

TABLE V
RESULTS OF TRACER EXPERIMENTS ON REACTION OF
THALLIUM(I) AND OZONE

Medium	E_{solid}	E_{soln}^b	No. of O per Tl_2O_3 from	
			Solvent	Ozone
Strongly alk.	6.614	7.265	2.59	0.31
Init. neut. to strongly acid	3.981	7.361	1.41	1.59
Acetate buffer ^a	3.962	7.651	1.57	1.43
Acetate buffer ^a	4.243	6.651	1.72	1.28

^a Initially, 0.2 *F* Tl(I), 0.3 *F* HOAc, 0.3 *F* OAc⁻, 0.4 *F* SO₄²⁻; after reaction, 0.5 *F* HOAc, 0.1 *F* OAc⁻, 0.4 *F* SO₄²⁻. ^b Corrected for isotope fractionation during equilibration.

thallium(III) oxide that results from oxidation with ozone in the latter two instances appears more crystalline than the slime-like gel that results from the reac-

tion in strongly basic solution. Table V presents results of these tracer experiments.

The experiments show that transfer takes place also when Tl⁺ is oxidized by O₃. In view of the fact that the oxide appears to be hydrous, and this affords opportunity for dilution by solvent oxygen of the oxygen transferred from O₃, it is remarkable that the observed transfer is as large as it is, and it is not impossible that it corresponds to one O for each Tl⁺ oxidized.

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A Crystal Field Model for the Spectral Relationships in Monoacidopentaammine and Diacidotetraammine Complexes of Cobalt(III)^{1a}

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The observed spectral band splittings of some monoacidopentaammine and *trans*-diacidotetraamminecobalt(III) complexes are reviewed and interpreted in terms of crystal field theory. It is shown that the ligand field strength of an acido group in a tetragonal complex may be measured in terms a new empirical parameter Dt' , which is related in turn to the octahedral field strength Dq of the acido group. Analysis of available spectral data shows that Dt' and hence Dq values of a given acido group are constant to within 5 to 10% irrespective of the compound. A similar analysis of spectral data for some chromium(III) complexes is presented. The possibility of a spectral "trans effect" is discussed.

The spectra of monoacidopentaammine and *trans*-diacidotetraammine complexes of trivalent cobalt have been the subject of numerous studies from which have emerged several empirical relationships concerning band splittings as a function of the ligands.²⁻¹²

Various complementary theoretical interpretations have been offered. Moffitt and Ballhausen¹³ have given the matrix elements for the tetragonal perturbation in terms of the crystal field model which they used qualitatively to predict the signs of the tetragonal splittings. Furthermore, they have discussed the

polarized crystal spectrum of $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}\cdot\text{HCl}\cdot 2\text{H}_2\text{O}$ and tentatively assigned the observed transitions on the basis of a vibrational analysis.

The qualitative aspects of molecular orbital theory for such compounds were first pointed out by Griffith and Orgel.¹⁴ They suggested for *trans*-dichlorotetraammine compounds that the one-electron octahedral level e_g ought to split with $E(x^2 - y^2) > E(3z^2 - r^2)$ in either theory. However, for the t_{2g} level the molecular orbital theory predicts $E(xz, yz) > E(xy)$ on account of the π -antibonding effect of the chloride anion. This is just the opposite order from that predicted by naïve crystal field theory since the ammonia groups have a greater crystal field than the chloride ion leading to the prediction $E(xy) > E(xz, yz)$. However, as we shall see, the formal crystal field theory can accommodate either ordering when empirical parameters are used.

Yamatera¹⁵ in his pioneering paper has provided a thorough treatment of both the crystal field and molecular orbital models for CoA_6 , CoA_5L , CoA_4L_2 , and CoA_3L_3 compounds. He suggested a molecular orbital

(1) (a) Supported by the National Science Foundation and Alfred P. Sloan Foundation; (b) Alfred P. Sloan Foundation Fellow.

(2) M. Linhard and M. Weigel, *Z. anorg. allgem. Chem.*, **264**, 321 (1951).

(3) M. Linhard and M. Weigel, *ibid.*, **266**, 49 (1951).

(4) M. Linhard and M. Weigel, *ibid.*, **267**, 113 (1951).

(5) M. Linhard and M. Weigel, *ibid.*, **267**, 121 (1951).

(6) M. Linhard and M. Weigel, *ibid.*, **271**, 101 (1952).

(7) M. Linhard and M. Weigel, *Z. physik. Chem. (Frankfurt)*, **11**, 308 (1957).

(8) S. Yamada, A. