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Complex Compounds of Molybdenum and Tungsten Pentahalides[1]

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Received April 10, 1967

The reaction of molybdenum(V) and tungsten(V) halides with the ligands 2,4,6-trimethylpyridine and benzonitrile has been investigated. Although reduction of these halides has been observed with ligands such as pyridine and acetonitrile, stable complexes of the type $[MoCl_4(C_8H_{11}N)_2]Cl$ and $[WX_4L_2]X$ (X = Cl, Br; L = $C_8H_{11}N$, C_7H_5N) were obtained in this study. $MoCl_5$ was observed to undergo reduction with benzonitrile to the +4 oxidation state. Conductivity studies indicate that the metal(V) complexes most likely exist as 1:1 electrolytes in nitromethane. It is proposed that these species are $[M^VX_4L_2]^+$ and a halide ion. Solution and reflectance spectra indicate that these compounds also exist in this form in the solid state. The magnetic moments of these complexes (0.6–1.5 BM) are in the range found for M(V) compounds.

Introduction

Previous studies[2–4] have shown that the reactions of molybdenum pentachloride and the hexa- and pentahalides of tungsten with various nitrogen-containing ligands such as pyridine, 2,2′-dipyridyl, acetonitrile, etc., almost always lead to complexes of the type $M^{IV}X_4L_2$ (L = monodentate ligand) or $M^{IV}X_4B$ (B = bidentate ligand). Only in the reactions of tertiary amines (NR_3; R = methyl and ethyl) and molybdenum pentachloride were simple adducts of the type $MoCl_5(NR_3)$ obtained without reduction of molybdenum.[5] In the case of tungsten(V) chloride and bromide, secondary amines (NHR_2) as well as tertiary amines (NR_3) caused reduction of the metal. With primary amines, however, aminobasic tungsten(V) halides were obtained with no evidence for any reduction.[6]

As a result, the literature contains reports of only the hexahalo anions, $MoCl_6^-$ and WX_6^- (X = Cl, Br),[7–9] the octacyano derivative,[10] and a number of oxyhalide complexes[11,12] of molybdenum(V) and tungsten(V). For this reason it was felt that a study of the reactions of the metal pentahalides with various ligands which were not capable of readily bringing about reduction might lead to the formation of stable +5 complexes. Such compounds would then allow informative comparisons to be made with similar compounds containing the metal in different oxidation states.

Experimental Section

General Precautions.—Since the halides of molybdenum and tungsten, as well as their complexes, were unstable in air, all operations were carried out using standard vacuum line techniques or in a dry nitrogen atmosphere.

Materials.—Powdered tungsten metal, supplied by the General Electric Co., was thoroughly degassed by heating to 500° at *ca.* 10^{-5} mm for several hours. Molybdenum pentachloride (Alfa Inorganics, Inc.) and tungsten hexachloride (City Chemical Corp.) were purified just before use by repeated sublimation. Reagent grade bromine, initially dried over anhydrous phosphorus pentoxide for 48 hr, was distilled, *in vacuo*, onto freshly outgassed phosphorus pentoxide for storage. 2,4,6-Trimethylpyridine, purchased from Eastman Chemicals, was refluxed over phosphorus pentoxide for 12 hr and then fractionally distilled. The constant-boiling fraction was dried over phosphorus pentoxide and then outgassed to *ca.* 10^{-5} mm. Benzonitrile, from Eastman Chemicals, was outgassed to *ca.* 10^{-5} mm pressure and then distilled onto previously outgassed Linde Type 4A Molecular Sieves. Other solvents used in this work were either reagent grade or spectrograde and were allowed to stand over phosphorus pentoxide for 48 hr and then outgassed to *ca.* 10^{-5} mm. The solvents were then vacuum distilled into clean, dry flasks containing a small amount of thoroughly outgassed P_2O_5 for storage under vacuum.

Analytical Work.—Molybdenum and tungsten were determined by treating the sample with hot, concentrated HNO_3 and digesting the solution until conversion to the trioxide was complete. These elements were weighed as MO_3 after ignition. The halide was determined as previously described.[2] Carbon, hydrogen, and nitrogen analyses were done by Midwest, Inc., Indianapolis, Ind., or Galbraith Laboratories, Inc., Knoxville, Tenn. The apparent oxidation state of the metal in the complexes was determined by oxidation with excess potassium dichromate. The excess dichromate was treated with KI, the liberated iodine being titrated with standard sodium thiosulfate.

