THE INVESTIGATION OF ZINC (II), NICKEL (II) AND PLATINUM (II) CHLORIDE COMPLEXES WITH SOME 1-SUBSTITUTED TETRAZOLES

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ABSTRACT

THE INVESTIGATION OF ZINC(II), NICKEL(II) AND PLATINUM(II) CHLORIDE COMPLEXES WITH SOME 1-SUBSTITUTED TETRAZOLES

by George L. Gilbert

The investigation of the zinc(II) chloride, nickel(II) chloride and platinum(II) chloride complexes of some 1-substituted tetrazoles was carried out. The coordination involved the molecular tetrazole coordinating with the metal chloride. The general formula for the solid products was MT_2Cl_2 (where T = 1-methyltetrazole, 1-cyclohexyltetrazole or 1-phenyltetrazole).

The crystalline products were obtained with the formula $Zn(C_2N_4H_4)_2Cl_2$, $Zn(C_7N_4H_6)_2Cl_2$, $Zn(C_7N_4H_{12})_2Cl_2$, $Ni(C_2N_4H_4)_2Cl_2$, $Ni(C_7N_4H_{12})_2Cl_2$, $Pt(C_2N_4H_4)_2Cl_2$ and $Pt(C_7N_4H_{12})_2Cl_2$. These solids are generally insoluble in common reagents with the exception of the zinc compounds which are moderately soluble in tetrahydrofuran and simple alcohols. Ethanolic solutions of the zinc complexes with 1-methyltetrazole and 1-phenyltetrazole yielded clear crystals with hexagonal platelet and rhombic shapes respectively.

The nickel and zinc complexes decomposed to the free tetrazole and metal chloride in water, but the platinum complexes were unaffected in this medium. The dichlorobis(1-methyltetrazole) platinum(II) compound dissolved with decomposition in concentrated nitric acid and concentrated aqueous ammonia, whereas the 1-cyclohexyltetrazole platinum(II) complex was not affected by these solvents.

The solid complexes decompose without melting when heated, often explosively. X-ray diffraction data indicate a large unit cell.

Stability constant studies on cobalt and nickel with 1-substituted tetrazoles in ethanol and tetrahydrofuran yielded similar values for 1-methyltetrazole and 1-cyclohexyltetrazole and somewhat larger values with 1-phenyltetrazole.

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By

George L. Gilbert

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF TABLES - Continued

TABLE Page

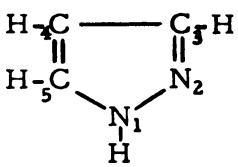
LIST OF FIGURES

I. HISTORICAL

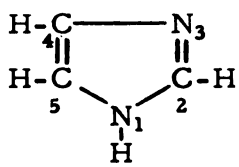
According to the theory of Sidgwick (1) and Lowry (2), a co-ordinate bond may be formed between any atom or ion which can act as an electron pair donor and any atom or ion which can act as an electron pair acceptor. The class of compounds resulting from this type of interaction is called coordination compounds.

It has also been found that certain olefin and ring systems form coordination compounds where the interaction is that of the π-electron cloud of the species with the acceptor atom or ion. A full understanding of the nature of this interaction requires the use of a molecular orbital treatment of the system.

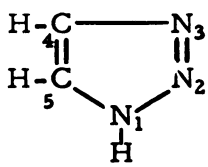
Azole ring systems containing two or more nitrogen atoms have also been studied as coordinating groups. The ring systems referred to are shown below:



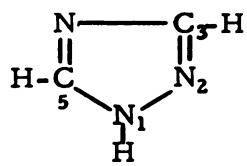
pyrazole



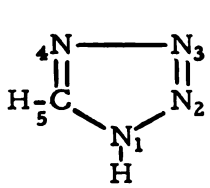
imidazole



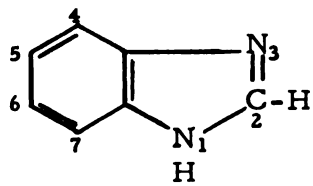
1, 2, 3-triazole



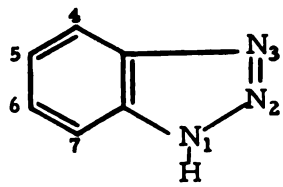
1, 2, 4-triazole



tetrazole



benzimidazole



benzotriazole

Structurally these rings might be expected to coordinate at the ring nitrogen or by interaction of the π-electrons associated with the ring.

A review and discussion of some coordination compounds of these ring systems has recently been given (3).

Solid complexes have been prepared between pyrazole and silver and cobalt but they have received little study.

The reaction of imidazole with silver and zinc has also produced solid compounds (4, 5) as have substituted imidazoles with Cu(I), Cu(II), Mg, Ni, Co, Zn, Cd, Mn and Pb (6, 7, 8, 9, 10, 11). The imidazole system is found to coordinate as the anion, neutral species, or cation, depending on the acidity of the solution.

The solid compounds of benzimidazole with silver, platinum(II), copper, mercury, and cobalt are found to form in most instances after the loss of hydrogen from the 1-position (12, 13). The stability of the silver salt has led to its use for quantitative precipitation of the silver ion (14). Substitution in the 1-position results in a much weaker coordination species as shown by the lack of interaction of 1-phenylbenzimidazole, 2-benzylimidazole and 1, 6- dimethylbenzimidazole with Cd, Co, Zn or Ag.

The silver compound with 1, 2, 3-benzotriazole (15) and a series of 1, 2, 3-benzotriazole compounds with palladium, rhodium, and osmium have been reported (16, 17, 18, 19). In the latter group of compounds the 1, 2, 3-benzotriazole is found to coordinate both as the anion and the neutral molecule.

In a slightly basic aqueous medium, coordination of 1, 2, 4-triazoles with Ni^{++}, Co^{++}, and Cu^{++} occurs as the neutral molecule (20, 21) whereas anionic interaction is exhibited in more basic solutions (22, 23).

Tetrazole and 5-substituted tetrazoles have been shown to form good compounds with the alkaline earth metals, and early workers reported compounds with mercury, copper and silver (22, 24, 25).

More recent studies have yielded crystalline materials from copper, nickel, cobalt and iron(II) with 5-substituted tetrazoles (26, 27, 28, 29).

Brubaker and Daugherty prepared a series of copper 5-substituted tetrazole compounds where the tetrazole coordinates as an anion or as the neutral species depending on the nature of the substituent on the ring. The work of Jonassen, utilizing the more basic 5-trifluoromethyltetrazolyl anion, has led to the preparation of cobalt, nickel and iron(II) compounds.

Disubstitution or 1-substitution on the tetrazole ring appears to give less stable compounds. The only reported instances of compound formation being those with Pt(IV), silver and cadmium (30, 31, 32). Polarographic studies by Popov using metrazole was found to yield no interaction with Co^{++}, Tl^{+}, and Cd^{++} in aqueous media.

The 5-azotetrazole-metal compounds have found uses as detonators while silver salts with 5-thiotetrazole have been used in photography.

The interaction of the various azole ring systems with metal ions in solution has also received attention. Stability constant studies and solution studies of imidazole with cobalt, copper, nickel, cadmium and zinc (33, 34, 35) and methylimidazole with cadmium (36) have been reported. The stability constants of tetrazole with various metal ions have yielded meaningful results only in the case of 5-aminotetrazole-copper(II) (26).

Infrared studies of the various azole compounds discussed have not elucidated the exact structure of the materials involved. The study of a series of metals with various substituted imidazoles has, however, resulted in the discovery of a regular shift in the 8μ region due to the metal present in the order Cu > Mg > Ni > Co > Zn, Cd, Mn > Pb (11). The copper-5-aminotetrazole complex has been shown by absence of a shift in the amino NH stretch to involve bonding by the copper to the ring.

Studies of the quantitative effect on coordination of various substituents in the 1-position can be hoped to clarify the character of the

bond more fully. Investigation of reactions of 1-substituted tetrazoles with the view of preparing metal-tetrazolates would also be of scientific interest.

II. EXPERIMENTAL

Materials Used

Reagent grade chemicals were used throughout this investigation with the exception of the following:

Sodium azide - Eastman Kodak yellow label

Formanilide - Eastman Kodak yellow label

N-methylformamide - Eastman Kodak yellow label

Tetrahydrofuran - the Baker Analyzed grade chemical was purified by distillation from either CaH_2 or $LiAlH_4$. The fraction boiling at 65°C was collected and used.

The following chemicals were prepared in this laboratory:

Formanilide: The method of Fallon (37) was used with the modification that after addition of an excess of formic acid to freshly distilled aniline and distillation to remove excess formic acid, water and unreacted aniline, the slightly yellow residue was collected and used without further purification.

N-methylformamide: A slight excess of ethyl formate was added, with cooling, to a 40% aqueous solution of methylamine. The resulting solution was refluxed for two hours and then distilled to remove water and ethyl formate. The remaining solution was distilled, the desired N-methylformamide fraction was collected at 195-216°C.

N-cyclohexylformamide: A slight excess of ethyl formate was added to newly distilled cyclohexylamine and the resultant solution was refluxed for four hours. This solution was subsequently distilled to remove water and excess ethyl formate. The N-cyclohexylformamide was collected at 260° C.

Preparation of Tetrazoles

1-Methyltetrazole: The preparation of methyl isocyanide of Ugi and Meyr (38) was utilized. Distillation of the isocyanide-chloroform mixture thus obtained into an 8% solution of hydrazoic acid in toluene was accomplished. This mixture was then refluxed for twenty-four hours to promote reaction. Evaporation to dryness under an air jet gave a crude yield of approximately twenty per cent. Sublimation of the crude material under reduced pressure gave a white crystalline product whose melting point was 37-8° C. The infrared spectra of 1-methyltetrazole can be found in Figure 1.

