free-radical ion in the solid is varied by using different cations:

(1) **The Monomer–Dimer Effect.**—The potassium salt in solution or in a mixed crystal with potassium hydroxylamine disulfonate exists as a monomer, but in the pure solid it is dimerized. Yamada and Tsuchida[8] conclude that steric conditions, along with visible, ultraviolet, and infrared spectra, suggest a structure having a peroxide linkage

$$^-O_3S \diagdown N{-}O \qquad SO_3^- \\ ^-O_3S \diagup \qquad O{-}N \diagup \diagdown SO_3^-$$
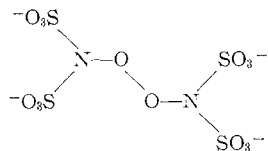
Nothing is known from X-ray crystal studies about the actual structure of the dimer. As the cation size increases a critical size is reached above which the cation prevents dimerization, probably owing to steric hindrance. As shown in Table III, this size is about that of the rubidium ion. Hoffman and Henderson reported[9] the preparation of the stable di-*t*-butyl nitroxide free radical, $[(CH_3)_3C]_2NO$. It was suggested that steric hindrance of the two *t*-butyl groups on the nitrogen prevents dimerization.

(2) **Exchange and Hyperfine Splitting Effects.**—With tetraphenylstibonium ion in the pure solid and in a 0.5 M solution only one broad peak was observed.[10]

(8) S. Yamada and R. Tsuchida, *Bull. Chem. Soc. Japan*, **32**, 721 (1959).
(9) A. K. Hoffman and A. T. Henderson, *J. Am. Chem. Soc.*, **83**, 4671 (1961).
(10) G. Pake, J. Townsend, and S. Weissman, *Phys. Rev.*, **85**, 682 (1952).

TABLE III
ION SIZE AND MAGNETIC PROPERTIES

Cation	Radius, Å	Magnetic properties of the salt
Na^+	0.97	Diamagnetic
K^+	1.33	Diamagnetic
Rb^+	1.47	Not measured; its color suggests it is a mixed crystal of both the monomer and the dimer
Cs^+	1.67	Paramagnetic
$(CH_3)_4N^+$	~2.4[a]	Paramagnetic
$(C_6H_5)_4As^+$	~6.3[a]	Paramagnetic
$(C_6H_5)_4Sb^+$	~6.5[a]	Paramagnetic
$Co(NH_3)_6^{3+}$	~2.8	Paramagnetic

[a] Calculated from data of R. C. L. M. Slater, *Acta Cryst.*, **12**, 187 (1959).

This is due to spin–spin interaction of nearby free-radical neighbors. When the concentration of the radicals is lowered the hyperfine splittings appear, as was noted in this study with a sample diluted with a diamagnetic salt or partially decomposed. The broad line split into three equidistant peaks of about 13-G separation, comparable to the splitting observed in very dilute solutions by the nitrogen nuclear spin.

Of interest to clarify the monomer–dimer situation will be X-ray crystal studies, preliminary phases of which are under way in our laboratories, and single-crystal anisotropy epr studies, once the problem of preparing suitable stable crystals is solved.

It should also be possible to correlate the spin–spin interaction effect with the distance of separation of the free radicals, both in solution and in solid salts once this structure information is available.

Some Tetrazole Complexes of Transition Metal Halides

BY DELORES M. BOWERS AND ALEXANDER I. POPOV

Anhydrous complexes of pentamethylenetetrazole (PMT) were prepared with first-row transition metal chlorides and bromides. Two types of complexes were isolated, $M^{II}(PMT)X_2$ and $M^{II}(PMT)_2X_2$. Both types of compounds are quite insoluble in polar and nonpolar liquids and have high melting or decomposition points. Magnetic and spectral evidence indicate that the metal ions in the $M^{II}(PMT)X_2$ complexes are in octahedral environments while $M^{II}(PMT)_2X_2$ complexes may be tetrahedral. The former compounds are probably polymeric and contain halogen bridges, while complexes containing two molecules of the ligand are probably monomeric and have tetrahedral structure.