The molybdenum content of the solutions used for the spectral and conductance work was determined in a manner similar to that reported by Snell and Snell.[13] The tungsten content of similar solutions was determined according to the procedure outlined by Norwitz.[14]

Preparation of 2,4,6-Trimethylpyridinium Chloride.—The 2,4,6-trimethylpyridinium chloride was prepared by bubbling HCl gas through a solution of 25 ml of 2,4,6-trimethylpyridine in 100 ml of 1-butanol for 30 min. Upon cooling the solution to 0°, the salt crystallized out of the solution. The salt was collected on a sintered-glass filtering funnel, washed with cold 1-butanol and cold benzene, and air dried. *Anal.* Calcd for $C_8H_{11}N\cdot HCl$: Cl, 47.3. Found: Cl, 47.1.

Preparation of Halides.—Tungsten pentachloride was prepared by the disproportionation of tungsten tetrachloride.[15] The

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[1] Presented before the Division of Inorganic Chemistry at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 28–31, 1966, and abstracted in part from a thesis submitted by B. Ruble to the Graduate School of Arizona State University, Tempe, Ariz., 1966.

[2] R. E. McCarley and T. M. Brown, *Inorg. Chem.*, **3**, 1232 (1964).

[3] E. A. Allen, B. J. Brisdon, and G. W. A. Fowles, *J. Chem. Soc.*, 4531 (1964).

[4] W. M. Carmichael, D. A. Edwards, and R. A. Walton, *ibid.*, 97 (1966).

[5] D. A. Edwards and G. W. A. Fowles, *ibid.*, 24 (1961).

[6] B. J. Brisdon and G. W. A. Fowles, *J. Less-Common Metals*, **7**, 102 (1964).

[7] S. M. Horner and S. Y. Tyree, Jr., *Inorg. Chem.*, **2**, 568 (1963).

[8] D. M. Adams, J. Chatt, J. M. Davidson, and J. Ganalt, *J. Chem. Soc.*, 2189 (1962).

[9] B. J. Brisdon and R. A. Walton, *ibid.*, 2274 (1965).

[10] P. C. H. Mitchell and R. J. P. Williams, *ibid.*, 4570 (1962).

[11] E. A. Allen, B. J. Brisdon, D. A. Edwards, G. W. A. Fowles, and R. G. Williams, *ibid.*, 4649 (1963).

[12] P. C. H. Mitchell, *J. Inorg. Nucl. Chem.*, **25**, 963 (1963).

[13] F. D. Snell and C. T. Snell, "Colorimetric Methods of Analysis, Vol. II, 3rd ed, D. Van Nostrand Co., Inc., New York, N. Y., 1949, p 478.

[14] C. Norwitz, *Anal. Chem.*, **33**, 1253 (1961).

[15] T. M. Brown, unpublished doctoral thesis, Iowa State University for Science and Technology, Ames, Iowa, 1963, p 22.

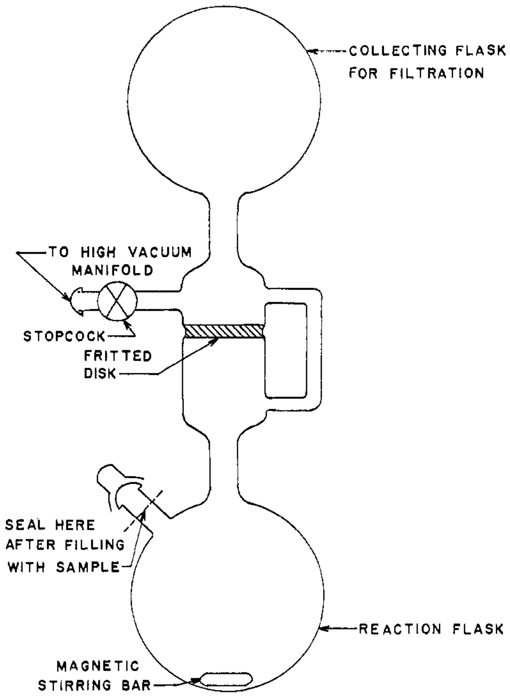

Figure 1.—Apparatus for the preparation of complexes.

material was identified by X-ray analysis and by tungsten determination. *Anal.* Calcd for WCl_5: W, 50.9. Found: W, 51.0.

