(5\text{-}p\text{-}CH_3OC_6H_4CN_4)_{1.8} \cdot H_2O$	3.83	3.49	2.65	225
$Ni(5\text{-}p\text{-}ClC_6H_4CH_2CN_4)_{1.8} \cdot H_2O$	3.60	3.57	2.52	———
$Cu(5\text{-}o\text{-}ClC_6H_4CN_4)_2 \cdot H_2O$	1.96	1.89	1.42	100
$Cu(5\text{-}p\text{-}ClC_6H_4CN_4)_2 \cdot H_2O$	1.75	1.56	.78	———
$Cu(5\text{-}C_6H_5CN_4)(OH)$	1.34	1.01	.79	300
$Cu(5\text{-}p\text{-}CH_3OC_6H_4CN_4)(OH)$	1.06	1.39	.75	———
$Cu(5\text{-}p\text{-}ClC_6H_4CH_2CN_4)_2 \cdot 3H_2O$	———	1.05	.73	200

Continued

Table XXVI. - Continued

Compound	295°K	195°K	77°K	θ (°K)
$Cr(5\text{-}p\text{-}CH_3OC_6H_4CN_4)_2OH \cdot 6H_2O$	3.06	3.15	3.64	0
$Cr(5\text{-}p\text{-}ClC_6H_4CN_4)_2OH \cdot 4H_2O$	5.33	4.82	3.60	206
$Cr(5\text{-}C_6H_5CN_4)_2OH \cdot 4H_2O$	4.68	4.17	3.18	210
$Cr(5\text{-}o\text{-}ClC_6H_4CN_4)_2OH \cdot 4H_2O$	3.91	3.77	3.12	75
$Cr(5\text{-}p\text{-}ClC_6H_4CH_2CN_4)_2OH \cdot 4H_2O$	5.22	4.99	4.60	180

[a] In units of Bohr Magnetons

Electron Spin Resonance Spectra

The esr parameters for the copper(II) complexes are displayed in Table XXVII. The g_{avg} values of 2.12 to 2.15 for these complexes compare very favorably with the g_{avg} values of copper(II) complexes with other nitrogen donors (66). Likewise, the $g_{\perp}$ and $g_{||}$ values are similar to the $g_{||}$ and $g_{\perp}$ values found for the copper(II) complexes of pyridine, 4-cyanopyridine, and pentamethylenetatrazole (66).

Unfortunately in the absence of any accurate estimation of $A_{\perp}$, the extent of tetragonal distortion is difficult to estimate. However, the value of $[g_{||} - g_{\perp}]$, which is a measure of splitting within the e_g level is almost directly proportional to the extent of diviation from octahedral symmetry (67).

It is proposed that no signal is seen with the undiluted copper(II) complexes of 5-p-chlorophenyltetrazole and 5-phenyltetrazole due to spin-spin broadening. Similarly, the broad unresolvable band found for the copper(II) complex of 5-p-methoxyphenyltetrazole is possibly due to spin-spin broadening.

The temperature dependence of the 95:1 (Zn:Cu) sample is rather unusual and is not readily explainable.

The esr spectra of most of the cobalt(II) complexes are

very complex. It was impossible to calculate g values for these complexes with the exception of bis(5-o-chlorophenyl-tetrazolato)cobalt(II) monohydrate. This complex shows rather unusual behavior. Apparently the g value changes with temperature. The g values of 2.55, 2.82, 2.87, and 3.01 at -40° C, -100° C, -130° C, and -160° C. This increase in g values with a decrease in temperature may be due to structural changes which accompany changes in temperature.

The esr spectra of the chromium(III) complexes are displayed in Table XXVIII. The g_{avg} value of 1.98 is similar to that of other octahedral chromium(III) complexes (68).

The esr spectra of the nickel complexes consisted of unresolved bands.

Table XXVII. Esr parameters for the Copper(II) Complexes of Various 5-Substituted Tetrazoles