Introduction

In previous communication from this laboratory[1,2] we reported the preparation and some properties of complexes formed by pentamethylenetetrazole (PMT) with some first-row transition metal perchlorates.

$$\begin{array}{c} N{=}C{-}CH_2{-}CH_2 \\ N \diagdown \qquad \qquad \qquad CH_2 \\ N{\Diagup\!\!\!\!} \\ N{-}N{-}CH_2{-}CH_2 \end{array}$$
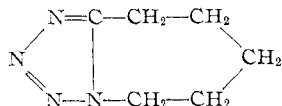
(1) H. A. Kuska, F. M. D'Itri, and A. I. Popov, *Inorg. Chem.*, **5**, 1272 (1966).
(2) F. M. D'Itri and A. I. Popov, *ibid.*, **5**, 1670 (1966); **6**, 597, 1591 (1967).

These complexes had the general formula $M^{II}(PMT)_6$-$(ClO_4)_2$ with M^{II} being Fe, Mn, Co, Ni, Zn, or Cu. It was shown that the complexes had octahedral or a distorted octahedral configuration. They were soluble in water and in a number of polar nonaqueous solvents. Magnetic susceptibility measurements have indicated that the complexes were of high-spin type.

Initial studies were carried out with perchlorates since we desired to minimize the possibility of interference from the anion and the formation of mixed complexes. The ligand, however, does not seem to have very strong donor properties and more polarizable

Table I

Analysis and Some Properties of Transition Metal Halide Complexes with Pentamethylenetetrazole

Complex	Mp, °C	Color	C Found	C Calcd	H Found	H Calcd	N Found	N Calcd	X Found	X Calcd
Cr(PMT)₂Cl₂	160 dec	Lt blue-green	36.04	36.10	4.92	5.05	28.09	28.07	17.86	17.76
Mn(PMT)Cl₂	>300	Pale pink	27.37	27.29	3.83	3.82	21.05	21.23	26.70	26.86
Fe(PMT)Cl₂	140 dec	Yellow	27.18	27.20	3.84	3.80	21.22	21.15	26.78	26.77
Co(PMT)Cl₂	>300	Pink	26.94	26.89	3.76	3.76	20.86	20.91	26.40	26.46
Ni(PMT)Cl₂	>300	Lt green	27.03	26.91	3.84	3.76	20.82	20.93	26.40	26.48
Cu(PMT)Cl₂	250 dec	Lt green	26.38	26.43	3.74	3.70	20.47	20.56	25.85	26.01
Zn(PMT)₂Cl₂	107–109	White	34.93	34.92	4.85	4.88	27.12	27.16	17.24	17.18
Mn(PMT)Br₂	>300	Lt pink	20.46	20.42	2.78	2.86	15.49	15.88	45.31	45.29
Co(PMT)₂Br₂	159–161	Royal blue	29.00	29.17	4.07	4.07	22.67	22.63	32.35	32.28
Ni(PMT)Br₂	>300	Yellow-green	19.93	20.20	3.00	2.83	15.60	15.71	44.68	44.81
Cu(PMT)Br₂	190 dec	Rust brown	19.86	19.93	2.74	2.79	15.04	15.50	43.29	44.21
Zn(PMT)₂Br₂	154–156	White	28.66	28.73	4.05	4.02	22.13	22.35	31.77	31.87

anions may well compete successfully with PMT for the coordination positions around the metal ion. In an extension of this work, therefore, we decided to study the influence of anions upon complexation reactions of tetrazoles.

Experimental Section

Reagents.—Technical grade 2,2-dimethoxypropane (hereafter abbreviated as DMP) and methanol were refluxed over granulated barium oxide and then distilled at reduced pressure. Other reagents such as anhydrous ethyl ether, reagent grade dichloromethane, chloroform, and acetone, as well as reagent grade hydrated transition metal halides, were used without further purification. Pentamethylenetetrazole was obtained from the Knoll Pharmaceutical Co., Orange, N. J.