Tungsten pentabromide was obtained by passing bromine over tungsten metal heated to 650°. Since the desired product was contaminated with tungsten(VI) bromide, repeated sublimation at 250° was necessary to purify the WBr_5. The excess bromine released during this decomposition of the tungsten(VI) bromide was trapped by means of a Dry Ice–acetone bath. X-Ray analysis and tungsten determination confirmed that pure pentabromide had been obtained. *Anal.* Calcd for WBr_5: W, 31.5. Found: W, 31.5.

Preparation of Complexes.—The reactions were carried out in the all-glass reaction vessel shown in Figure 1. This type of apparatus allowed for filtration and extraction of the product to be carried out in the same vessel. A finely ground sample of the pentahalide, typically 2–5 g, was placed in the reaction flask. The vessel and its contents were then outgassed on the vacuum line. Approximately a tenfold excess of ligand and 30–40 ml of dichloromethane were vacuum distilled into the vessel and the reaction was allowed to proceed with stirring for 75–100 hr at room temperature. At the end of the given time period, the reaction mixture was filtered by inverting the vessel and the solid product was continuously extracted with dichloromethane for 6–10 hr. The residue was vacuum dried at *ca.* 10^{-5} mm for at least 24 hr. This procedure was found to be desirable as it was noted that in some of the reactions with excess ligand, undesirable side reactions occurred after prolonged reaction times of approximately 1 week. Analytical data for the resulting compounds are given in Table I.

Table I

Analytical Data of Molybdenum(V) and Tungsten(V) Complexes

Complex	% calcd M	X	C	H	N	% found M	X	C	H	N	Oxidn state	Color
$MoCl_5(C_8H_{11}N)_2$	18.6	34.4	37.3	4.3	5.4	18.4	34.2	...	...	5.4	...	Red
$WCl_5(C_8H_{11}N)_2$	30.5	29.4	31.8	3.7	4.6	30.7	29.8	31.3	3.6	4.5	...	Gray
$WBr_5(C_8H_{11}N)_2$	22.2	48.4	23.3	2.7	3.4	22.1	48.8	23.0	2.8	3.5	...	Green
$WCl_5(C_7H_5N)_2$	32.4	31.3	29.6	1.8	4.9	32.3	31.2	29.7	1.9	4.9	5.1	Yellow
$WBr_5(C_7H_5N)_2$	23.3	50.6	21.3	1.3	3.5	23.4	50.4	21.2	1.4	3.4	5.0	Red-brown

Physical Measurements.—Spectral and conductivity measurements were carried out by methods previously described.[16] Nuclear magnetic resonance spectra were obtained from a Varian A-60 using deuterated dimethyl sulfoxide as a solvent. For magnetic susceptibility data, a powdered sample was placed in a Teflon container 13 mm long and 7 mm in diameter. Magnetic susceptibility measurements were made at room temperature using a Faraday balance. Correction for the diamagnetism of the Teflon container was made in all cases.

Stability Determination.—The stability of a typical complex with respect to temperature was determined by placing a small amount of the complex in an L-shaped tube in the drybox. The tube was evacuated and sealed off. The end containing the complex was placed in an oil bath while the opposite end was kept in a Dry Ice–acetone bath. The temperature of the bath was slowly increased and the volatile substances were collected.

Results and Discussion

The solids $WX_5(C_7H_5N)_2$ and $WX_5(C_8H_{11}N)_2$, where X = Cl or Br, were obtained from the reactions of the pentahalides and the corresponding ligand in dichloromethane at room temperature. Only in the reaction of molybdenum pentachloride with 2,4,6-trimethylpyridine was an analogous +5 molybdenum complex obtained. In the presence of benzonitrile, molybdenum pentachloride was observed to undergo reduction, the ultimate product being $MoCl_4(C_7H_5N)_2$. During the course of this reaction, the solution became quite warm and the evolution of HCl was observed. Analysis and equivalent weight determinations confirmed the presence of the molybdenum(IV) diadduct. Considering the reduction of molybdenum pentachloride with other aromatic compounds,[17] one might expect either 4-chlorobenzonitrile or 4,4′-dicyanobiphenyl as the oxidation product. The higher oxidation states of tungsten are, in general, more stable than the corresponding oxidation states of molybdenum so that the above reduction was not completely unexpected.