1-Cyclohexyltetrazole: The cyclohexylisocyanide used was prepared according to the procedure of Ugi et al. (39). A modification of this procedure was made in that the crude product was not distilled, as suggested, but mixed directly with the 8% hydrazoic acid in toluene and this mixture was refluxed for approximately twenty-four hours. Removal of the solvent under an air jet yielded a reddish-brown solid, the color being caused by resinification of cyclohexylisocyanide. The crude product was sublimed under reduced pressure to yield a white crystalline solid melting at 46-7° C. The infrared spectra of 1-cyclohexyltetrazole can be found in Figure 2.

1-Phenyltetrazole: The procedure of Herbst and Fallon (40) was followed. Purification of the crude product by recrystallization from cyclohexane proved to be a lengthy process and gave only nearly-pure material. Sublimation at reduced pressure, however, gave a white crystalline solid melting at 65-6° C. The infrared spectra of 1-phenyltetrazole can be found in Figure 3.

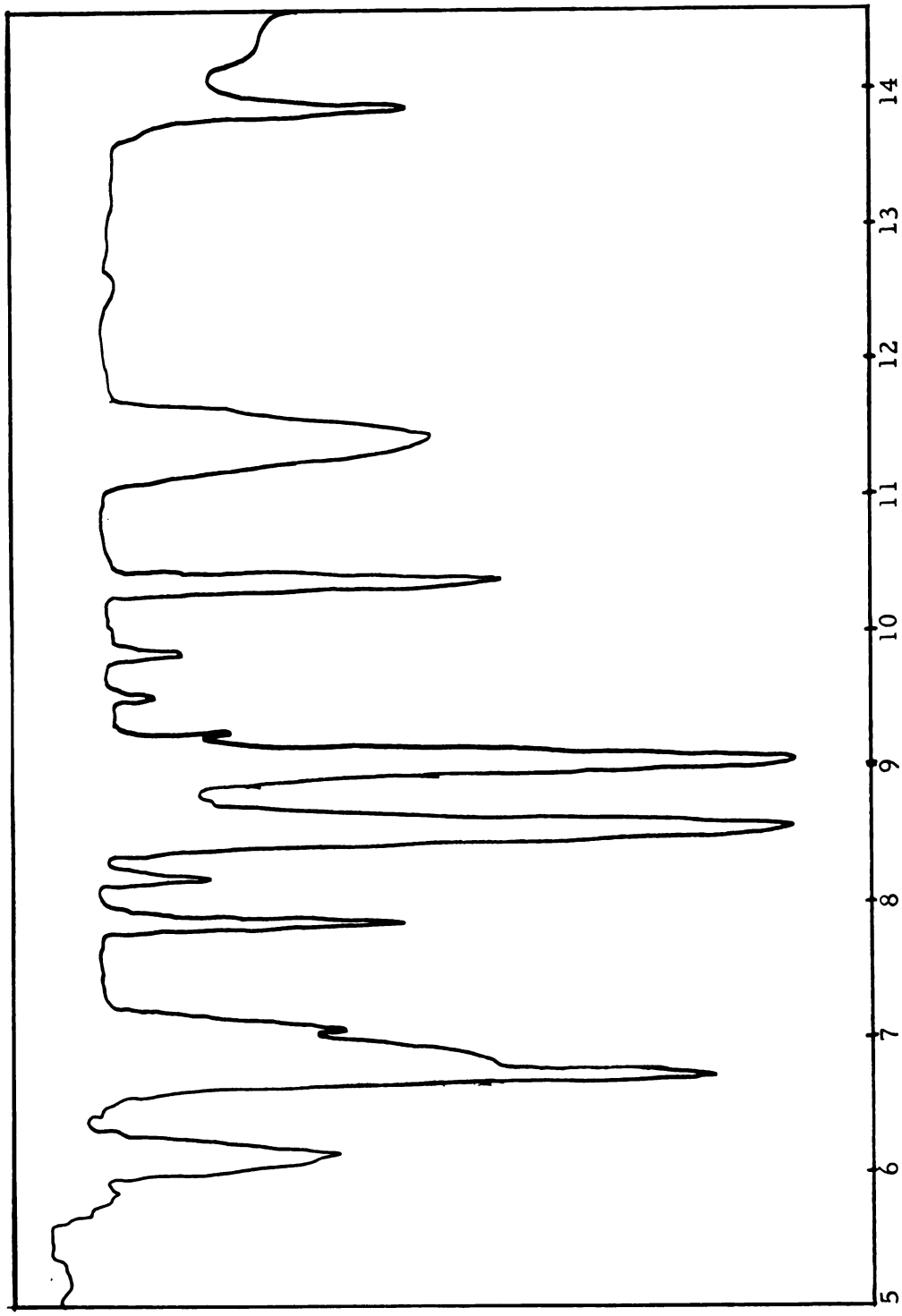


Figure 1. Infrared absorption spectra (in microns) of 1-methyltetrazole. Potassium bromide disc.

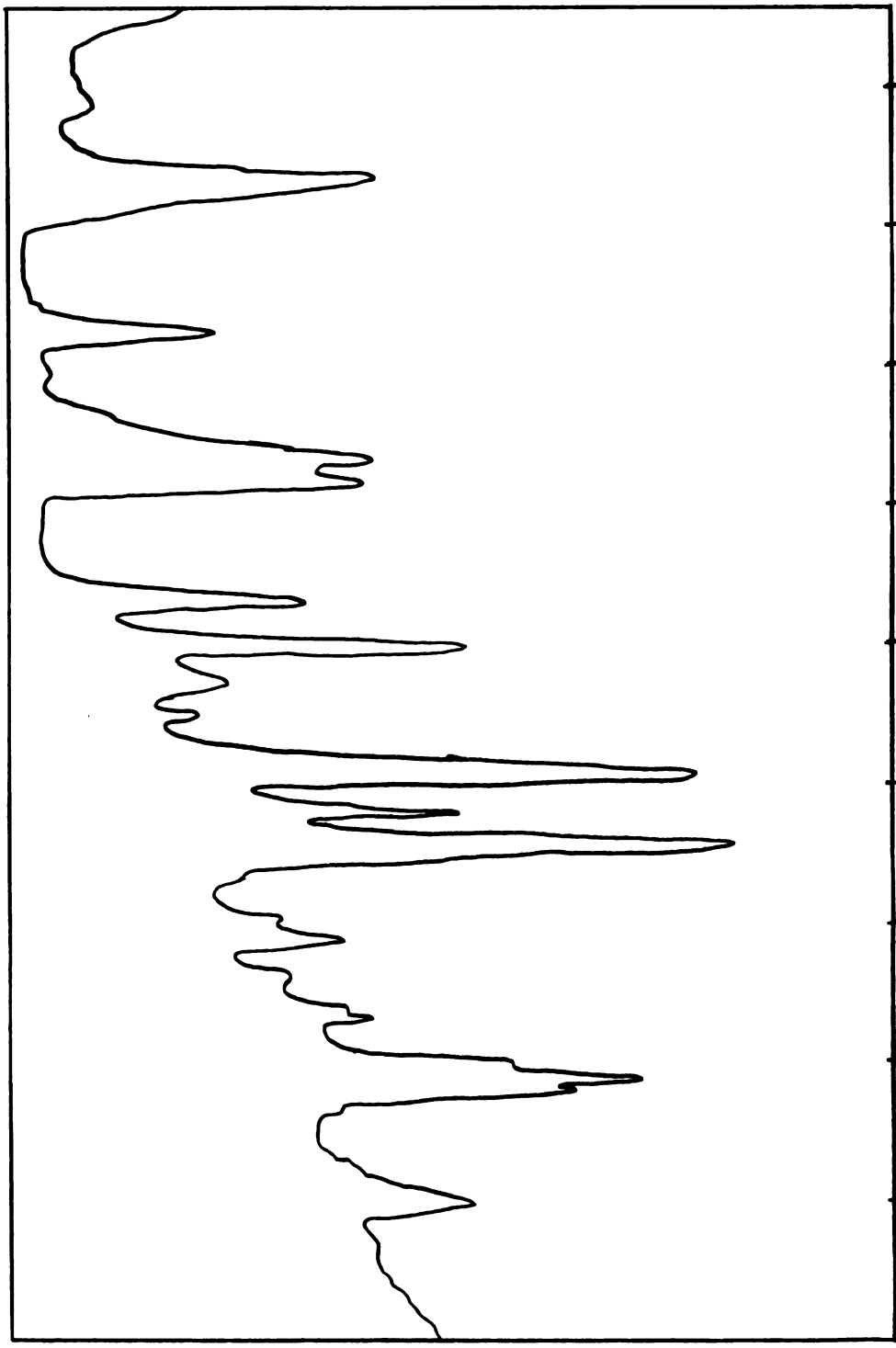


Figure 2. Infrared absorption spectra (in microns) of 1-cyclohexyltetrazole. Potassium bromide disc.

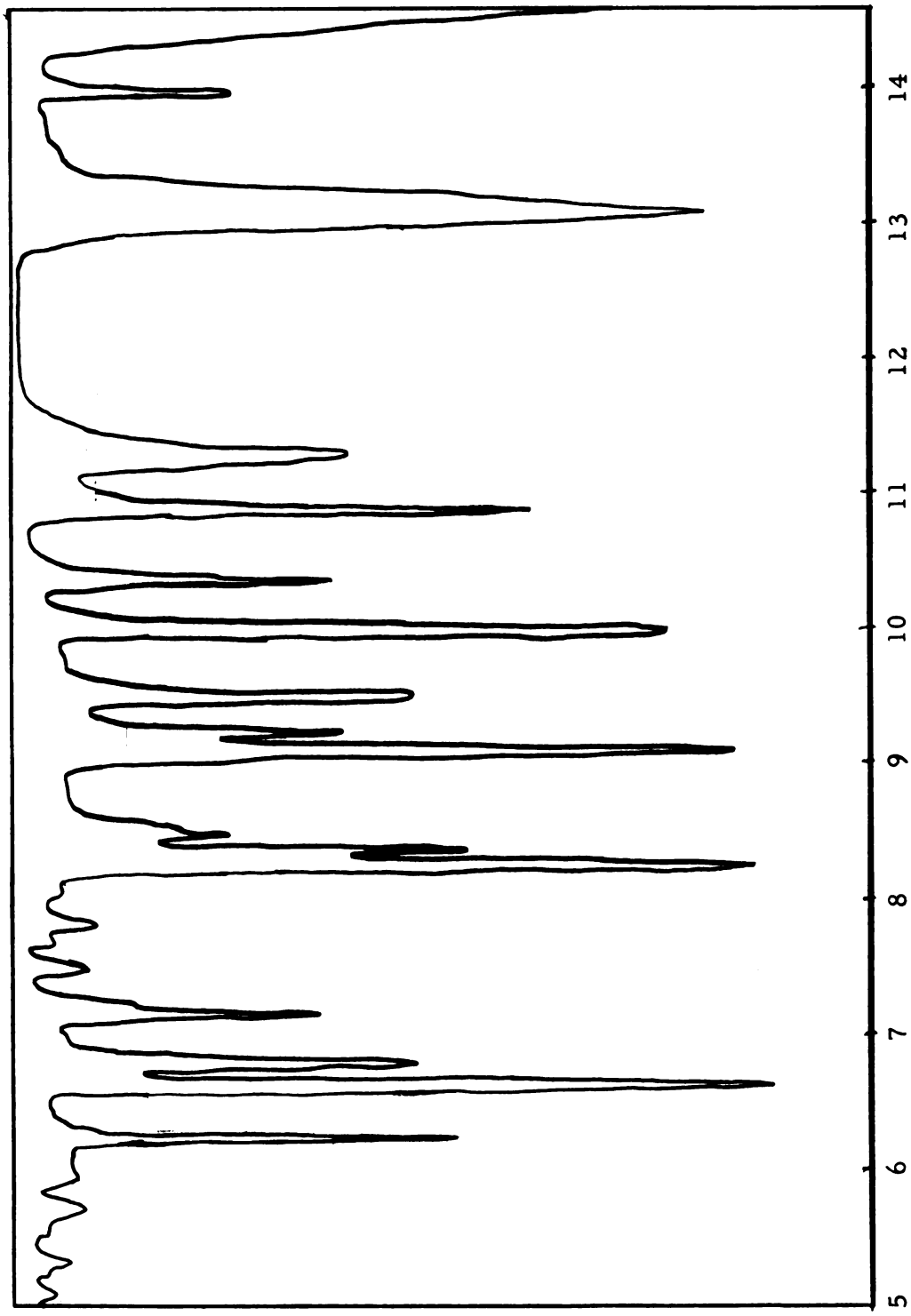


Figure 3. Infrared absorption spectra (in microns) of 1-phenyltetrazole. Potassium bromide disc.

Preparation of the Metal Chlorides

Platinum(II) chloride: The reduction of H_2PtCl_6 by hydrazine hydrochloride (41) was carried out.

Cobalt chloride: Dehydration of the hexahydrate was accomplished by prolonged heating at 110° C, to give blue, solid cobalt chloride.

Nickel chloride: The anhydrous salt was donated by Mr. R. A. D. Wentworth who had dehydrated the hydrated salt by use of thionyl chloride and subsequent removal of remaining water under vacuum. The analysis reported for chloride was: Anal. calculated for $NiCl_2$: Cl, 54.7. Found: Cl, 54.7.

Analytical Methods

The solid complexes of 1-methyl-, 1-phenyl-, and 1-cyclohexyltetrazole and certain metal chlorides were prepared in this investigation. The solids thus obtained were dried at 60° C under vacuum and analyzed for metal, chloride, and carbon, hydrogen, and nitrogen by the procedures below.

Chloride analysis: Samples of the nickel and zinc complexes were dissolved in 50 ml of 0.1M nitric acid and were titrated potentiometrically, using a glass electrode-silver-silverchloride electrode system, with 0.1N silver nitrate.

The platinum chloride complexes were analyzed for chloride by Spang Microanalytical Laboratory.

Zinc analysis: The potentiometric procedure (42) using a platinum-calomel electrode system and titrating with 0.1N potassium hexacyanoferrate(II) was slightly modified for this work.

To the titrating vessel was added the sample, five milliliters of 15M aqueous ammonia, six milliliters of 18M hydrochloric acid,

37 ml of water and three drops of 0.001 potassium hexacyanoferrate(III). The resulting solution was titrated potentiometrically, using a platinum electrode-calomel electrode system, with 0.1N potassium hexacyanoferrate(II).

Platinum analysis: A weighed portion of the complex was heated carefully in a tared platinum crucible to 600° C until a constant weight was found.

Nickel analysis: The procedure utilized by Daugherty (3) was slightly modified for use here. To the sample was added 20 ml of 0.05M potassium cyanide, 5 ml of concentrated aqueous ammonia and 0.2 ml of a potassium iodide solution containing 0.1 g/ml of potassium iodide. The excess cyanide was titrated to turbidity with 0.1N silver nitrate and the nickel was determined by the difference in volume between the sample and a blank prepared in the same manner but lacking the sample.

Carbon, hydrogen and nitrogen analysis: Samples of the complexes were analyzed by Spang Microanalytical Laboratory for carbon, hydrogen, and nitrogen. Some of the samples exploded on heating and only fair agreement between the two sets of analyses was found.

Preparation of the Complexes

The technique generally used for the preparation of the complexes was as follows: Add the tetrazole (0.02 mole) to approximately 75 ml of recently distilled tetrahydrofuran in a round bottomed flask. The metal chloride (0.01 mole) was placed in a soxhlet cup and refluxing of the tetrazole solution to extract the metal chloride as a weak complex with tetrahydrofuran (43) was begun. After twenty-four hours the solution was removed from reflux and the solvent removed by water vacuum.

A second technique, used for the preparation of the nickel and zinc complexes involved the addition of the tetrazole and metal chloride in a 2:1 molar ratio to approximately 40 ml of 95% ethanol and refluxing overnight. The resulting solution was allowed to evaporate slowly and the crystals formed dried over calcium chloride in a desiccator.

Nickel chloride-tetrazole complexes: These complexes were prepared by both techniques above, the lower solubility of nickel chloride in tetrahydrofuran giving a lower yield for the first method. A similar preparation involving the soxhlet apparatus but with ethanol as the extraction solvent was carried out. The infrared spectrum of this compound was found to be similar to that for the product of the tetrahydrofuran preparation. The analytical data for the nickel chloride complexes are shown below:

Dichlorobis (1-methyltetrazole) nickel(II)

Calculated for $NiCl_2C_4N_8H_8$: Ni, 19.7; Cl, 23.8; C, 16.1; N, 37.6; H, 2.7.

Found: Ni, 19.7; Cl, 23.6; C, 16.1; N, 37.6; H, 2.6.

Dichlorobis (1-cyclohexyltetrazole) nickel(II)

Calculated for $NiCl_2C_{14}N_8H_{24}$: Ni, 13.5; Cl, 16.3; C, 38.7; N, 25.8; H, 5.6.

Found: Ni, 12.0; Cl, 13.8; C, 38.3; N, 24.7; H, 6.1.

These solids were found to be insoluble in most common solvents, except water, where solution with decomposition to the metal chloride and free tetrazole occurs. They were green to dark green and appeared to be crystalline.

The infrared data for these compounds was tabulated and can be found in Tables I and II.

Table I. Infrared Absorption Bands (in cm^{-1}) of 1-Methyltetrazole, 1-Methyltetrazole hydrochloride, Dichlorobis(1-methyltetrazole) zinc(II), Dichlorobis(1-methyltetrazole) nickel(II) and Dichlorobis(1-methyltetrazole) platinum(II). Potassium Bromide Discs

$C_2N_4H_4$	$C_2N_4H_4 \cdot HCl$	$Zn(C_2N_4H_4)_2Cl_2$	$Ni(C_2N_4H_4)_2Cl_2$	$Pt(C_2N_4H_4)_2Cl_2$
3401 vs		3509-3390 ms		3401 m
3100 vs		3125 s	3096s	3077 s
2900 m				
1704 vw		1770-1751 vw	1754 w	1730 vw
1637 m		1610 vw	1621 m	1626-1613 w
1497 s		1524 s	1506 s	1517 s
1471 ms	1471 s	1471 m	1460 ms	1460 m
1418 m		1441 m	1412 m	
1277 m	1266 w	1311 m	1290 ms	1299 ms
1227 w		1236 w	1235 w	1247 w
1170 s	1167 s	1183 s	1171 s	1183 s
			1126 ms	
1109 s		1104 s	1105 s	1099 s
1083 w	1078 vw	1064 w	1074 w	1070 m
1053 vw		1027 m	1022 m	1020 m
1018 vw		1012 ms		
		996 s	993 s	
966 ms	959 s	890 s	880 s	889 w
877 w	869 s	882 s		862 s
			755-749 w	
		717 m	718 m	709 m
720 ms	719 m			

Table II. Infrared Absorption Bands (in cm^{-1}) of 1-Cyclohexyltetrazole, 1-Cyclohexyltetrazole hydrochloride, Dichlorobis(1-cyclohexyltetrazole) zinc(II), Dichlorobis(1-cyclohexyltetrazole) nickel(II), and Dichlorobis(1-cyclohexyltetrazole) platinum(II). Potassium Bromide Discs

$C_7N_4H_{12}$	$C_7N_4H_{12}\cdot HCl$	$Zn(C_7N_4H_{12})_2Cl_2$	$Ni(C_7N_4H_{12})_2Cl_2$	$Pt(C_7N_4H_{12})_2Cl_2$
			3322 s	
3100 m	3096 m	3058 m	3067 m	3077 vs
2899 s	2890 s	2915 s	2899 s	2882 vs
		2849 m	2833 m	2833 s
1672 m		1639 w	1634 m	
		1493 s	1488 m	1490 ms
1470 s	1464 m	1464 w		
	1441 s	1449 s	1449 s	1439 s
1366 w	1346 w	1368 s	1366 w	1366 w
		1346 w		
		1298 w		1290 m
1266 w	1264 w	1266 w		
1167 s	1167 s	1168 s	1174 s	1167 s
1139 m	1134 ms	1135 s	1136 m	1133 m
1101 s	1096 s	1089 s	1093 s	1081 s
			1079 w	
1054 w		1052 w		
1030 w	1027 vw	1014 s	1015 s	1024 ms
	999 ms			989 w
970 m	969 w	966 vw		
897 w	895 w	893 ms	893 ms	892 m
881 w	879 s	876 m		868 m
818 w	816 w	816 m	814 mw	810 w
749 m	746 ms	743 ms	754 s	743 ms
		715 w		

Zinc chloride tetrazole complexes: The solid complexes containing zinc were prepared by the general methods mentioned previously. The latter procedure, addition of the metal chloride and tetrazole to 95% ethanol and refluxing overnight yielded good crystalline products. These were observed to be clear planar hexagonal crystals in the case of 1-methyltetrazole and clear rhombic needles with 1-phenyltetrazole. Presently work is underway at St. Olaf College to determine their structure by X-ray single crystal studies.