Tetrazolate	Zn Cu	$g_{\perp}$ [c]	All	$g_{\perp}$ [b]	Temp	g_{avg}	A [a]
5-o-$ClC_6H_4CN_4$	1000:1	2.25	175	2.06		2.12	
5-o-$ClC_6H_4CN_4$	333: 1	2.25	180	2.06	-160°to 30°	2.12	
5-o-$ClC_6H_4CN_4$	60: 1	2.25	180	2.06		2.12	
5-o-$ClC_6H_4CN_4$	Neat					2.124	~100
5-p-$ClC_6H_4CN_4$	1000:1	2.24	130	(2.09,2.03)		2.12	
5-p-$ClC_6H_4CN_4$	500: 1	2.24	125	(2.08,2.03)		2.12	
5-p-$ClC_6H_4CN_4$	95: 1	2.24	130	(2.08,2.03)		2.12	
5-p-$ClC_6H_4CN_4$	Neat	No signal					
5-p-$ClC_6H_4CH_2CN_4$	1000:1	2.28	150	(2.11)		2.15	
5-p-$ClC_6H_4CH_2CN_4$	500: 1	2.28	145	(2.11)			
5-p-$ClC_6H_4CH_2CN_4$	95: 1					2.15	~73

a estimated by taking one third of the line width

b (values) the numbers represent gxx and gyy

c when two values are given for $g_{\perp}$, the value listed for $g_{\parallel}$ is actually gzz

Continued

Table XXVII. - Continued

Tetrazolate	Zn:Cu	$g_{\|\|}$[c]	$A_{\|\|}$	$g_{\perp}$[b]	Temp	g	A[a]
5-p-$ClC_6H_4CH_2CN_4$	95:1	2.29	230	2.15	30°	2.20	
5-p-$ClC_6H_4CH_2CN_4$	95:1	2.33	270	2.15	-40° to -100°	2.21	
5-p-$ClC_6H_4CH_2CN_4$	95:1	2.33	150	2.21	-120°	2.23	
5-p-$ClC_6H_4CH_2CN_4$	95:1			2.15	-130°	2.15	~90
5-$C_6H_5CN_4$	1000:1	2.40	70	2.09		2.11	53
5-$C_6H_5CN_4$	95:1						
5-$C_6H_5CN_4$	Neat	No signal					
5-p-$CH_3OC_6H_4CN_4$	1000:1					2.11	53
5-p-$CH_3OC_6H_4CN_4$	Neat	broad unresolvable band					

Table XXVIII. Esr Parameters for the Chromium(III) Complexes of Several 5-Substituted Tetrazoles [a]

Tetrazolate	Zn:Cr	g	A[c]	$g_{\|\|}$	$A_{\|\|}$	$g_{\perp}$	$A_{\perp}$	$g_{\perp}$
5-o-$ClC_6H_4CN_4$	1000:1			2.260[d]	180[d]	2.060[d]		2.010[d]
5-o-$ClC_6H_4CN_4$	0:1	1.970	320					
5-p-$ClC_6H_4CN_4$[b]	0:1	1.980	400					
5-p-$ClC_6H_4CH_2CN_4$[b]	0:1	1.970	350					
5-p-$CH_3OC_6H_4CN_4$[b]	0:1	1.970	420					
5-$C_6H_5CN_4$[b]	0:1	1.970	400					

a Hyperfine splittings are given in gauss ($10^{-4}cm^{-1}$)

b The spectra obtained at 1000:1 dilution did not permit calculation of g values.

c A is the line width

d These are due to copper(II) impurities

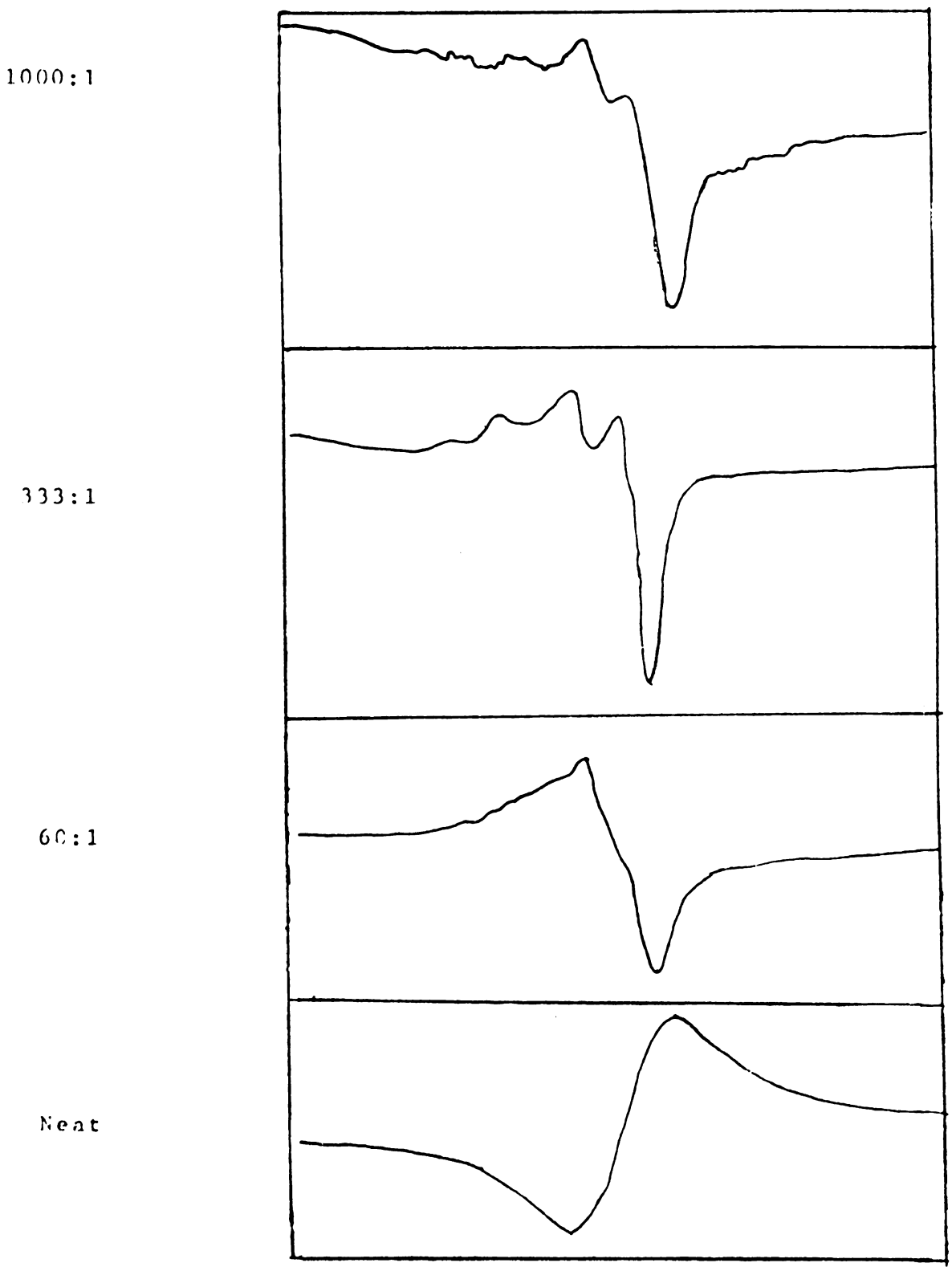


Figure 10. ESR Spectra of Bis(5-o-Chlorophenyltetrazolato) Copper(II) Monohydrate at Various Zn:Cu Ratios

