value of 94.6° for the two equatorial C–Fe–C bond angles in $[SFe(CO)_3]_2$, which is somewhat larger than the corresponding average value of 88.7° in $[C_2H_5SFe(CO)_3]_2$,[2] is much nearer the *idealized* magnitude of 90° expected for octahedral metal valency rather than the *idealized* value of 120° based on the trigonal bipyramidal metal valency. The similarly sharp Fe–S–Fe angles (Table VII) of approximately 69° for both the thio- and ethylthioiron carbonyl complexes suggest a similar Fe–S electronic interaction. Both these angles and the more acute S–Fe–S angles of average value 53.5 ± 0.1° for $[SFe(CO)_3]_2$ necessitate "bent" Fe–S bonds in order for each of the iron and sulfur atoms to utilize *two equivalent* orbitals in forming electron-pair bonds with one another. It should be emphasized that both theoretical models are only approximations. This discussion has neglected all refinements of these two extreme bonding representations, but nevertheless its purpose is to give some idea of the structural relationships of these type compounds.

Other isoelectronic dimeric carbonyl complexes with presumably similar configurations to that of $[SFe(CO)_3]_2$ include the recently prepared $[HNFe(CO)_3]_2$[39] and the as yet unreported $[RPFe(CO)_3]_2$ (R = H, alkyl, aryl group). This structural investigation certainly suggests that S_2 groups can be incorporated into other metal complexes as bridging groups (with a three-electron donor capacity per metal) to produce a number of new type compounds (*e.g.*, $[SCoC_5H_5]_2$ and $[SFe(NO)_2]_2$ with metal–metal bonds and the corresponding analogs $[SNiC_5H_5]_2$ and $[SCo(NO)_2]_2$ without metal–metal bonds). Finally, it is tempting to speculate that under appropriate conditions it may be possible to prepare nonbridging dithio complexes.

Acknowledgments.—The authors wish to acknowledge the financial support of both the Atomic Energy Commission of the United States and the Air Force Office of the Air Research and Development Command.[40] We also wish to acknowledge the use of the computing facilities of the Numerical Analysis Laboratory of the University of Wisconsin (CDC 1604) and those of the Midwestern Universities Research Association (IBM 704). We are indebted for helpful discussions with Professor Richard Fenske of Wisconsin.

---

[39] W. Hieber and H. Beutner, *Z. Naturforsch.*, **15b**, 324 (1960).

[40] Under Contract No. AF-AFOSR-518-64. Reproduction in whole or part is permitted for any purpose of the United States Government.

CONTRIBUTION FROM THE W. A. NOYES LABORATORY,
UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS

Transition Metal Ion Complexes of Tetramethylguanidine

BY RAYMOND LONGHI[1] AND RUSSELL S. DRAGO

Received June 24, 1964

Tetramethylguanidine (TMG), $HNC[N(CH_3)_2]_2$, complexes of Co(II), Cu(II), Zn(II), Pd(II), Ni(II), and Cr(III) are described. The assignment of the C═N stretching frequency of TMG in the infrared region is discussed and evidence is presented to indicate that the imine nitrogen is the donor site in the compounds reported. The conductance of each complex is evaluated. Spectral and magnetic data obtained for $[Co(TMG)_4](ClO_4)_2$ suggest that this complex is tetrahedral. Spectroscopic studies leading to the evaluation of the ligand field parameters Δ, β, and B' were carried out. A very large Δ value, 4454 cm.$^{-1}$, is obtained. The similarity in the X-ray powder diffraction patterns of $[Cu(TMG)_4](ClO_4)_2$ and $[Zn(TMG)_4](ClO_4)_2$, the latter being a tetrahedral complex, indicates that these compounds have similar configurations. Distortions are expected in the copper complex. Magnetic and spectroscopic data are presented for the copper(II) compound.