PMT Complexes with Manganese(II), Iron(II), Cobalt(II), Nickel(II), and Copper(II) Chlorides.—Each hydrated transition metal chloride (0.02 mol) was added to 75 ml of 50% DMP–CH₃OH solvent mixture and stirred for 5–10 min to remove the waters of hydration. A slight excess of PMT (0.04 mol) was dissolved in 25 ml of the solvent and added slowly from a dropping funnel. A finely divided solid complex formed which was filtered and dried.

Analytical results on this and other PMT complexes described below are given in Table I.

PMT Complex with Zinc(II) Chloride.—The procedure outlined above was followed. The product, however, was obtained in the form of a viscous oil. The oil was dissolved in dichloromethane and the solution was added slowly to anhydrous ethyl ether. A finely divided precipitate was obtained. In order to obtain pure product, the precipitation procedure was repeated several times.

PMT Complex with Chromium(II) Chloride.—Chromium(II) chloride was prepared by passing a solution of chromium(III) chloride through a Jones reductor. The effluent was passed into a solution of sodium acetate and chromium(II) acetate precipitated out. The precipitate was filtered, washed with chilled deoxygenated acetone, and transferred to a concentrated solution of hydrochloric acid held at −10° by a salt water–ice bath. Acetic acid and solid hydrated chromium(II) chloride were liberated. After stirring the mixture for 15–20 min the liquid was decanted from the solid and the precipitate was washed several times with cold concentrated hydrochloric acid.

Hydrated chromium(II) chloride was dissolved in 75 ml of 50% DMP–CH₃OH solvent mixture to remove the waters of hydration. Solid PMT in excess was added to the solution and the solid complex was obtained. The complex was filtered, washed with DMP, and dried under vacuum. The stability of the complex was tested by exposing a sample to moist atmosphere.

The color of the sample rapidly changed from blue to green, indicating formation of chromium(III) chloride. The oxidation also occurred, over a period of several days, in dry atmosphere.

PMT Complexes with Manganese(II), Cobalt(II), Copper(II), and Zinc(II) Bromides.—The same procedure as outlined for the PMT complex with manganese(II) chloride was used. Again finely divided solid complexes were obtained.

PMT Complex with Nickel(II) Bromide.—Since anhydrous nickel bromide was not very soluble in the chosen solvent mixture, it was dissolved in 75 ml of 90% acetone–water mixture. A slight excess (0.04 mol) of PMT also dissolved in acetone was slowly added from a dropping funnel. The system changed color but no solid formed until the volume was reduced and the solution was added to chloroform.

PMT Complexes with Iron(II) Bromide and Iron(III) Chloride.—Attempts were made to prepare these complexes by the same technique, but they were unsuccessful. In the case of iron(III) chloride no evidence for the complex formation could be obtained. The reaction of iron(II) bromide with PMT initially yielded an oil which was dissolved in an excess of DMP and a solid precipitate was obtained by the addition of ether. Analysis of the precipitate, however, showed that the compound was nonstoichiometric.

In a number of the above described preparations, we attempted to vary the stoichiometry of the complex by varying the PMT: M^{II}X₂ ratio in the reaction mixture. For example, in the case of nickel chloride the ligand : metal ion ratio was varied from 1 : 1 to 8 : 1. In all cases the product had the composition Ni(PMT)-Cl₂.

Magnetic Susceptibility Measurements.—Magnetic moments of the above complexes were determined by the Gouy method at 24.0°. Copper sulfate pentahydrate and mercury(II) tetracyanocobaltate(II) were used as reference materials. Obtained values are corrected for the diamagnetic susceptibility of PMT and the halide salts. The results are shown in Table II.

Reflectance Spectra.—Reflectance spectra of the complexes were obtained by the standard procedure with a Beckman DK-2 spectrophotometer.