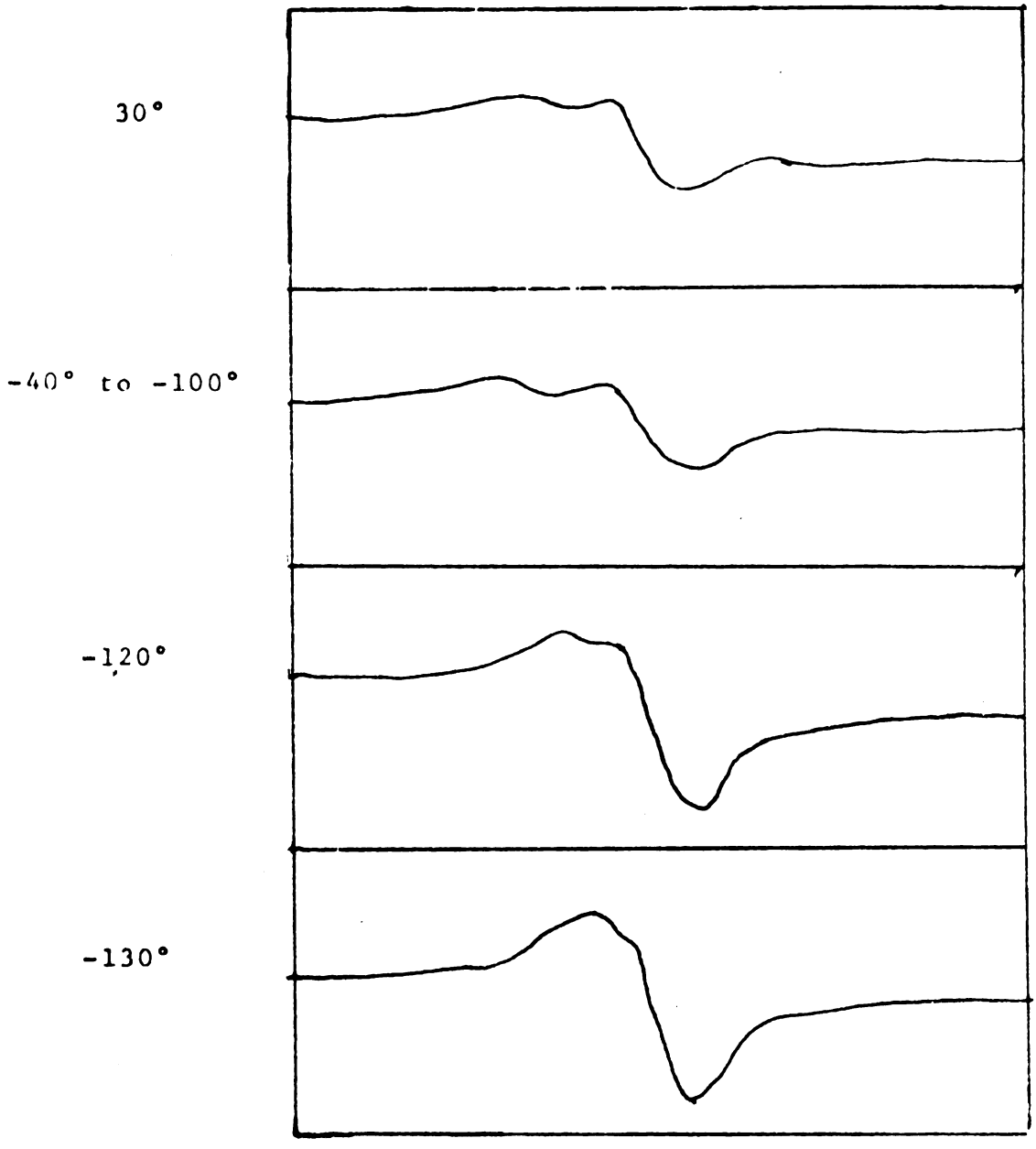


Figure 11. ESR Spectra at Various Temperatures of Bis(5-p-Chlorobenzyltetrazolato) Copper(II) Trihydrate Diluted by a Factor of 95:1 (Zn:Cu)