Introduction

In earlier articles,[2-5] the geometry and coordination number of complexes formed by several nonaqueous solvents were investigated and the positions of these solvents in the spectrochemical series were determined. Because of the multiplicity of coordination positions and the strongly basic character of tetramethylguanidine, $HN{=}C[N(CH_3)_2]_2$, this material is an interesting nonaqueous solvent. Consequently, it was of interest to prepare some complexes of this material, to determine their structure, and to locate tetramethylguanidine in the spectrochemical series. Transition metal ion complexes of TMG have not been previously reported.

Experimental

Chemicals and Purification of Materials.—All of the chemicals used in this research are commercially available. Some of the less common were obtained from the following sources: Metal perchlorates, G. F. Smith Chemical Co., Columbus, Ohio; anhydrous nickel(II) iodide and anhydrous nickel(II) bromide, Amend Drug and Chemical Co., New York, N. Y.; tetramethylguanidine, American Cyanamid Co., New York, N. Y.; and 2,2-dimethoxypropane, Dow Chemical Company, Midland, Mich.

Diethyl ether and hydrocarbon solvents were dried over sodium wire prior to use, but the 2,2-dimethoxypropane was used as received. Tetramethylguanidine was dried over anhydrous barium oxide and distilled from fresh BaO prior to use. Solvents were distilled from anhydrous barium oxide and kept dry during their storage and handling.

---

[1] Abstracted in part from the Ph.D. thesis of Raymond Longhi, University of Illinois, 1962.

[2] D. W. Meek, R. S. Drago, and T. S. Piper, *Inorg. Chem.*, **1**, 285 (1962).

[3] J. T. Donoghue and R. S. Drago, *ibid.*, **1**, 866 (1962).

[4] R. S. Drago, *et al.*, *ibid.*, **2**, 124 (1963).

[5] R. S. Drago, *et al.*, *ibid.*, **2**, 1056 (1963).

All products were filtered and handled in a drybox. After precipitating from solution, the products were washed with several portions of ether and dried under vacuum over anhydrous phosphorus(V) oxide for 24 hr.

Instrumentation.—Infrared spectra were obtained with a Perkin-Elmer Model 21 infrared spectrophotometer with sodium chloride optics. The instrument was frequency calibrated using ammonia, water vapor, and polystyrene.

Ultraviolet, visible, and near-infrared spectra were obtained with a Cary Model 14M recording spectrophotometer.

Reflectance spectra were obtained using a Bausch and Lomb Spectronic 505 recording spectrophotometer with a standard reflectance attachment. Magnesium carbonate blocks were used as the standard for white reflectance.

Conductance measurements were made with an Industrial Instruments, Inc., conductivity bridge, Model RC 16 B2.

A Gouy magnetic balance was used to determine magnetic susceptibilities. The Gouy tubes were calibrated using $Hg[Co(NCS)_4]$. The techniques for the determination and calculation of magnetic susceptibilities have been recently reviewed in detail.[6,7]

Data for X-ray powder patterns were obtained utilizing cobalt $K\alpha_1$ radiation (λ 1.78890 Å.). The samples were not ground due to the possible explosive nature of the compounds. A 12-hr. exposure time was used.

Tetrakis(tetramethylguanidine)cobalt(II) Perchlorate.—$Co(ClO_4)_2 \cdot 6H_2O$ (5.5 g.) was dehydrated in a 100% excess of 2,2-dimethoxypropane by stirring for 2 hr.[8] To this solution a sevenfold molar excess (based on four-coordinate cobalt) of tetramethylguanidine was added, and solid formed. After stirring for 2 hr. and allowing the mixture to cool slowly to room temperature, the solid was filtered, washed with ether, and dried. The dry, rose-violet powder obtained in 83% yield was only slightly hygroscopic. It decomposes in water but dissolves in many organic solvents.

Anal. Calcd. for $[Co((CH_3)_2NC{:}NHN(CH_3)_2)_4](ClO_4)_2$: C, 33.43; H, 7.29; N, 23.39; Co, 8.20. Found: C, 33.40; H, 7.42; N, 23.08; Co, 8.48.

Tetrakis(tetramethylguanidine)copper(II) Perchlorate.—$Cu(ClO_4)_2 \cdot 6H_2O$ (5.6 g.) was treated as described above for the cobalt complex. Upon filtration, a somewhat gummy solid was obtained. After washing several times with dry ether, a crystalline olive-green solid resulted. The vacuum-dried product represented a 98% yield.

Anal. Calcd. for $[Cu((CH_3)_2NC{:}NHN(CH_3)_2)_4](ClO_4)_2$: C, 33.22; H, 7.25; N, 23.24; Cu, 8.79. Found: C, 33.16; H, 7.45; N, 22.91; Cu, 8.78.

Tetrakis(tetramethylguanidine)zinc(II) Perchlorate.—A 74% yield of the white zinc complex was obtained by the procedure described for preparation of the cobalt complex.

Anal. Calcd. for $[Zn((CH_3)_2NC{:}NHN(CH_3)_2)_4](ClO_4)_2$: C, 33.13; H, 7.23; N, 23.19; Zn, 9.02. Found: C, 33.31; H, 7.21; N, 23.01; Zn, 9.13.

The product was soluble in dichloromethane, nitromethane, absolute ethanol, N,N-dimethylformamide, and N,N-dimethylacetamide.

Tetrakis(tetramethylguanidine)palladium(II) Chloride.—Palladium(II) chloride (3 g. of 60%, Engelhard Chemical Co.) was dissolved with heating in 75 ml. of absolute anhydrous ethanol. After filtering, 2.88 g. of tetramethylguanidine was added to the warm solution. Stirring was continued for 2 hr., and, after cooling to room temperature, the addition of 600 ml. of dry diethyl ether to this solution produced a tan-gray solid which was filtered and dried. The yield was 69%.

Anal. Calcd. for $[Pd((CH_3)_2NC{:}NHN(CH_3)_2)_4]Cl_2$: C, 37.63; H, 8.21; N, 26.33. Found: C, 37.38; H, 8.58; N, 26.44.

The product was soluble in the solvents listed under the zinc complex.

Attempts to Prepare Four- or Six-Coordinate Tetramethylguanidine Complexes of Nickel(II).—Neither four- nor six-coordinate complexes of nickel(II) could be prepared by the above procedure. These complexes could not be prepared by displacing ligand from either $Ni[CH_3C(O)N(CH_3)_2]_6(ClO_4)_2$ or $Ni[(CH_3)_2SO]_6(ClO_4)_2$.

When anhydrous nickel(II) chloride was added to a 100-fold excess (based on six-coordinate nickel(II)) of TMG at 120°, a blue color developed. After stirring and heating for 5 hr., a yellow hygroscopic solid precipitated on cooling to room temperature. The filtered product was vacuum dried at 100°.

Anal. Calcd. for $NiCl_2 \cdot 4TMG$: C, 40.69; H, 8.88; N, 28.48. Found: C, 40.61; H, 8.89; N, 28.91.

When the deep blue solution which resulted from stirring and heating at 120° was decanted from a green solid and added to a volume of dry pentane about ten times the volume of the blue solution, a green-blue solid formed which was filtered, washed with pentane, and vacuum dried at 100°.

Anal. Calcd. for $NiCl_2 \cdot 2TMG$: C, 33.37; H, 7.28; N, 23.35. Found: C, 33.36; H, 7.27; N, 23.46.

Attempts to prepare the four- or six-coordinated TMG complexes with nickel(II) bromide and nickel(II) iodide were unsuccessful. In both of the above chloro complexes, absorption in the infrared spectrum corresponding to free TMG was detected. Consequently, we can say very little about these materials. It is possible that the free TMG resulted from displacement by water, for these complexes are very hygroscopic.

Chromium(III) Chloride–Tetramethylguanidine Complexes.—Anhydrous chromium(III) chloride (1.58 g.) was dissolved in 40 ml. of reagent grade acetone by stirring and heating at 40° for 2 hr. in the presence of a trace of zinc dust. The addition of an eightfold molar excess of TMG immediately produced a green solid. The green powder obtained was only partially soluble in distilled water, but it gave a positive chloride test.

Anal. Calcd. for $CrCl_3 \cdot 4TMG$: C, 38.80; H, 8.47; N, 27.15. Found: C, 38.98; H, 9.02; N, 26.57.

The previous compound was placed in a 100-fold excess of TMG and stirred vigorously for 8 hr. at 120°. After cooling to room temperature, a gray-green solid was filtered from the solution, washed with dry ether, and vacuum dried at 100° (0.5 mm.) for 15 hr.

Anal. Calcd. for $CrCl_3 \cdot 6TMG$: C, 42.42; H, 9.26; N, 29.68. Found: C, 41.76; H, 8.94; N, 29.74.

Free TMG was detected in the infrared spectra of both chloro complexes and we are not able to characterize these products with confidence. Attempted preparations of the TMG complexes of Fe(II), Fe(III), and Mn(II) perchlorates were unsuccessful. In all cases hygroscopic, nonstoichiometric materials were obtained.

Results and Discussion

Tetramethylguanidine Complexes.—Lieber and coworkers[9] have studied the infrared spectra of 38 guanidine derivatives, and they assign absorption bands in the range 1724–1626 cm.$^{-1}$ to the C=N stretching frequency. The following assignments have also been made for this group: at 1602 cm.$^{-1}$ in diphenylketimine,[10] at 1618 cm.$^{-1}$ in phenyl-*t*-butylketimine,[10] at 1637 cm.$^{-1}$ in triphenylguanidine,[10] at 1639 cm.$^{-1}$ in *sym*-diphenylguanidine,[10] at 1611 cm.$^{-1}$ in $(CH_3S)(C_6H_5)C{=}NC_6H_5$,[11] at 1622 cm.$^{-1}$ in $(CH_3S)(C_6H_5)C{=}NCH_3$,[11] and at 1607 cm.$^{-1}$ in $[(CH_3S)(C_6H_5)C{=}N(CH_3)_2]^+I^-$.[11]

---

(6) B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishing Corp., New York, N. Y., 1960.

(7) R. S. Nyholm, *J. Inorg. Nucl. Chem.*, **8**, 401 (1958).

(8) K. Starke, *ibid.*, **11**, 77 (1956).

(9) E. Lieber, D. Levering, and L. Patterson, *Anal. Chem.*, **23**, 1594 (1951).

(10) P. L. Pickard and G. W. Polly, *J. Am. Chem. Soc.*, **76**, 5169 (1954).

(11) J. D. S. Goulden, *J. Chem. Soc.*, 997 (1953).

From the previous data and Bellamy's review[12] of unsaturated nitrogen compounds, the C–N stretching frequency in tetramethylguanidine was assigned at 1609 cm.$^{-1}$. The band at 1609 cm.$^{-1}$ is the only one in the 1500–1800 cm.$^{-1}$ region in the spectrum of TMG (5% solution in cyclohexane).

The infrared spectra of the Co(II), Cu(II), and Zn(II) tetramethylguanidine complexes show that the position of the C=N band is shifted toward lower wave numbers when TMG is complexed with transition metal ions. This indicates that the imine nitrogen is the donor site in these complexes. Pertinent infrared data are presented in Table I.

TABLE I
INFRARED SPECTRAL DATA FOR TETRAMETHYLGUANIDINE COMPLEXES

Compound	Medium	C=N stretch, cm.$^{-1a}$	Band shift, cm.$^{-1}$
$(CH_3)_2NC:HNH-(CH_3)_2$ (TMG)	Cyclohexane, 5%	1609	. . .
$[Co(TMG)_4](ClO_4)_2$	Nujol	1548	61
$[Cu(TMG)_4](ClO_4)_2$	Nujol	1542	67
$[Zn(TMG)_4](ClO_4)_2$	Nujol	1549	60
$[Pd(TMG)_4]Cl_2$	KBr	1567	42
$NiCl_2\cdot 2TMG$	KBr	1563 (1608)	46
$NiCl_2\cdot 4TMG$	KBr	1562 (1608)	47
$CrCl_3\cdot 4TMG$	Nujol	1563 (1605)	46
$CrCl_3\cdot 6TMG$	KBr	1562 (1608)	47

^{a} The values in parentheses are absorptions of noncoordinated tetramethylguanidine.