The analytical data for the zinc chloride complexes are shown below:

Dichlorobis (1-methyltetrazole) zinc(II):

Calculated for $ZnCl_2C_4N_8H_8$: Zn, 21.5; Cl, 23.3; C, 15.8; N, 36.8; H, 2.6.

Found: Zn, 21.6; Cl, 23.4; C, 15.8; N, 36.7; N, 2.6.

Dichlorobis (1-cyclohexyltetrazole) zinc(II):

Calculated for $ZnCl_2C_{14}N_8H_{24}$: Zn, 14.3; Cl, 15.0; C, 40.9; N, 26.5; H, 6.0.

Found: Zn, 14.8; Cl, 16.1; C, 38.2; N, 25.4; H, 5.5.

Dichlorobis (1-phenyltetrazole) zinc(II):

Calculated for $ZnCl_2C_{14}N_8H_{12}$: Zn, 15.2; Cl, 16.7; C, 39.2; N, 26.1; H, 2.8.

Found: Zn, 15.1; Cl, 16.5; C, 39.3; N, 26.2; H, 2.8.

These clear crystalline solids were moderately soluble in tetrahydrofuran and readily soluble in the simple alcohols. Solution of these complexes in water causes decomposition to free tetrazole and zinc chloride.

Infrared spectra of these compounds have been obtained and are shown in Figures 4, 5 and 6. A tabulation of the absorption maxima is reported in Tables I, II and III.

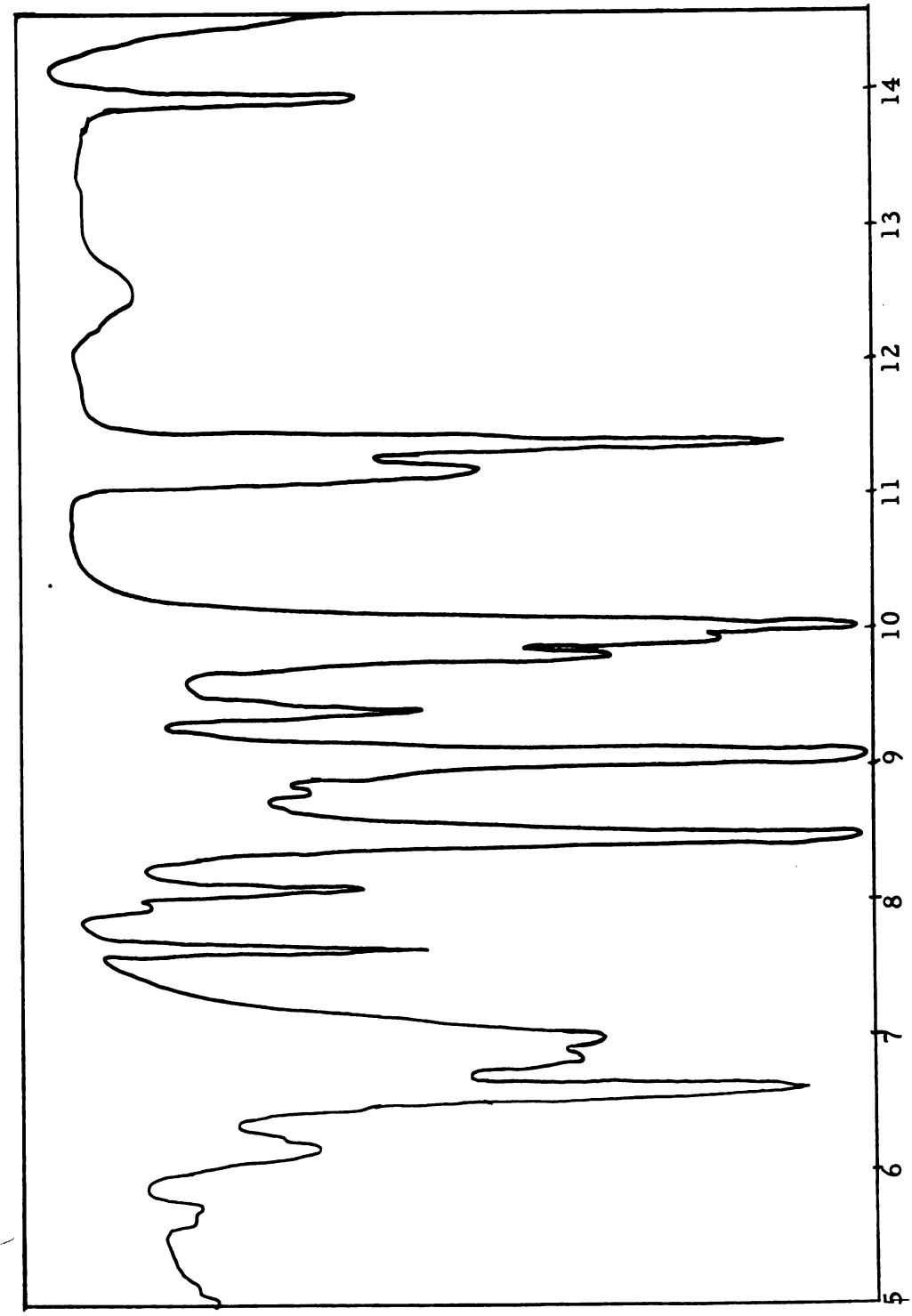


Figure 4. Infrared absorption spectra (in microns) of dichlorobis (1-methyltetrazole) zinc(II). Potassium bromide disc.

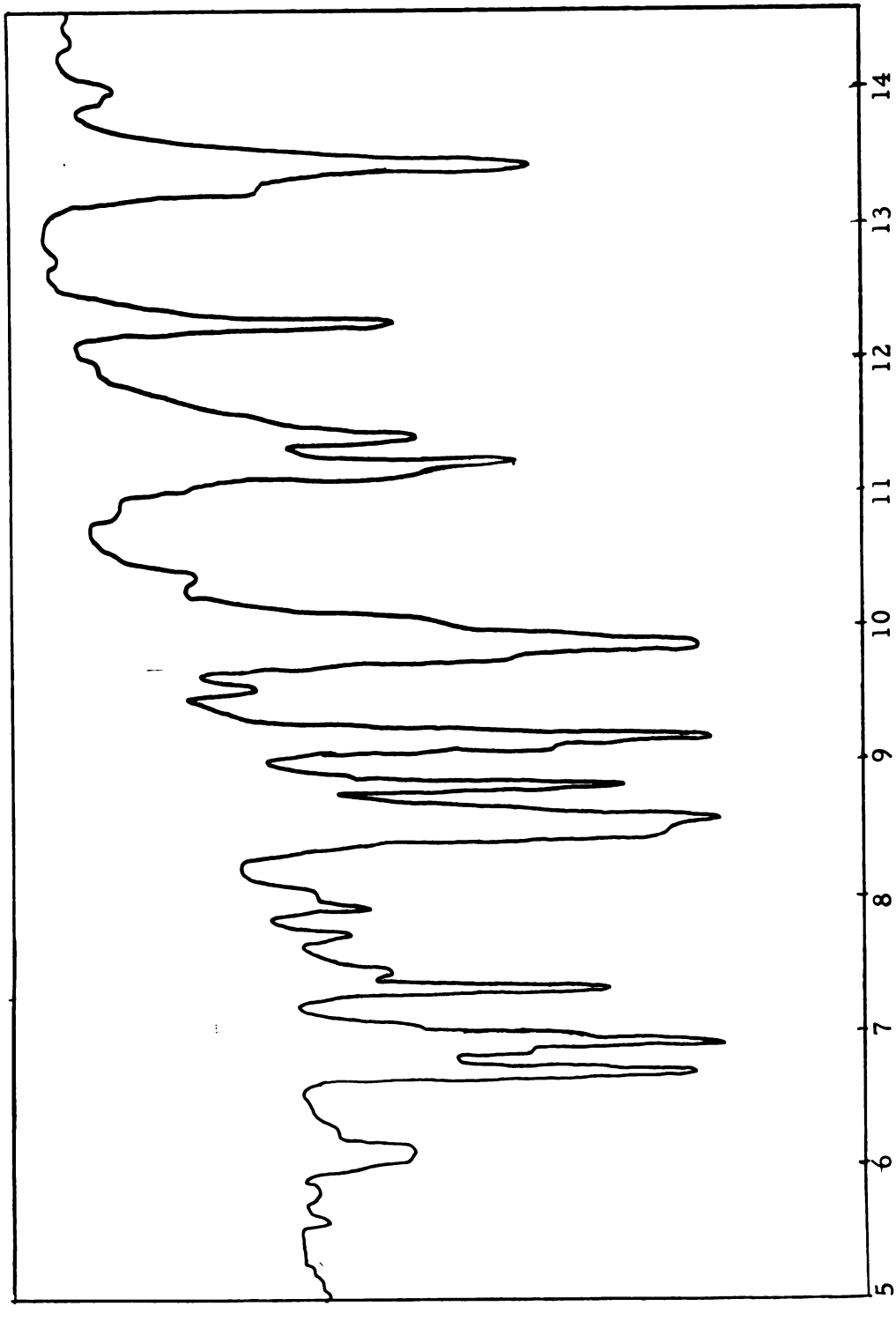


Figure 5. Infrared absorption spectra (in microns) of dichlorobis (1-cyclohexyltetrazole) zinc(II). Potassium bromide disc.