$Cu(5\text{-}o\text{-}ClC_6H_4CN_4)_2 \cdot H_2O$

$Cu(5\text{-}p\text{-}ClC_6H_4CN_4)_2 \cdot H_2O$

$Cu(5\text{-}p\text{-}ClC_6H_4CH_2CN_4)_2 \cdot 3H_2O$

$Cu(5\text{-}C_6H_5CN_4)(OH)$

$Cu(5\text{-}p\text{-}CH_3OC_6H_4CN_4)(OH)$

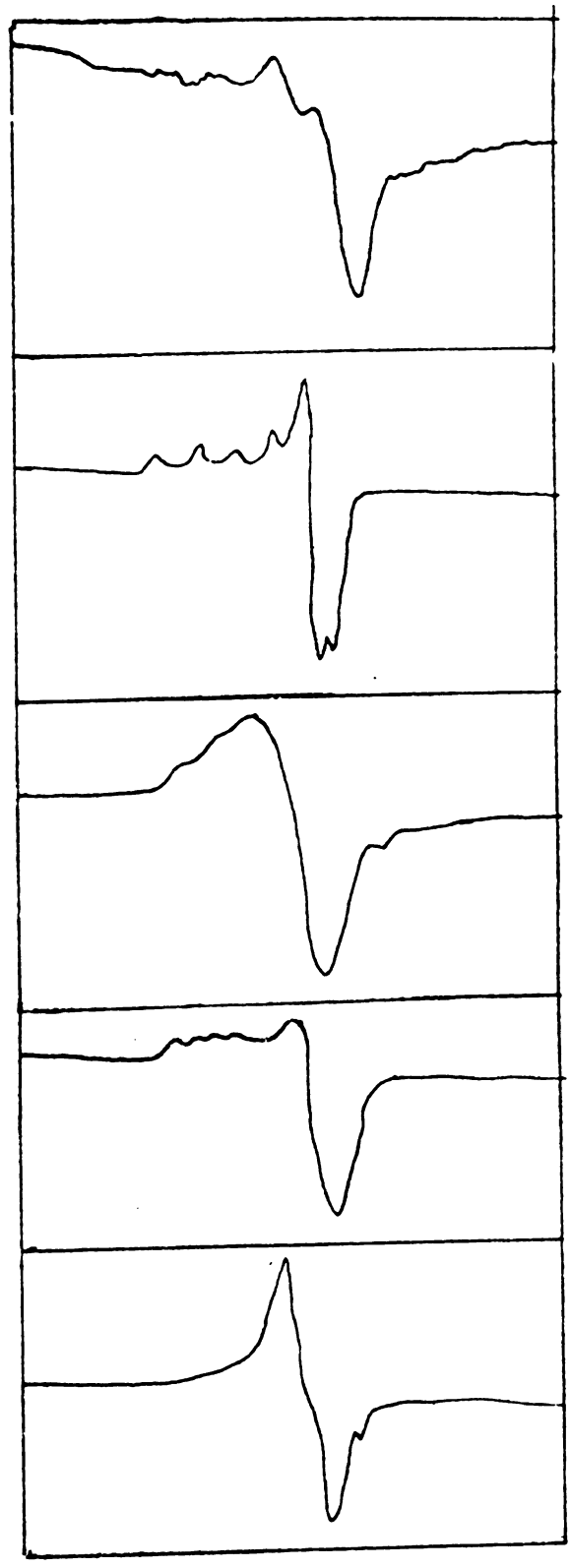


Figure 12. A Comparison of the ESR Spectra at -160° of the Copper(II) Complexes Diluted by 1000:1 (Zn:Cu)

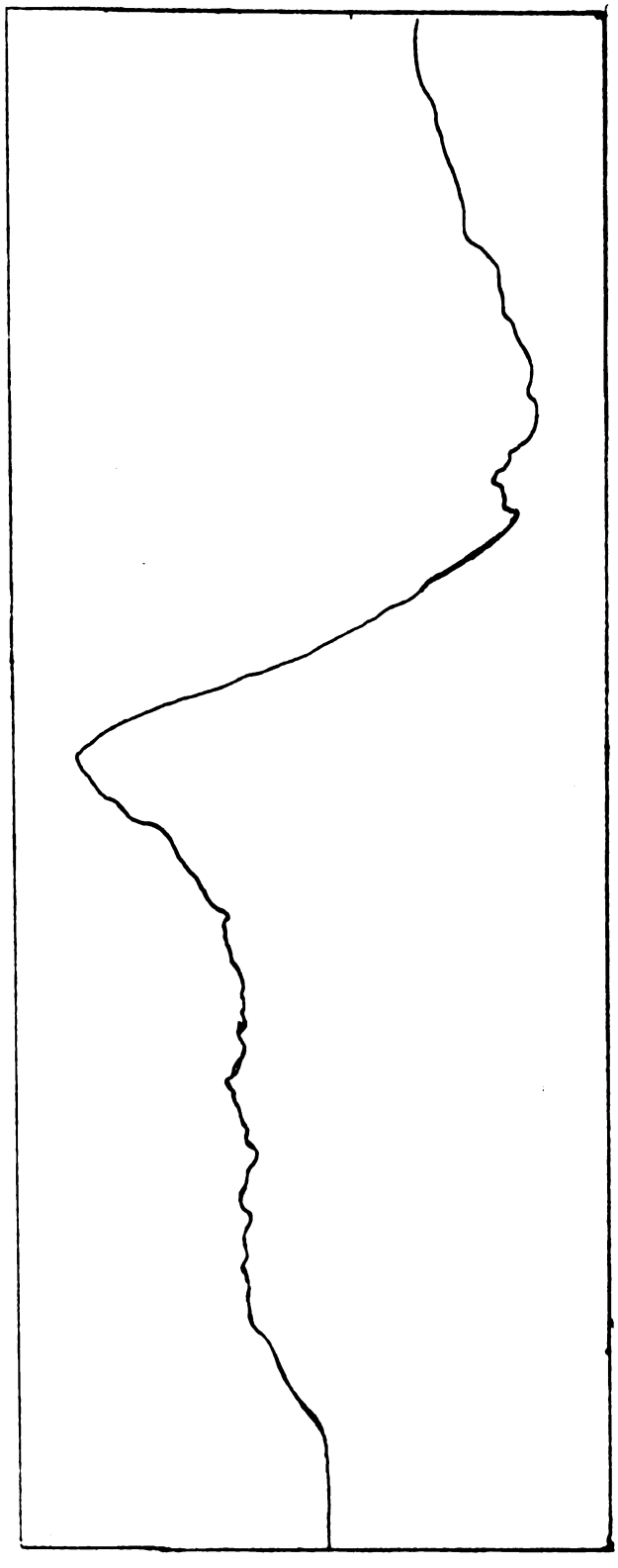


Figure 13. ESR Spectrum of Bis(5-o-Chlorophenyltetrazolato)Cobalt(II) Monohydrate at -40°

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