The +5 oxidation state for tungsten in the benzonitrile complexes was confirmed from equivalent weight data. Although a number of methods for determining the equivalent weight of the 2,4,6-trimethylpyridine complexes were tried, none was successful owing to the oxidation of the 2,4,6-trimethylpyridine by the oxidizing agent. Strong oxidizing agents such as permanganate have been shown to oxidize the methyl groups to carboxyl groups.[18] Analysis of the compounds indicated the presence of two coordinated 2,4,6-trimethylpyridine ligands. If reduction of the metal had occurred during the reaction, one would expect to find

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(16) T. M. Brown and G. S. Newton, *Inorg. Chem.*, **5**, 1117 (1966).

(17) M. L. Larson and F. W. Moore, *ibid.*, **5**, 801 (1966).

(18) E. Klingsberg, Ed., "Pyridine and its Derivatives," Interscience Publishers, Inc., New York, N. Y., 1961, Part 2, p 184.

any of a number of possible oxidation products of the 2,4,6-trimethylpyridine. That none was present in the reaction product was verified from infrared and nuclear magnetic resonance data. The infrared spectra of the complexes were in agreement with that expected for coordinated 2,4,6-trimethylpyridine. In addition, nmr data indicated the expected number of methyl groups attached to the pyridine ring for 2,4,6-trimethylpyridine.

Magnetic Susceptibility.—The magnetic moments of the various compounds (Table II) are somewhat lower than the spin-only value for a d^1 system, but are similar to values reported for other Mo(V) and W(V) complexes.[19]

TABLE II

MAGNETIC PROPERTIES OF MOLYBDENUM(V) AND TUNGSTEN(V) COMPLEXES

Compd	Temp, °K	$10^6\chi'_M$	μ_{eff}, BM
$MoCl_5(C_8H_{11}N)_2$	297.7	837	1.41
$WCl_5(C_8H_{11}N)_2$	297.3	777	1.36
$WBr_5(C_8H_{11}N)_2$	295.6	888	1.45
$WCl_5(C_7H_5N)_2$	295.4	167	0.63
$WBr_5(C_7H_5N)_2$	294.4	684	1.27

Stability.—The 2,4,6-trimethylpyridine complexes were not particularly stable at higher temperatures. At 60°, $MoCl_5(C_8H_{11}N)_2$ began to decompose giving rise to a small amount of 2,4,6-trimethylpyridine. At 100°, reduction of the complex was observed along with the formation of a white volatile material which was shown by infrared data to be the hydrochloride salt of 2,4,6-trimethylpyridine.

Conductivity.—The compounds were only slightly soluble in the more common organic solvents such as acetonitrile, benzene, chloroform, dichloromethane, and nitromethane. Nevertheless, it was possible to recrystallize small amounts of these compounds unchanged from dichloromethane. The conductivities of the compounds (Table III) indicate that the molybdenum(V) and tungsten(V) complexes most likely exist as 1:1 electrolytes in nitromethane. On this basis we have proposed structures of the type $[MX_4L_2]X$ for these compounds in which the metals are six-coordinate. It is, of course, not possible at this time to classify these compounds unambiguously as containing six-coordinate molybdenum or tungsten. However, additional coordination through halogen bridging is unlikely in the presence of good electron donors such as 2,4,6-trimethylpyridine and benzonitrile.

Spectra.—The infrared results obtained for these compounds over the range 600–4000 cm^{-1} indicated peaks typical of the coordinated ligands and provided no evidence for structures other than those in which the ligands are coordinated to the metal(V) halide; thus the absence of the broad band between 2200 and 3000 cm^{-1}, typical of the hydrohalide salt of 2,4,6-trimethylpyridine, in the 2,4,6-trimethylpyridine compounds completely eliminates the possibility of 2,4,6-trimethylpyridinium cations as being present. Shifts toward higher frequencies of 40 and 30 cm^{-1} for the $WCl_5(C_7H_5N)_2$ and $WBr_5(C_7H_5N)_2$ complexes, respectively, of the infrared-active C–N stretching frequencies were in accord with that expected for the coordinated benzonitrile[20] and also indicated that little or no π bonding takes place from nitrile to metal. Such an interaction would be expected to cause a shift to lower frequencies. At high resolution, the C–N stretching frequency for $WBr_5(C_7H_5N)_2$ was resolved into two peaks. Walton[21] has indicated that this splitting may be indicative of a *cis* configuration. The absence of a strong band in the 900–1000-cm^{-1} region eliminates any possibility of M=O species being present in the compounds.