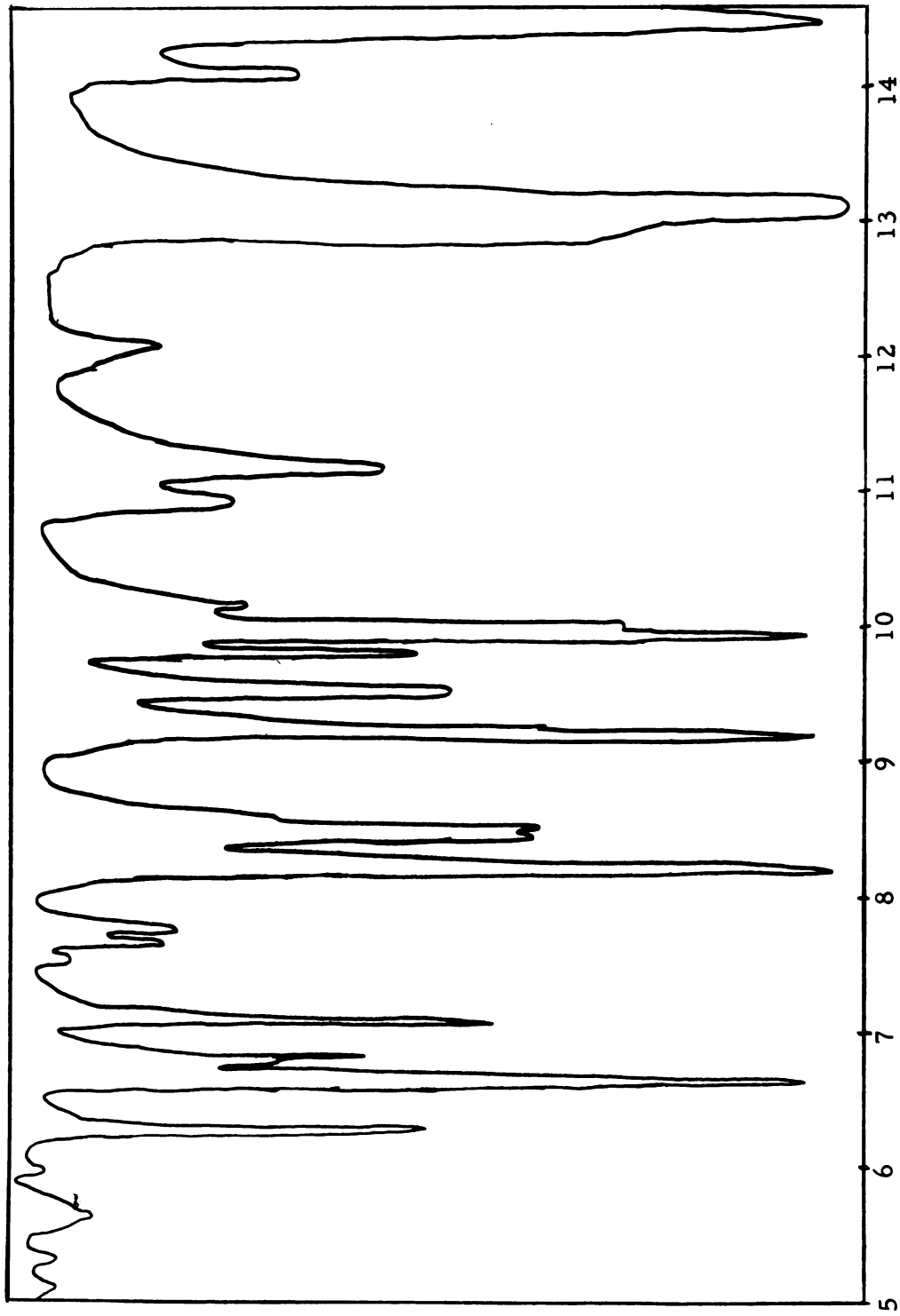


Figure 6. Infrared absorption spectra (in microns) of dichlorobis (1-phenyltetrazole) zinc(II). Potassium bromide disc.

Table III. Infrared Absorption Bands (in cm^{-1}) of 1-Phenyltetrazole, 1-Phenyltetrazole hydrochloride and Dichlorobis (1-phenyltetrazole) zinc(II). Potassium Bromide Discs

$C_7N_4H_6$	$C_7N_4H_6 \cdot HCl$	$Zn(C_7N_4H_6)_2$
3436 m	3367 m	3497 w
3025 ms	3077 ms	3077 s
1605 m	1592 ms	1600 ms
1504 s	1490 s	1511 s
1471 m	1460 ms	1473 m
1397 mw	1389 m	1416 ms
1337 vw	1330 vw	
		1311 w
		1292 w
1280 vw	1272 w	
1211 s		1221 s
1196 m	1198 s	
1181 s	1186 m	1185 ms
	1172 m	1176 ms
1096 s		
1083 mw	1086 s	1088 s
	1075 w	
1053 m		1053 m
		1008 s
1000 ms	993 ms	1000 m
966 m	962 m	985 w
919 ms	913 m	917 w
886 m	881 mw	896 mw
		832 w
762 s	756 s	763-760 s
717 w	713 w	712 mw

Platinum(II) chloride-tetrazole complexes: The solid platinum complexes were available only by the tetrahydrofuran procedure but were found to be more stable to decomposition than the zinc or nickel complexes. The analytical data for the platinum(II) complexes are shown below:

Dichlorobis (1-methyltetrazole) platinum(II):

Calculated for $PtCl_2C_4N_8H_8$: Pt, 44.9; Cl, 16.3; C, 16.3; N, 25.8; H, 1.9.

Found: Pt, 45.0; Cl, 16.2; C, 15.5; N, 26.0; H, 1.6.

Dichlorobis (1-cyclohexyltetrazole) platinum(II):

Calculated for $PtCl_2C_{14}N_8H_{24}$: Pt, 34.9; Cl, 12.4; C, 29.5; N, 19.6; H, 4.2.

Found: Pt, 34.2; Cl, 12.4; C, 29.4; N, 19.7; H, 4.2.

These yellow solids were found to be generally insoluble in common solvents--the 1-methyltetrazole complex being soluble with decomposition in concentrated aqueous ammonia or concentrated nitric acid. The cyclohexyltetrazole complex was unattacked by even these reagents.

Purification of these compounds was accomplished due to their very slight solubility in tetrahydrofuran. They were extracted in a soxhlet apparatus and the yellow powder thus obtained dried as previously mentioned.

Infrared spectra were obtained for these complexes and the data tabulated in Tables I and II.

Infrared Spectra

The infrared spectra of the free tetrazoles, the tetrazole hydrochlorides and the metal chloride-tetrazole complexes were obtained in potassium bromide salt pellets. A small portion ($\sim$0.01 g) was added

to approximately 0.5 g of dried potassium bromide and the mixture ground for one minute in a Wigglebug grinder. The clear pellet was run on a Perkin Elmer Model 221 double beam instrument using a potassium bromide pellet in the reference beam.

The infrared spectra were also obtained in Nujol mulls to determine to what extent any interaction with the potassium bromide medium may have occurred. The resulting spectra were similar to those in potassium bromide although the peaks appeared broadened in all cases. This was probably due to the larger particle sizes in the mulls.

Stability Constants

The interaction between cobalt and nickel in absolute alcohol and cobalt in tetrahydrofuran and the tetrazoles were observed spectrophotometrically using a Beckmann DU Spectrophotometer.

Cobalt-tetrazole complexes: The determination of a Beer's Law adherence for cobalt in both tetrahydrofuran at 660 mμ and in absolute ethanol at 605 mμ and 650 mμ was made. No evidence for a species of composition CoT^{++} (where T = tetrazole) was found by using varying, but dilute tetrazole and a fixed, but large metal concentration.

A series of solutions containing fixed, high tetrazole concentrations and low, varying metal concentrations yielded the extinction coefficient for the species CoT_2^{++} in each medium.

Absorbancy readings were taken on solutions containing 0.001 M $CoCl_2.6H_2O$ in tetrahydrofuran and tetrazole concentrations from 0.001 M to 0.1M. Data on the 1-phenyltetrazole complex with cobalt was not obtained due to the lack of solubility of this tetrazole in tetrahydrofuran to the extent necessary for definitive measurements.

The absorbancy measurements in absolute ethanol were made on solutions containing 0.005M $CoCl_2.6H_2O$ and tetrazole concentrations varying from 0.01M to 0.5M.

The data from these experiments is tabulated in Tables IV-VIII.

Nickel-tetrazole complexes: The solutions of nickel chloride hexahydrate in absolute ethanol were found to obey Beer's Law at 400 mμ and 420 mμ in the concentration range used. In accordance with the cobalt data no evidence for any species other than Ni^{++} and NiT_2^{++} was found.

Absorbancy measurements were made at 400 mμ and 420 mμ on solutions containing 0.01M $NiCl_2.6H_2O$ and tetrazole concentrations ranging from 0.002 M to 0.5 M.

The data from these experiments are tabulated in Table IX, X and XI.

Zinc chloride-tetrazole complexes: An attempt was made to determine the stability constants for complexes between zinc and the tetrazoles in these media. The first technique used was the addition of varying amounts of zinc to solutions of fixed cobalt and tetrazole concentration in tetrahydrofuran--the method of corresponding solutions (44). The results obtained were highly scattered and no conclusion concerning the complex could be made. It was observed, however, that a precipitate formed in the solution and a color change from blue to colorless to pink to a yellow brown occurred over a 24 hours period. This latter seems to indicate some interaction between zinc and cobalt in the medium in the presence of tetrazole.

A second procedure was the addition of an excess of zinc chloride to tetrahydrofuran solutions containing varying amounts

Table IV. Absorbancies and $\bar{n}$ Values for 1-Methyltetrazole and 0.001M Cobalt chloride hexahydrate in Tetrahydrofuran

[Tz]	- Log [Tz]	$A_{605\ m\mu}$	$\bar{n}$
0.001	3.00	.123	.163
0.002	2.70	.131	.245
0.003	2.52	.138	.316
0.004	2.40	.145	.388
0.005	2.30	.153	.469
0.006	2.22	.159	.530
0.007	2.15	.165	.592
0.008	2.10	.171	.653
0.009	2.05	.174	.683
0.010	2.00	.180	.745
0.030	1.52	.230	1.255
0.050	1.30	.247	1.428
0.060	1.22	.239	1.346
0.100	1.00	.256	1.520

Table V Absorbancies and $\bar{n}$ Values for 1-Cyclohexyltetrazole and 0.001M Cobalt chloride hexahydrate in Tetrahydrofuran

[Tz]	- Log [Tz]	$A_{605\ m\mu}$	$\bar{n}$
0.010	2.00	.185	.773
0.012	1.92	.190	.829
0.014	1.86	.198	.917
0.016	1.80	.202	.961
0.018	1.74	.209	1.028
0.020	1.70	.209	1.028
0.040	1.40	.238	1.359
0.060	1.22	.265	1.657
0.080	1.10	.278	1.801
0.100	1.00	.290	1.934

Table VI. Absorbancies and $\bar{n}$ Values for 1-Methyltetrazole and 0.005M Cobalt chloride hexahydrate in Absolute Ethanol

[Tz]	- Log [Tz]	$A_{605\ m\mu}$	$\bar{n}$
0.050	1.30	.466	.377
0.060	1.22	.460	.407
0.070	1.15	.440	.508
0.080	1.10	.431	.553
0.090	1.05	.413	.644
0.100	1.00	.414	.639
0.150	0.82	.387	.774
0.200	0.70	.338	1.021
0.250	0.60	.298	1.222
0.300	0.52	.255	1.439
0.350	0.46	.231	1.559
0.400	0.40	.212	1.655
0.450	0.35	.183	1.801
0.500	0.30	.179	1.821

Table VII. Absorbancies and $\bar{n}$ Values for 1-Cyclohexyltetrazole and 0.005M Cobalt chloride hexahydrate in Absolute Ethanol

[Tz]	- Log [Tz]	$A_{660\ m\mu}$	$\bar{n}$
0.002	2.70	.253	.120
0.004	2.40	.249	.180
0.006	2.22	.245	.240
0.008	2.10	.239	.330
0.010	2.00	.237	.360
0.020	1.70	.216	.675
0.030	1.52	.202	.885
0.040	1.40	.188	1.095
0.050	1.30	.179	1.230
0.060	1.22	.165	1.440
0.070	1.15	.156	1.575
0.080	1.10	.142	1.785
0.090	1.05	.139	1.830
0.100	1.00	.138	1.845

Table VIII. Absorbancies and $\bar{n}$ Values for 1-Phenyltetrazole and 0.005M Cobalt chloride hexahydrate in Absolute Ethanol

[Tz]	- Log [Tz]	$A_{605\ m\mu}$	$\bar{n}$
0.004	2.40	.558	.058
0.006	2.22	.571	.141
0.008	2.10	.567	.116
0.010	2.00	.569	.129
0.020	1.70	.641	.592
0.030	1.52	.669	.772
0.040	1.40	.679	..836
0.060	1.22	.722	1.112
0.070	1.15	.731	1.170
0.080	1.10	.752	1.305
0.090	1.05	.759	1.350
0.100	1.00	.771	1.427
0.150	0.82	.860	2.000

Table IX. Absorbancies and $\bar{n}$ Values for 1-Methyltetrazole and 0.01M Nickel chloride hexahydrate in Absolute Ethanol

[Tz]	- Log [Tz]	$A_{420\ m\mu}$	$\bar{n}$
0.02	1.70	0.096	.265
0.03	1.52	0.094	.313
0.04	1.40	0.090	.410
0.05	1.30	0.085	.530
0.06	1.22	0.079	.675
0.07	1.15	0.074	.795
0.08	1.10	0.070	.892
0.09	1.05	0.066	.988
0.10	1.00	0.063	1.012
0.20	0.70	0.038	1.663
0.30	0.52	0.030	1.856
0.40	0.40	0.026	1.952
0.50	0.30	0.024	2.000

Table X. Absorbancies and $\bar{n}$ Values for 1-Cyclohexyltetrazole and 0.01M Nickel chloride hexahydrate in Absolute Ethanol

[Tz]	-Log [Tz]	$A_{420\ m\mu}$	$\bar{n}$
0.50	0.30	0.030	2.000
0.45	0.35	0.038	1.792
0.40	0.40	0.033	1.920
0.30	0.52	0.025	2.120
0.25	0.60	0.041	1.715
0.20	0.70	0.048	1.536
0.10	1.00	0.066	1.075
0.09	1.05	0.071	.947
0.08	1.10	0.073	.896
0.07	1.15	0.077	.794
0.06	1.22	0.079	.742
0.05	1.30	0.082	.666
0.04	1.40	0.087	.538
0.03	1.52	0.092	.410
0.02	1.70	0.097	.282
0.01	2.00	0.104	.077

Table XI. Absorbancies and $\bar{n}$ Values for 1-Phenyltetrazole and 0.01M Nickel chloride hexahydrate in Absolute Ethanol

[Tz]	-Log [Tz]	$A_{400\ m\mu}$	$\bar{n}$
0.	.	.063	--
0.002	2.70	.064	--
0.004	2.40	.070	.119
0.006	2.22	.077	.257
0.008	2.10	.081	.337
0.010	2.00	.087	..455
0.20	0.70	.130	1.307
0.30	0.52	.143	1.564
0.40	0.40	.150	1.703
0.50	0.30	.165	2.000

of the tetrazoles. The solutions were allowed to equilibrate in a water bath at 24.97° C for three days at which point they were removed. After filtration to remove excess solid zinc chloride, the potentiometric titration of an aliquot for zinc with potassium hexacyanoferrate(II) in the manner previously discussed yielded only erratic results.

III. RESULTS AND DISCUSSION

As a part of this investigation a series of compounds were prepared which involved 1-methyl-, 1-cyclohexyl-, and 1-phenyltetrazole interacting with nickel chloride, zinc chloride and platinum(II) chloride. The composition for these compounds as dichlorobis (1-substituted tetrazole)metal(II) was confirmed by the analytical data.

The solid species were found to be insoluble in common solvents with the exception of the zinc complexes which were fairly soluble in the lower alcohols and tetrahydrofuran. This solubility was utilized in the purification of the zinc compounds. It was also found that, although the crystallization of the zinc complexes from tetrahydrofuran yielded no well shaped crystalline species, crystallization from alcohol gave excellent crystals with the 1-methyl and 1-phenyltetrazole complexes. These crystals were of sufficient purity and definition that they were submitted to Dr. George Hardgrove of St. Olaf College for single crystal studies. Elucidation of their structure by this means may offer valuable information concerning the nature of the bonding within these complexes. Preliminary x-ray diffraction studies indicate a large unit cell.

The nickel complexes were found to be powdery substances insoluble in common solvents except water in which they decompose. The platinum complexes were very slightly soluble in tetrahydrofuran as previously mentioned, but extremely insoluble in common solvents.

The infrared studies were found to yield no definite information concerning the nature of the bonding within the various complexes. While shifts were observed for certain of the absorbancy maxima, the lack of assignment of the particular vibrations within the ring made correlations impossible. The band at 1470 cm^{-1} has been assigned to the ring C-H (37) but was not found to vary in the three tetrazoles used

in this study indicating no great difference in the relative acidities of the ring C-H. Bands assigned to ring vibration (45) were found shifted in the complexes and hydrochlorides of the tetrazoles. The tetrazole-metal complex shift occurred towards higher wave numbers while the hydrochlorides were shifted towards lower wave numbers. The purpose of preparing the hydrochlorides was to establish, if possible, whether the primary bonding was to the substituted ring nitrogen. This is the most likely position for interaction in the hydrochloride and a similarity in the infrared shift between the metal complex and hydrochloride and free tetrazole would lend evidence to this hypothesis. Unfortunately no such similarity in shift was observed.

The stability constant studies were performed using spectrophotometric measurements on the tetrazoles and nickel chloride or cobalt chloride in absolute ethanol or tetrazoles and cobalt chloride in tetrahydrofuran. The treatment of the absorbancy data was as follows (46):

The degree of formation was found by use of the relationship

$$\alpha = \frac{A-A_o}{A_\infty - A_o}$$ where A = observed absorbancy, A_o = absorbancy of metal ion solution

A_∞ = limiting absorbancy of tetrazole-metal in solution

or

$$\alpha = \frac{A_o - A}{A_o - A_\infty}$$ when the interaction was observed by a loss in the absorbancy peak of the metal due to complexation by the tetrazole.

The average number of ligands bound per metal, $\bar{n}$, ion is (46):

$$\bar{n} = 2\alpha = 2x\frac{A-A_o}{A_\infty - A_o} \quad \text{or} \quad \bar{n} = 2\alpha = 2x\frac{A_o - A}{A_o - A_\infty}.$$

Assuming the ligand concentration remaining in solution to be approximately that added, due to the low degree of formation of the

complex, and the relatively low concentration of metal ions, the formation constants can be determined.

The formation constant, β_n, for the species ML_n, where M = metal, and L = ligand, is defined by the expression: $\beta_n = [ML_n]/[M][L]^n$(47). The analytical concentration of metal C_M can be calculated from the expression

$$C_M = \sum_{n=0}^{n=N} \beta_n[M][L]^n$$

and the total concentration of ligand can be calculated from

$$C_L = [L] + \sum_{n=0}^{n=N} n \beta_n[M][L]^n.$$

The average number of ligands per metal, $\bar{n}$, can be found as follows:

$$\bar{n} = (C_L - [L])/C_M$$

or

$$\bar{n} = \sum_{n=1}^{n=N} n \beta_n[L]^n / \sum_{n=0}^{n=N} \beta_n[L]^n$$

or

$$\sum_{n=0}^{n=N} (\bar{n}-n) \beta_n[L]^n = 0.$$

For the case of the formation of two complexes this expression rearranges to yield

$$\frac{\bar{n}}{(1-\bar{n})[L]} = \beta_1 + \beta_2 \frac{(2 - \bar{n})[L]}{1 - \bar{n}}$$

Thus knowledge of $\bar{n}$ and L allows determination of β_1 and β_2 from a plot of $\bar{n}/(1-\bar{n})[L]$ vs $\frac{(2-\bar{n})[L]}{1 - \bar{n}}$. The slope of the line obtained is equal to β_2, the intercept of β_1.

The data obtained for the complexes mentioned was treated in this manner and a least squares treatment of the data thus calculated was carried out. The values for the formation constants are given in Table XII. Typical graphs showing lines obtained from the least squares treatment are given in Figures 7, 8 and 9 for cobalt and 1-methyltetrazole in tetrahydrofuran, cobalt and 1-methyltetrazole in absolute alcohol and nickel and 1-methyltetrazole in absolute alcohol, respectively.

Whereas a Beer's Law relationship had been established for nickel in absolute alcohol up to 0.01M and for cobalt in tetrahydrofuran and absolute ethanol up to 0.001M, it was found that a higher concentrations of cobalt in absolute ethanol a deviation from linearity occurred. The nature of the cause of this deviation is unknown but appears most probably due to the greatly increased activity of water as the concentration of cobalt chloride hexahydrate is increased.

The plot of absorbancy vs concentration at these higher cobalt concentrations in absolute ehtanol is found to deviate slightly from linearity so that plots of the data calculated from absorbancy measurements fits moderately well the line determined by a least squares treatment, as previously mentioned. This deviation does, however, make the values of the stability constants thus calculated of questionable merit.

The stability constants indicate a similarity in basicity for the 1-methyl- and 1-cyclohexyltetrazole. These stability constants have values of an order of magnitude below those of 1-phenyltetrazole. This would not be predicted from the lack of shift for the ring C-H band as was mentioned, but may be due to a resonance interaction between the phenyl ring and the tetrazole ring. Expected resonance forms are shown

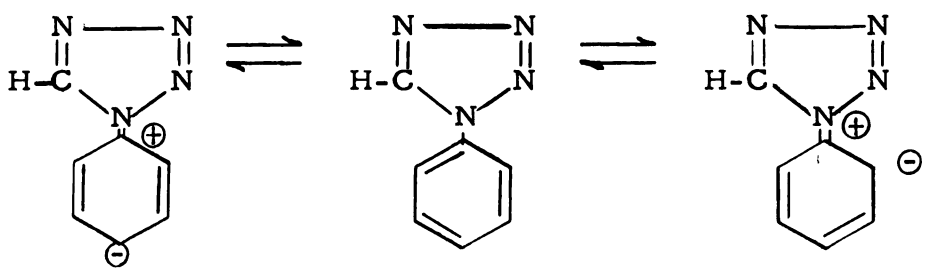


Table XII. Table of Formation Constants for Cobalt with 1-Methyltetrazole and 1-Cyclohexyltetrazole in Tetrahydrofuran, Cobalt with 1-Methyltetrazole, 1-Cyclohexyltetrazole, and 1-Phenyltetrazole in Absolute Ethanol and Nickel with 1-Methyltetrazole, 1-Cyclohexyltetrazole, and 1-Phenyltetrazole in Absolute Ethanol

Metal Chloride	Tetrazole	β_1	β_2	Solvent
Cobalt chloride	1-Methyltetrazole	91.8	2520	Tetrahydrofuran
Cobalt chloride	1-Cyclohexyltetrazole	45.2	3240	Tetrahydrofuran
Cobalt chloride	1-Methyltetrazole	4.15	26.6	Absolute ethanol
Cobalt chloride	1-Cyclohexyltetrazole	36.3	1180	Absolute ethanol
Cobalt chloride	1-Phenyltetrazole	45	428	Absolute ethanol
Nickel chloride	1-Methyltetrazole	13.8	112	Absolute ethanol
Nickel chloride	1-Cyclohexyltetrazole	3.7	112	Absolute ethanol
Nickel chloride	1-Phenyltetrazole	42.6	3840	Absolute ethanol

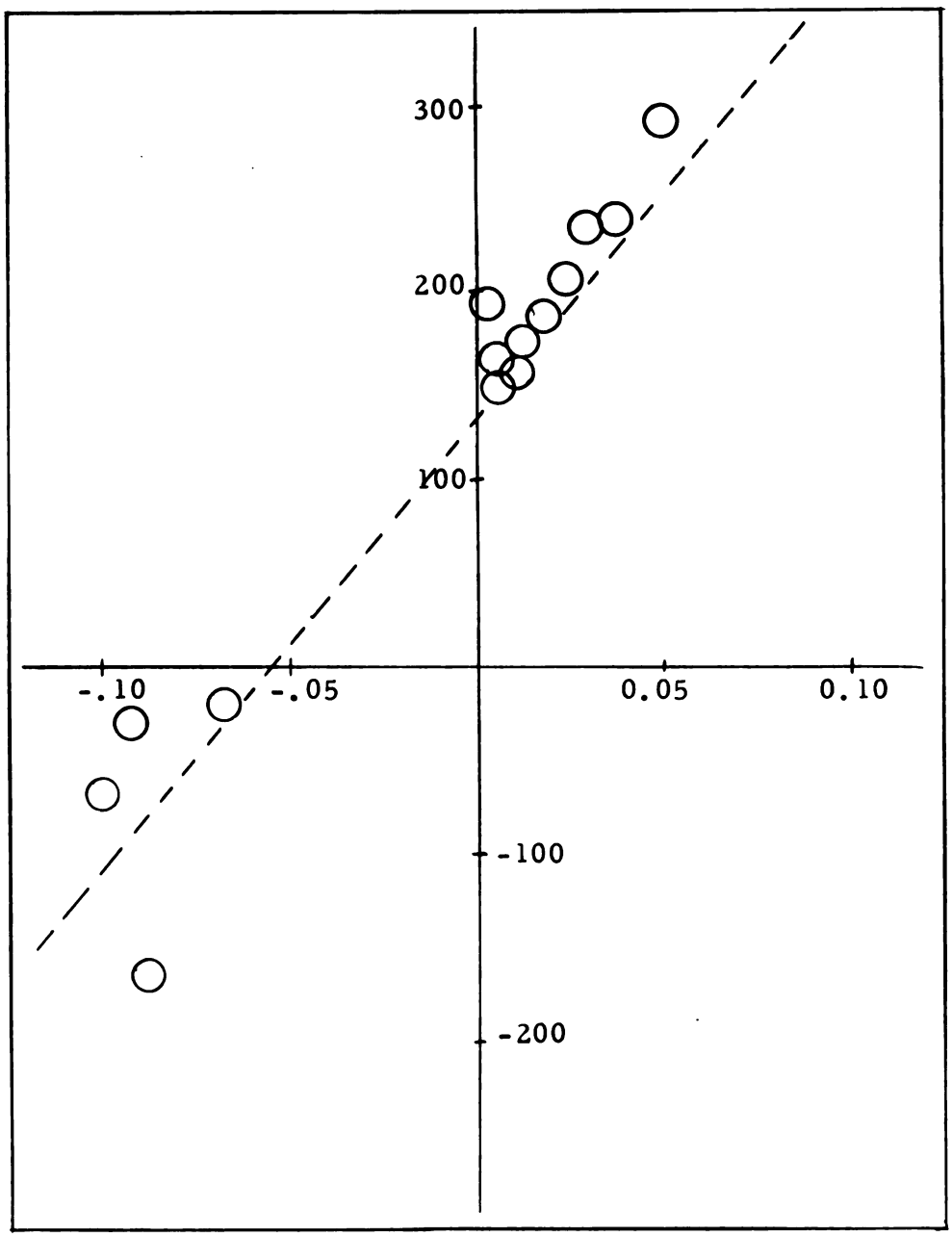


Figure 7. Graph of $\bar{n}/(1-\bar{n})[L]$ vs $(2-\bar{n})/(1-\bar{n})$ [L] for cobalt chloride and 1-methyltetrazole in tetrahydrofuran.