Infrared Spectra.—Measurements in the 5000–650-cm⁻¹ spectral region were carried out on a Unicam 200 spectrometer or on a Beckman IR-7 spectrometer when better resolution was needed. Spectra in the 650–100-cm⁻¹ region were obtained with a Perkin-Elmer 301 spectrometer. In all cases the complexes were dispersed in Nujol mulls.

Results and Discussion

As seen from Table I, the stoichiometry of the metal halide complexes is radically different from that of the perchlorate complexes. It was indeed surprising that only one or at most two PMT molecules would coordinate with a metal halide while six PMT molecules coordinated with a metal perchlorate.

Physical properties of the metal halide complexes were likewise quite different from those of the perchlorates. In particular, halide complexes, especially

TABLE II

MAGNETIC MOMENTS OF TRANSITION METAL HALIDE COMPLEXES WITH PENTAMETHYLENETETRAZOLE

	Spin-free complexes		
Complex	μ_{eff} (found), BM	No. of unpaired electrons	μ_{eff}(exptl), BM
Cr(PMT)$_2$Cl$_2$	4.55	4	4.40-4.90
Mn(PMT)Cl$_2$	5.44	5	5.65-6.10
Fe(PMT)Cl$_2$	5.32	4	5.1-5.5
Co(PMT)Cl$_2$	5.12	3	4.30-4.80 (tetra) 4.80-5.20 (octa)
Ni(PMT)Cl$_2$	3.28	2	2.80-3.50
Cu(PMT)Cl$_2$	1.55	1	1.70-2.20
Zn(PMT)$_2$Cl$_2$	0.00	0	...
Mn(PMT)Br$_2$	5.63	5	5.65-6.10
Co(PMT)$_2$Br$_2$	4.48	3	4.30-4.80 (tetra) 4.80-5.20 (octa)
Ni(PMT)Br$_2$	3.29	2	2.80-3.50
Cu(PMT)Br$_2$	1.55	1	1.70-2.20
Zn(PMT)$_2$Br$_2$	0.00	0	...

TABLE III

REFLECTANCE SPECTRA

	Obsd bands		Octahedral[a]	Lit. values (soln spectral), cm⁻¹ Tetrahedral or planar[b]
Complex	mμ	Cm⁻¹		
Mn(PMT)Cl$_2$	355	28,200	29,700	23,250[f]
	376	26,600	28,000	22,500
	426	23,500	25,150[c]	
	472	21,200	24,900	
	560	17,900	23,000	
	1190	8,200	18,800	
	1390	7,200		
Mn(PMT)Br$_2$	360	27,800		27,000[f]
	379	26,400		23,000
	432	23,100		22,100
	473	21,100		21,500
	554	18,000		
	1200	8,300		
	1390	7,200		
				Charge transfer beyond
Fe(PMT)Cl$_2$	1080	9,300	10,400[e]	20,000[g]
	1412	7,100		
Co(PMT)Cl$_2$	508	19,700	21,550[d]	16,900[f]
	560	17,900	19,400	16,300
	692	14,400	16,000	15,700
	1500	6,700	8,000	15,000 14,400
Co(PMT)$_2$Br$_2$	387	25,800		16,200[f]
	432	23,100		15,500
	447	22,400		15,000
	560	17,900		14,300
	628	15,900 vs		13,800
	1095	9,100		
	1395	7,200		
Ni(PMT)Cl$_2$	422	23,700	25,500[c]	16,400[f]
	698	14,300	18,500	15,150
	1190	8,400	15,400	14,300
	1435	7,000	13,500	
	1935	5,200	8,600	
Ni(PMT)Br$_2$	435	23,000		16,500[f]
	720	13,900		15,300
	1195	8,400		14,300
	1455	6,900		
	1945	5,100		
Cu(PMT)Cl$_2$	780	12,800	12,600[c]	27,800[f] 23,000 11,200
Cu(PMT)Br$_2$	800	12,500		27,100[f] 23,100 15,600 11,500