TABLE III

CONDUCTIVITY DATA FOR MOLYBDENUM(V) AND TUNGSTEN(V) COMPLEXES IN NITROMETHANE AT 25°

Compd	Concn, *M*	Λ_M, cm^2 mole^{-1} ohm^{-1}
$MoCl_5(C_8H_{11}N)_2$	1.80×10^{-3}	65.6
$WCl_5(C_8H_{11}N)_2$	2.30×10^{-3}	60.0
$WBr_5(C_8H_{11}N)_2$	1.37×10^{-3}	75.9
$WCl_5(C_7H_5N)_2$	1.35×10^{-3}	98.5
$WBr_5(C_7H_5N)_2$	5.79×10^{-4}	60.6
$(C_2H_5)_4NBr^a$	9.80×10^{-4}	103

[a] 1:1 electrolytes, such as $(C_2H_5)_4NI$, generally have Λ_M of 80–100 cm^2 ohm^{-1} mole^{-1} in this solvent: N. S Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959).

The visible and ultraviolet spectra (Table IV) of the complexes are very complex. The spectra of these compounds in nitromethane and acetonitrile were essen-

TABLE IV

VISIBLE AND ULTRAVIOLET SPECTRA OF MOLYBDENUM(V) AND TUNGSTEN(V) COMPLEXES

Complex	Conditions	Peak positions, cm^{-1} (extinction coefficients in parentheses)
$[MoCl_4(C_8H_{11}N)_2]Cl$	Solid	18,900, 22,000, 32,400, 37,000
	Nitromethane	19,200 (260), 21,700 (280)
$[WCl_4(C_8H_{11}N)_2]Cl$	Solid	18,200, 28,600 sh, 31,800, 36,900
	Nitromethane	17,700 (140), 26,300 sh (500)
$[WBr_4(C_8H_{11}N)_2]Br$	Solid	18,900, 23,400, 27,300, 31,400, 37,000
	Nitromethane	18,900 (100), 22,700 (731), 25,300 (1450)
$[WCl_4(C_7H_5N)_2]Cl$	Solid	16,700, 23,300, 26,200, 29,400, 33,500, 35,800, 37,200, 37,700, 43,900
	Acetonitrile	16.900 (700), . . . , 25,800 (4100), 29,500 (5100), 33,600 (6000)
$[WBr_4(C_7H_5N)_2]Br$	Solid	16,100, 19,200, 21,300, 25,100, 35,800, 37,200, 37,700, 43,900
	Acetonitrile	16,500 (250), 18,800 (700), 20,800 (1600), 24,900 (2600), 30,000 (5400), 36,100 (9300), 37,000 (8900)

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(19) B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers Ltd., London, 1960, pp 444–445.

(20) H. J. Colver and C. Curran, *J. Am. Chem. Soc.*, **80**, 3522 (1958).

(21) R. A. Walton, *Quart. Rev.* (London), **18**, 126 (1964).

tially identical with the diffuse reflectance spectra of the solid compounds, suggesting that similar species are present in the solid and in solution. A slight decrease in the intensity of the peaks occurred over a period of time which may have been due to dissociation of the complex ion in nitromethane. Addition of ligand to the solutions suppressed the change in spectra. No change was observed in the conductance of these solutions indicating that, if dissociation occurs, it probably involves the coordinated nitrogen ligand. One might consider assigning the first two bands to the $^2E_g \rightarrow {}^2A_{1g}$ and $^2E_g \rightarrow {}^2B_{1g}$ ligand field transitions expected for a tetragonal distortion. The extinction coefficients however are much higher than those expected for simple d–d transitions. This may be an indication that there is some degree of ligand–metal orbital overlap involved which obscures the distinction between d–d transitions and charge transfer. The remaining bands are undoubtedly charge transfer in nature and it is not possible at this time to make any detailed assignments. The high-energy bands at 35,800, 37,200, and 43,900 cm^{-1} in the benzonitrile complexes can be attributed to charge transfer within the ligand as can the band at 37,000 cm^{-1} in the 2,4,6-trimethylpyridine complexes.[22]

Acknowledgment.—We wish to thank the National Science Foundation for financial support of this research under Grant No. GP-3810.

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(22) P. M. Boorman, N. N. Greenwood, M. A. Hildon, and R. V. Parish, *Inorg. Nucl. Chem. Letters*, **2**, 377 (1966), have recently reported the preparation of $[WCl_4(dipy)^+]Cl^-$, which supports our results on the formation of stable +5 compounds.