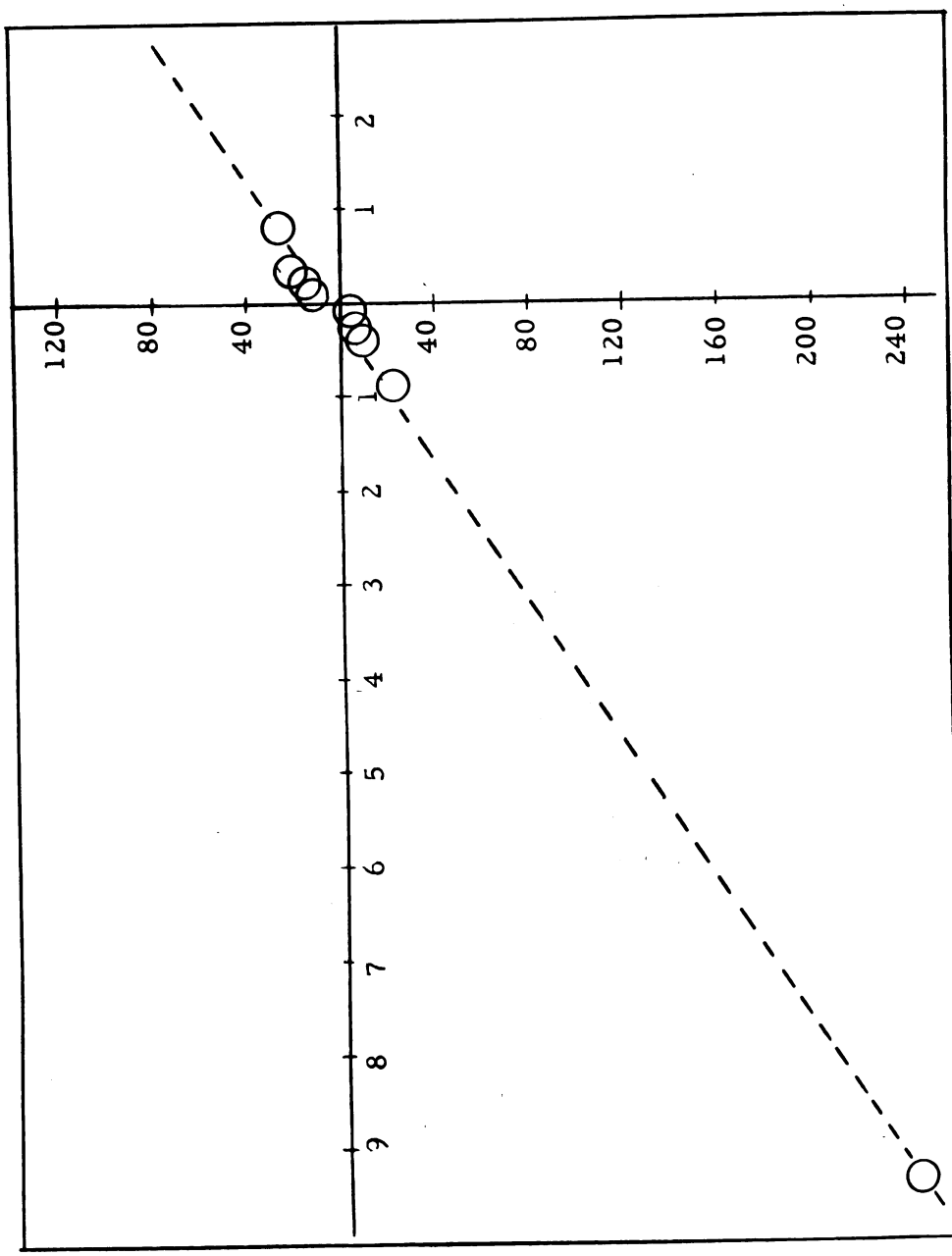


Figure 8. Graph of $\bar{n}/(1-\bar{n})[L]$ vs $(2-\bar{n})/(1-\bar{n})$ [L] for cobalt chloride and 1-methyltetrazole in absolute ethanol.

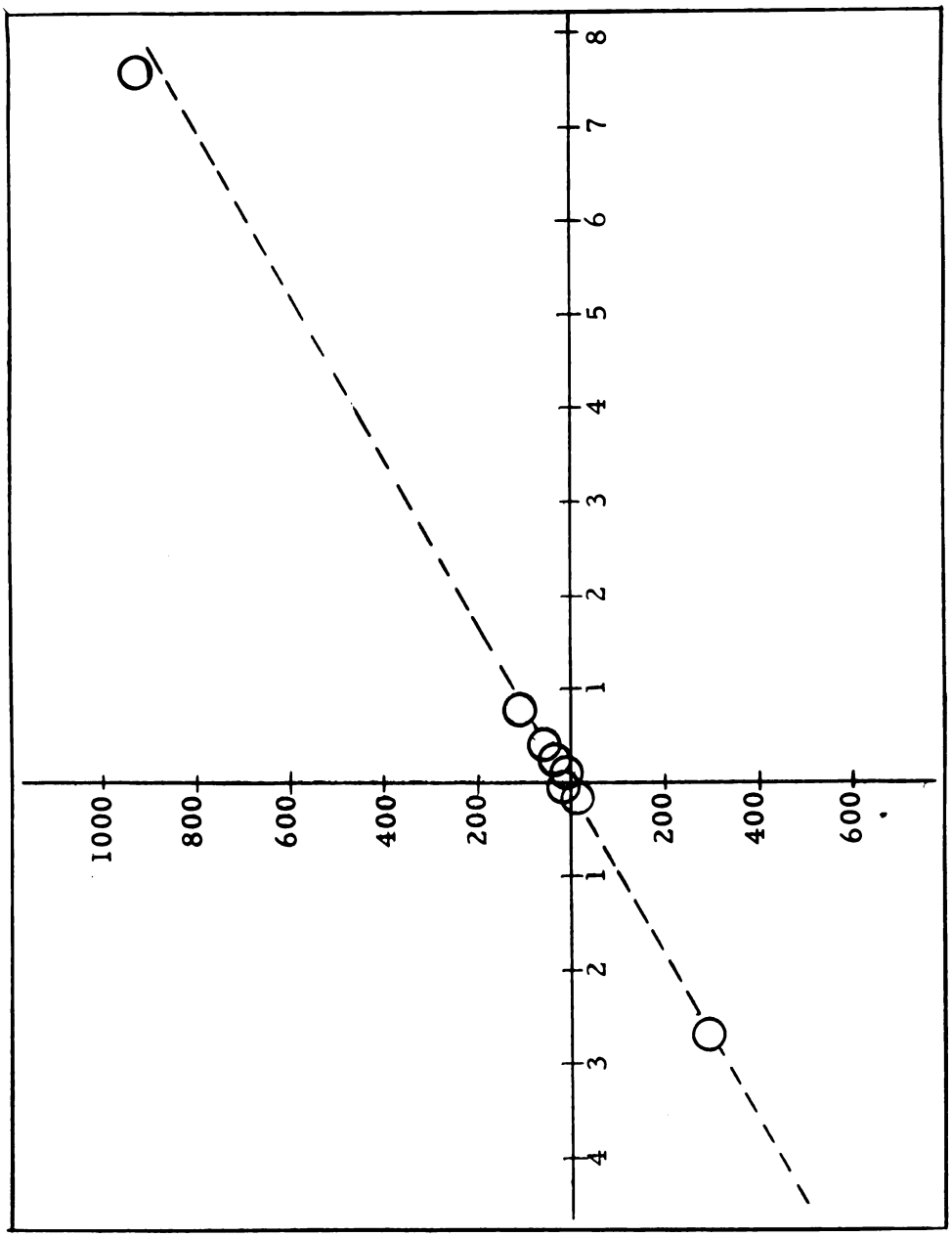


Figure 9. Graph of $\bar{n}/(1-\bar{n})[L]$ vs $(2-\bar{n})/(1-\bar{n})$ [L] for nickel chloride and 1-methyltetrazole in absolute ethanol.

Two of these resonance forms would tend to pull electrons away from the tetrazole ring thus reducing its ability to donate electrons. This effect should manifest itself as weaker complexes which would not be expected to contribute greatly to the species in solution.

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APPENDIX

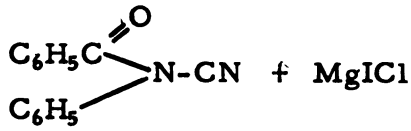
Attempted preparation of metal-1-substituted tetrazolates

The initial success in the preparation of the dichlorobis (1-substituted tetrazole) metal(II) work led to attempts to prepare metal tetrazolate compounds.

Of the possible paths to these compounds, the first utilized was the preparation of the sodium compounds of tetrazole by removal of the ring hydrogen. The reaction of sodium ethoxide with the tetrazole in ethanol was one path used to prepare the desired sodium 1-substituted tetrazolate. Infrared spectra of the solid obtained by removal of the excess ethanol revealed no characteristic tetrazole peaks.

Reaction of lithium and sodium amide in liquid ammonia with the tetrazoles yielded a solid product which did not dissolve in common solvents except with decomposition and was found to be non-reactive towards the metal halides used in this investigation.

The work of Stollé (48) involved preparation of the Grignard reagent of 1-phenyltetrazole (1-phenyltetrazolemagnesium iodide). This was formed when 1-phenyltetrazole was added to methylmagnesium iodide in ether. The evolution of methane was noted during this addition. Subsequent addition of benzoyl chloride formed an intermediate which lost nitrogen to yield:



This work suggested the addition of the tetrazoles to methylmagnesium iodide or other Grignard reagents to yield a material which

could subsequently react with the metal halides to produce the desired tetrazolates.

It was found that addition of 1-phenyltetrazole to methylmagnesium iodide in ether caused bubbling although no attempt to determine the nature of any gas evolved was made. Subsequent reaction of portions of the solution with small amounts of the metal chlorides yielded black solids in all cases. These solids changed in appearance upon exposure to air with the exception of the platinum chloride reaction product. The reaction appeared to have reduced the metal chlorides to the metal in all instances.

In order to fully understand the nature of this interaction, work was carried out to prove the existence of the tetrazolemagnesium iodide intermediate. Thus solutions were prepared containing the methylmagnesium iodide and slightly less than stoichiometric amounts of tetrazole were added. To these solutions were added carbon dioxide, acetaldehyde, benzaldehyde and excess iodine. Subsequent addition of water to produce the tetrazole derivative gave no new species as shown by infrared spectra and melting point determinations.

The necessity of determining whether the ring hydrogen was sufficiently acid to be removed by this interaction seemed apparent. This was accomplished by utilizing a Zerewittenoff apparatus and adding lithium aluminum hydride in tetrahydrofuran to a tared sample of the solid tetrazole. A blank correction on the data indicates that no quantitative conclusion could be made, but a qualitative indication of reaction was found.

In order to achieve somewhat higher reaction temperatures, it was decided to use tetrahydrofuran as the solvent medium.

The removal of residual water was found to be more critical in this reaction and it was necessary to distill the tetrahydrofuran from lithium aluminum hydride instead of the calcium hydride previously used.

Both methylmagnesium iodide and ethylmagnesium bromide were prepared in tetrahydrofuran. To each of these was added the tetrazole and a definite heating and bubbling noted. Once more the attempt to prepare derivatives was found to yield no new species. Similarly, reaction with the metal halides produced the same black reduction products recorded previously.

Further work remains since it seems probable that metal-1-substituted tetrazolate compounds should be possible to prepare. One such procedure would be to use n-butyllithium and tetrazole to prepare a lithium tetrazolate which could subsequently react with the metal halides to produce the desired tetrazolate.