[a] Spectra for octahedral aquo complexes $M^{II}(H_2O)_6{}^{2+}$. [b] Spectra for the corresponding tetrahalides $M^{II}X_4{}^{2-}$. [c] T. M. Dunn in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers Inc., New York, N. Y., 1960, p 229 ff. [d] C. K. Jørgensen, *Acta Chem. Scand.*, **9**, 116 (1955). [e] C. K. Jørgensen, *ibid.*, **8**, 1502 (1954). [f] R. S. Nyholm and N. S. Gill, *J. Chem. Soc.*, 3997 (1959). [g] N. S. Gill, *ibid.*, 3512 (1961).

those with one molecule of PMT, were quite insoluble in water and in most polar or nonpolar solvents. In a few isolated cases some solubilization of complexes was observed but only when the solvent (such as dimethylformamide or pyridine) had strong donor properties. In such cases, however, absorption spectra of the resulting solutions showed that the dissolved complex was completely decomposed into metal salt and PMT.

The two classes of complexes sharply differ in their decomposition temperatures. Complex compounds with the structure $M^{II}(PMT)X_2$ in general are quite stable thermally and decompose at 100-150° higher than the $M^{II}(PMT)_2X_2$ compounds.

Magnetic moments of the complexes, listed in Table II, in general agree rather well with the values predicted for the spin-free complexes. It is interesting to note that there is a definite difference in the moments of the cobalt complexes with Co(PMT)$_2$Br$_2$ having a moment of 4.48 BM and Co(PMT)Cl$_2$ having a moment of 5.12 BM. These data seem to indicate that the first complex has a tetrahedral configuration while the second has an octahedral configuration.

The magnetic moment of the copper complex seems to be abnormally low. Such values are often indicative of some metal–metal bonding such as has been observed, for example, for the copper acetate. The data available at this time, however, do not allow an unambiguous identification of Cu–Cu bonds in the CuX$_2$–PMT complexes.

Since the complexes could not be dissolved in any solvent, it was impossible to study their spectra in solutions. Reflectance spectra of the powders, however, were obtained and the observed absorption bands are listed in Table III. Literature data on the principal absorption bands of the corresponding octahedral hexaaquo complexes and of the tetrahalide complexes (tetrahedral or planar) are also listed for comparison. It is seen that the reflectance spectra of the M^{II}-(PMT)X$_2$ complexes closely resemble those reported for the octahedral complexes of the same metals. For example, the Co(PMT)Cl$_2$ complex has a strong band at 17,900 cm⁻¹ characteristic of the octahedral cobalt

complexes. On the other hand, the Co(PMT)$_2$Br$_2$ complex has a very strong absorption band at 15,400 cm⁻¹ typical of the tetrahedral cobalt complexes.

A comparison of the near-infrared spectra of PMT with that of a representative PMT complex shows that two noticeable changes in the spectrum of the ligand occur upon complexation. A quartet of bands at 1100 cm⁻¹ is transformed into two sets of bands and the PMT band at 1000 cm⁻¹ is not observed in the spectrum of the complex. Similar spectral changes have been reported for the solid Ag(PMT)$_2$NO$_3$ complex in a previous publication.[3] They could not, however, be observed in the $M^{II}(PMT)_6(ClO_4)_2$ complexes[2] because of the broad perchlorate band in that region.

(3) A. I. Popov and R. D. Holm, *J. Am. Chem. Soc.*, **81**, 3250 (1959).

The far-infrared spectra of PMT show a total of ten absorption bands in the 700–110-cm^{-1} region. The location and the relative intensities of these bands are compared (Figures 1 and 2) with those of the PMT complexes with the transition metal halides.
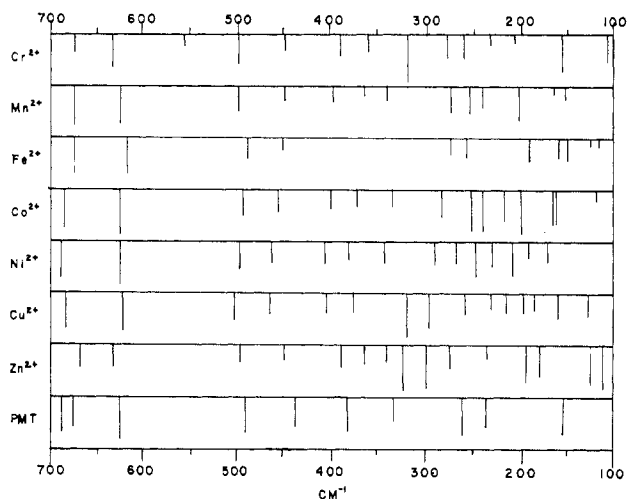

Figure 1.—Line drawing representing the infrared spectra of PMT and of PMT–metal chloride complexes in the 700–100-cm^{-1} spectral region. Line lengths are proportional to band intensities.
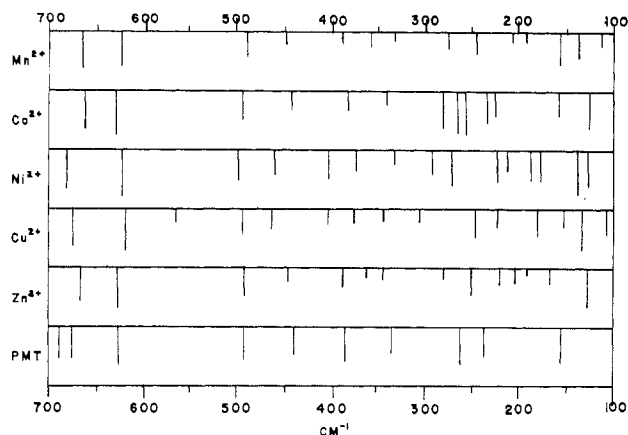

Figure 2.—Line drawing representing the infrared spectra of PMT and of PMT–metal bromide complexes in the 700–100-cm^{-1} spectral region. Line lengths are proportional to band intensities.

Transition metal complexes of PMT should show some similarity with those of pyridine and a comparison of the far-infrared spectra of the two types may be instructive. A variety of complexes with several different configurations are formed in metal halide–pyridine systems. Thus tetrahedral, octahedral, distorted polymeric octahedral, polymeric octahedral, and planar complexes have been prepared and their far-infrared spectra have been reported. Clark and Williams[4] have found that for the distorted polymeric octahedral complexes with the composition $CuX_2 \cdot 2py$ (X = Cl, Br) there are two metal–halogen vibrational modes of Cu–Cl at 294 and 235 cm^{-1} while Cu–Br vibrations occur at 255 and 202 cm^{-1}. In the case of polymeric

(4) R. J. H. Clark and C. S. Williams, *Inorg. Chem.*, **4**, 350 (1965).

octahedral complexes $MCl_2 \cdot 2py$ (M = Mn, Fe, Co, or Ni), the spectra consist of broad, badly resolved bands in the 200–260-cm^{-1} spectral region. Goldstein, *et al.*,[5] have reported that in-plane bending modes for distorted polymeric octahedral complexes $CuX_2 \cdot 2py$ occur at 175 cm^{-1} for the chloro complex and at 130 cm^{-1} for the bromo complex. Ahuja, *et al.*,[6] who have studied far-infrared spectra of bridged complexes with the general formula MLX_2 and ML_2X_2 (M = Mn, Co, Ni, Cu, Zn, Cd; X = halogen; L = monodentate heterocyclic amine) report that M–Cl vibrations occur at *ca.* 230 cm^{-1} and M–Br vibrations are located below 200 cm^{-1}.

It seems somewhat more difficult to interpret our spectra in view of the fact that PMT has an abundance of bands in this region, some of which, undoubtedly, are displaced owing to complex formation.