Conductivity data for $[M(TMG)_4](ClO_4)_2$, were M = Co(II), Cu(II), and Zn(II), and $[Pd(TMG)_4]Cl_2$ show that these complexes are 1:2 electrolytes in nitromethane. These values may be found in Table II.

TABLE II
CONDUCTANCE DATA FOR TETRAMETHYLGUANIDINE COMPLEXES

Compound	Molar concn. (solvent)	Temp., °C.	Molar conductivity
$[Co(TMG)_4](ClO_4)_2$	1.01×10^{-2} (CH_3NO_2)	28.6	182
$[Cu(TMG)_4](ClO_4)_2$	1.01×10^{-2} (CH_3NO_2)	27.9	184
$[Zn(TMG)_4](ClO_4)_2$	1.10×10^{-2} (CH_3NO_2)	26.8	174
$[Pd(TMG)_4]Cl_2$	1.00×10^{-2} (CH_3NO_2)	29.4	182
$[(C_2H_5)_4N]Cl$	1.07×10^{-2} $(CH_3CON(CH_3)_2)$	29.2	61
$[Zn(TMG)_4](ClO_4)_2$	1.02×10^{-2} $(CH_3CON(CH_3)_2)$	28.0	115

The reference standards for molar conductivities were determined by Gill and Nyholm[13] for nitromethane solutions at 20°.

The Structure of $[Co(TMG)_4](ClO_4)_2$, Dq, and β for TMG.—A magnetic susceptibility (μ_{eff}), corrected for diamagnetism, of 4.77 ± 0.1 B.M. was determined for this complex at 25°. The values for Pascal's constants were taken from Figgis and Lewis,[6] and their method of calculation was followed. The following parameters were determined: $\chi_M \times 10^6 = 9046$; diamagnetic correction $\times 10^6 = 362$; $\chi_{M'} \times 10^6 = 9408$. This value is in the range found for tetrahedral cobalt(II) complexes.[14,15]

Figures 1 and 2 show the visible and near-infrared spectra of the complex in dichloromethane. The similarity of the solid reflectance spectrum to that in solution (Figure 1) indicates that a gross change has not occurred by dissolving the complex in dichloromethane.

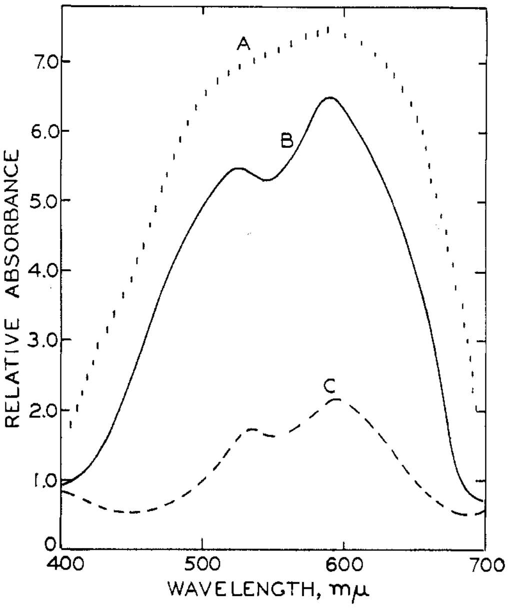

Figure 1.—Visible spectrum of $[Co(TMG)_4](ClO_4)_2$: A, solid reflectance; B, CH_2Cl_2 solution, 1.0×10^{-2} *M;* C, CH_2Cl_2 solution, 1.65×10^{-3} *M.*