Contribution from the Department of Chemistry, Indiana University, Bloomington, Indiana, and the Mellon Institute, Pittsburgh, Pennsylvania

Interpretation of the Spectra of Cyanoaquo Complexes of Chromium(III) by the Theory of Noncubic Ligand Fields[1]

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Received November 21, 1966

The visible and ultraviolet absorption spectra of a series of mixed cyanoaquo complexes of chromium(III) are measured and resolved by Gaussian analysis. The complexes studied include $Cr(CN)_5(H_2O)^{2-}$, *cis*-$Cr(CN)_4(H_2O)_2^-$, *cis*-$Cr(CN)_3(H_2O)_3$, *cis*-$Cr(CN)_2(H_2O)_4^+$, and $Cr(CN)(H_2O)_5^{2+}$, all of which have been isolated and characterized in this laboratory. The parent complex ions of the series, $Cr(CN)_6^{3-}$ and $Cr(H_3O)_6^{3+}$, have also been included in this study for comparison. The ligand field theory of cubic and noncubic fields, in the strong-field formalism and in the limit of zero spin–orbit interaction, is applied to interpret and assign the observed absorption bands of the spectra of these systems. The bands in the absorption spectrum of the trisubstituted complex do not show splittings and hence can be interpreted on the basis of ligand fields of pseudo-cubic symmetry. The observed bands are nevertheless assigned the trigonal symmetry designations, and the energies of the absorption maxima are in agreement with those of the calculated trigonal levels using axial ligand field parameters of small magnitude. The spectra of the monosubstituted complexes, $Cr(CN)_5(H_2O)^{2-}$ and $Cr(CN)(H_2O)_5^{2+}$, are treated on the basis of axial perturbations applied to the cubic field potentials of their parent ions, $Cr(CN)_6^{3-}$ and $Cr(H_2O)_6^{3+}$, respectively. The *cis* complexes, $Cr(CN)_4(H_2O)_2^-$ and $Cr(CN)_2(H_2O)_4^+$, are similarly treated in relation to their parent molecule of pseudo-cubic symmetry, *cis*-$Cr(CN)_3(H_2O)_3$. The $^4T_{2g}$ cubic band splits into two well-defined components in the penta- and the dicyano complexes, while in the monocyano species the splitting of this band is manifested only by appreciable asymmetric broadening. These components are given tetragonal assignments, and the Dt value has been evaluated by fitting to be -300 cm^{-1} for the substitution of CN^- by H_2O, and $+300$ cm^{-1} for the reverse substitution. With a Dt value of appropriate sign and a consistent set of parametric values for B, C, Dq, and κ $(= Ds/Dt)$, the remaining portions of these spectra and the spectrum of *cis*-$Cr(CN)_4(H_2O)_2^-$ are interpreted. Alternate assignments are found to be possible for the components of the second cubic band. Since *cis*-disubstituted complexes are monosubstituted derivatives of the pseudo-cubic, symmetrically trisubstituted *cis* complex, justification is provided for treating them under tetragonal fields on the basis of the crystal-field model. This treatment in turn leads to some interesting predictions of spectral relations for the *cis* and *trans* isomers of d^3 complexes which can serve as spectral criteria for distinguishing between such isomers. The spectra of the known *cis–trans* pairs of Cr(III) complexes conform to these predictions.

I. Introduction

The ligand field theory has been used successfully for the interpretation of the magnetic and spectral phenomena of transition metal complexes in cubic symmetry. The optical spectra may be favorably described in terms of a single ligand field parameter, Dq, in addition to the Racah electron correlation parameters, A, B, and C. These are generally viewed as empirical parameters to be determined from experimental spectra. In ligand fields of symmetries lower than cubic, such as tetragonal and trigonal, which can arise by the superposition of an axial perturbation along the 4-fold or the 3-fold axis of an octahedral potential, two additional parameters, $D\mu$ $(\mu = s, \sigma)$ and $D\nu$ $(\nu =$

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[1] (a) This work was supported in part by the U. S. Atomic Energy Commission under Contract No. AT(11-1)-256 (Document No. COO-256-63). (b) Presented in part before the Division of Inorganic Chemistry at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966, at the 9th International Conference on Coordination Chemistry, St. Moritz-Bad, Switzerland, Sept 1966, and at the 153rd National Meeting the American Chemical Society, Miami Beach, Fla., April 1967.

[2] (a) Taken in part from a thesis submitted by R. Krishnamurthy to the Graduate School of Indiana University in partial fulfillment of the requirements for the Ph.D. degree in Chemistry, 1966. (b) Indiana University. (c) Mellon Institute.