Purely by comparison one can very tentatively assign the 206-, 253-, 300-, and 299-cm^{-1} bands of Mn-(PMT)Cl$_2$, Ni(PMT)Cl$_2$, Cu(PMT)Cl$_2$, and Zn-(PMT)$_2$Cl$_2$, respectively, to the metal–halogen vibration. Inspection of the spectra also reveals that Ni-(PMT)Cl$_2$ and Ni(PMT)Br$_2$ complexes both have a band at 174 cm^{-1} which cannot be ascribed to ligand vibration. This band may represent metal–ligand vibration. Similar reasoning leads us to consider the 220-cm^{-1} bands in the Cu(PMT)X$_2$ complexes and the $\sim$190-cm^{-1} band in the Zn(PMT)$_2$X$_2$ complexes as metal–ligand vibrations.

In the case of other complexes, the data do not allow, at this time at least, to make even tenuous band assignments. In the case of cobalt, no comparison between the spectra of the chloro and the bromo complexes can be made since the two seem to have quite different structures. In the case of Cr(II) and Fe(II) halides, only the complex chlorides could be prepared, and, again, the data do not appear to be adequate for the interpretation of the far-infrared spectra.

It is evident that octahedral complexes containing only one molecule of PMT must have either metal–metal bonds or bridging ligands. The evidence for metal–metal bonds is, at best, very tenuous for the copper complexes and nonexistent for the other complexes. On the other hand, in all previous work PMT was found to act as a monodentate ligand. The reluctance of the tetrazole ring to form more than one bond is also illustrated by the PMT–halogen complexes such as PMT·ICl, where as shown by a recent crystallographic study,[7] iodine monochloride is bound to N(2) nitrogen. Nevertheless it seems that in the case of metal halides, the polymeric form of the complex forces the tetrazole ring into the bridging position. It should be noted that the crystal structure of the copper(II) chloride complex with 1,2,4-triazole[8] indicates that the copper is octahedrally coordinated and that the tri-

(5) M. Goldstein, E. F. Mooney, A. Anderson, and H. A. Gebbie, *Spectrochim. Acta*, **21**, 105 (1965).

(6) I. S. Ahuja, D. H. Brown, R. H. Nuttall, and D. W. A. Sharp, *J. Inorg. Nucl. Chem.*, **27**, 1625 (1965).

(7) N. C. Baenziger, A. D. Nelson, A. Tulinsky, J. H. Bloor, and A. I. Popov, *J. Am. Chem. Soc.*, **89**, 6463 (1967).

(8) J. A. J. Jarvis, *Acta Cryst.*, **16**, 964 (1962).

azole ring acts as a bridging ligand. It is quite possible that our complexes have a similar structure.

CONTRIBUTION FROM THE WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES, UNIVERSITY COLLEGE, LONDON, W.C.1, ENGLAND

Electronic Spectra and Magnetism of Some Vanadium(III) Halogeno Complexes

BY A. T. CASEY AND R. J. H. CLARK

The electronic spectra of a number of octahedral and tetrahedral complexes of vanadium(III) have been recorded over the range 5500–45,000 cm^{-1}, and the relevant ligand field parameters were derived. Of special interest are the values found for $10Dq$ for the tetrahedral VCl_4^- and VBr_4^- ions; these are 5530 and 5200 cm^{-1}, respectively. The magnetic susceptibilities of the complexes have also been determined in the range 300–90°K. The magnetic moments of the tetrahedral species VCl_4^- and VBr_4^- are essentially independent of temperature, after allowance is made for temperature-independent paramagnetism, as expected for species possessing $^3A_2$ ground terms. The magnetically dilute octahedral complexes of vanadium(III) (ground term $^3T_{1g}$) have magnetic moments which fall slightly with decreasing temperature (from ~2.7 to ~2.5 BM in the range stated). The splitting of the ground term due to the asymmetry of the ligand field is estimated to be ~800 cm^{-1} in the ions $VX_4 \cdot 2CH_3CN^-$ (X = Cl or Br). The magnetism of the complex $[(C_2H_5)_4N]_3V_2Cl_9$ has been interpreted in terms of the binuclear spin system with $S_1 = S_2 = 1$. The exchange integral J is estimated to be ~ −40 cm^{-1}.