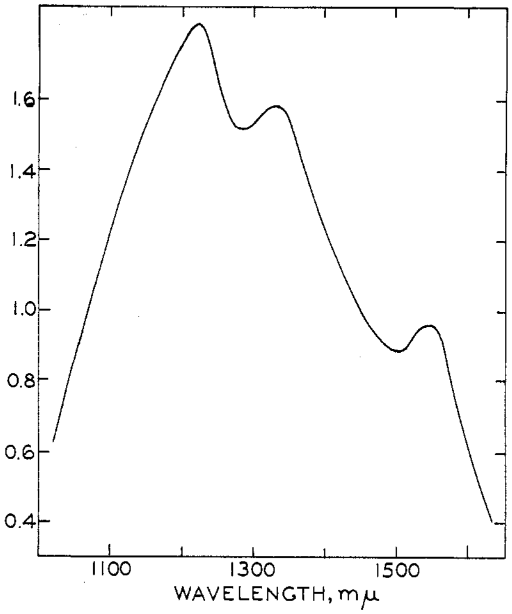

Figure 2.—Near-infrared spectrum of $[Co(TMG)_4](ClO_4)_2$: CH_2Cl_2 solution, 2×10^{-2} *M.*

---

(12) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co., Ltd., London, 1958, pp. 267–271.

(13) N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959).

(14) B. N. Figgis, *Nature*, **182**, 1568 (1958).

(15) F. A. Cotton, O. D. Faut, D. M. L. Goodgame, and R. H. Holm, *J. Am. Chem. Soc.*, **83**, 1780 (1961).

The data indicate a tetrahedral complex in which four TMG molecules are coordinated to the cobalt in both the solid and in methylene chloride solution.

A detailed procedure has been reported[16] for evaluation of the ligand field strength modulus, Δ, and the Racah interelectronic repulsion integral, B', for tetrahedral cobalt(II) complexes. In a field of tetrahedral symmetry the ^4F ground state of cobalt(II) is split to give $^4A_2$, $^4T_2$, and $^4T_1(F)$. The frequencies of the transitions $^4A_2 \rightarrow {}^4T_2$, $^4A_2 \rightarrow {}^4T_1(F)$, and $^4A_2 \rightarrow {}^4T_1(P)$ are designated as ν_1, ν_2, and ν_3, respectively.[16] Using a visual estimate of the center of gravity, a value of 17,908 cm.$^{-1}$ is assigned to ν_3 and one of 7692 cm.$^{-1}$ to ν_2 in the TMG complex. From these, values of 4454 cm.$^{-1}$ for Δ, 816 cm.$^{-1}$ for B', and 0.844 for β are obtained (here $\beta = B'$ (complex)/B (free ion)).

A meaningful X-ray powder pattern could not be obtained for the cobalt(II) complex of TMG. Since it was obtained as a fine powder, a considerable degree of "background" on the X-ray film and a resultant broadening of the strong bands were observed. Hence many bands of weak intensity were masked and those present could not be accurately measured. A visual comparison of this pattern with that of $[Zn(TMG)_4](ClO_4)_2$ suggested a similarity. Several unsuccessful attempts were made to obtain larger crystals.

$[Cu(TMG)_4](ClO_4)_2$.—Magnetic studies of this complex produced the following parameters: $\chi_M \times 10^6 = 1629$; diamagnetic correction $\times 10^6 = 362$; $\chi_{M'} \times 10^6 = 1991$. The effective magnetic moment (μ_{eff}) was determined to be 2.1 ± 0.1 B.M. This value is the same as that predicted by Figgis[14] for a tetrahedral copper(II) species. However, it should be pointed out that it is difficult to use magnetic susceptibility measurements for structure determinations of copper complexes since the predicted differences between values for six-coordinate and tetrahedral complexes are often small (octahedral copper(II) has a predicted moment of 1.9 B.M.).[14]

The X-ray powder diffraction data in Table III for $[Cu(TMG)_4](ClO_4)_2$ and $[Zn(TMG)_4](ClO_4)_2$ indicate that they have similar structures. The zinc compound is not expected to show distortion from pure tetrahedral symmetry. This would indicate that distortion from tetrahedral symmetry in $[Cu(TMG)_4](ClO_4)_2$ is not large.