Introduction

The electronic spectra and magnetism of vanadium-(III) complexes have been less extensively studied than those of the later, first-row transition elements.[1] As part of a continuing program of research in this area, it was thought desirable to obtain the spectra of the unusual tetrahedral species[2] VCl_4^- and VBr_4^- under good resolution (the counterions are $(C_6H_5)_4As^+$ for the VCl_4^- ion and $(C_6H_5)_4As^+$ and $(C_2H_5)_4N^+$ for the VBr_4^- ion). Moreover, the magnetic moments of these ions over a temperature range should be of interest in comparison with those of octahedral vanadium(III) complexes. The spectral and magnetic properties of two magnetically dilute octahedral complexes have also been investigated, and these are compared with previous results on related complexes.[3]

The binuclear species $[(C_2H_5)_4N]_3V_2Cl_9$ has also been studied, and it is found that both its spectral and magnetic properties imply appreciable vanadium–vanadium interaction. Surprisingly, the salt $[(C_2H_5)_4N]VCl_4$ has similar magnetic behavior, and, from this and other data, it is concluded that the anion is octahedral polymeric in this salt, whereas it is tetrahedral monomeric in the tetraphenylarsonium salt.

Experimental Section

Compounds.—The compounds were prepared under oxygen-free nitrogen in a vacuum system by methods outlined previously.[2,4] The compounds gave satisfactory analysis for C, H, N, Cl or Br, and V in each case.

One compound is characterized here for the first time, although its existence was implied previously.[2] It is $(C_6H_5)_4As[VCl_4 \cdot 2CH_3CN]$, prepared by addition of $(C_6H_5)_4AsCl$ to a solution of VCl_3 in acetonitrile. It is yellow, like other salts of the $VCl_4 \cdot 2CH_3CN^-$ ion. *Anal.* Calcd for $C_{28}H_{26}AsCl_4N_2V$: C, 50.3; H, 3.55; Cl, 21.9; N, 3.0; V, 8.25. Found: C, 51.1; H, 4.0; Cl, 21.5; N, 4.25; V, 7.75.

Spectra.—The electronic spectra of the compounds were recorded on a Cary 14 spectrophotometer both by diffuse reflectance and also, where possible, in solution. All of the complexes are very unstable to air and to moisture, and therefore their diffuse reflectance spectra were recorded on samples held between silica plates, the edges of which had been greased.

Magnetism.—The magnetic susceptibilities of the compounds were recorded by use of an electromagnet with a field strength of 8150 ± 50 Oe; the field strength was checked every six runs. The thermocouple was calibrated by reference to the susceptibility of $HgCo(NCS)_4$. The temperatures are believed to be correct to ±0.5° at 300°K and to ±0.8° at 90°K.

The magnetic parameters for the $VCl_4 \cdot 2CH_3CN^-$ and $VBr_4 \cdot 2CH_3CN^-$ ions were initially derived by graphical procedures and then refined by Dr. D. J. Machin by use of the University of Manchester Atlas computer.

Results

Spectra.—The band maxima found for the tetrahedral complexes are given in Table I, while those for the octahedral complexes are given in Table II.

Magnetism.—The magnetic susceptibilities and moments of the tetrahedral complexes at the various measured temperatures are given in Table III, together with the suceptibilities and moments corrected for a temperature-independent contribution to the susceptibility (TIP) of 300 cgsu. The magnetic data for the octahedral species are given in Table IV. The appropriate diamagnetic corrections are indicated in each case and are subtracted from the observed sus-

(1) R. J. H. Clark, "The Chemistry of Titanium and Vanadium," Elsevier Publishing Co., Amsterdam, 1968.
(2) R. J. H. Clark, R. S. Nyholm, and D. E. Scaife, *J. Chem. Soc., A*, 1296 (1966).
(3) D. J. Machin and K. S. Murray, *ibid.*, 1498 (1967).
(4) G. J. Wessel and D. J. W. Ijdo, *Acta Cryst.*, **10**, 466 (1957).