The solid reflectance spectrum of the copper(II) complex shows no maxima in the region 400 to 700 mμ. In dichloromethane (4.69×10^{-4} M) a very intense band is observed in the ultraviolet region at 246 mμ (ϵ 3800). At a concentration of 1.61×10^{-2} M, very intense absorption throughout the entire visible region is noted, and in the near-infrared region a very weak band at 1517 mμ (6592 cm.$^{-1}$) with ϵ 2.8 and a shoulder at 1534 mμ (6519 cm.$^{-1}$) with ϵ 2.3 are observed. The deep green solution gradually takes on a yellow color when diluted and at a concentration of 1.88×10^{-3} M a band is observed at 598 mμ.

TABLE III[a]

X-RAY POWDER PATTERN DATA

$[Zn(TMG)_4](ClO_4)_2$		$[Cu(TMG)_4](ClO_4)_2$	
d_{hkl}, Å.	Intensity	d_{hkl}, Å.	Intensity
11.07	s	11.07	s
8.44	vs	8.44	vs
6.59	s	6.63	s
6.12	s	6.09	vs
5.58	m	5.57	m
5.13	w	5.13	w
4.71	s	4.70	s
4.20	m	4.19	m
3.98	vs	3.98	vs
3.63	s	3.62	s
3.38	vw	3.38	vw
3.28	vw	3.28	vw
3.17	m	3.16	m
2.99	w	2.98	w
2.87	w	2.87	w
2.76	m	2.76	m
2.63	vw	2.63	vw
2.36	w	2.36	w
2.18	vw	2.18	vw
2.09	w	2.09	w

[a] Cobalt $K_{\alpha 1}$ X-rays were used with an exposure time of 12 hr. The intensities were visually estimated: s, strong; m, medium; w, weak; v, very. The term d_{hkl} is the familiar parameter defined in the modified Bragg relationship $\lambda = 2d_{hkl} \sin \theta_{hkl}$.

Liehr[17] has predicted that tetrahedral copper(II) should show a transition in the region 5000–7000 cm.$^{-1}$ and should show no transition in the visible region. We observe a band at 6592 cm.$^{-1}$ for a concentrated solution of $[Cu(TMG)_4](ClO_4)_2$ in dichloromethane. In addition, the solid reflectance spectrum shows no maxima in the visible region.

The magnetic, X-ray, and spectral studies indicate that $[Cu(TMG)_4](ClO_4)_2$ does not show large distortion (say around 5°) from tetrahedral symmetry in the solid state and most probably is close to tetrahedral in concentrated dichloromethane solutions.

$[Zn(TMG)_4](ClO_4)_2$.—Since the four-coordinate zinc complex should be tetrahedral, this complex was prepared for the purpose of providing an X-ray powder pattern to which the copper(II) compound could be compared. The compound was found to be a 1:2 electrolyte in nitromethane (Table II). Its infrared spectrum shows that the TMG molecules are coordinated at the imine nitrogen site (Table I).

$[Pd(TMG)_4Cl_2$.—This compound behaves as a 1:2 electrolyte in nitromethane and is diamagnetic in the solid state. A solution of this complex 1.01×10^{-3} M in dichloromethane shows a strong absorption at 374 mμ (ϵ 376). No band maxima were observed in the ultraviolet region. Bonding of the TMG is through the imine nitrogen site (Table I).

Acknowledgment.—The authors wish to thank the U. S. Army Research Office (Durham) for their generous support of this research under Grant No. DA-ARO(D)-31-124-672.

---

(16) F. A. Cotton and M. Goodgame, *J. Am. Chem. Soc.*, **83**, 1777 (1961).

(17) A. D. Liehr, *J. Phys. Chem.*, **64**, 43 (1960).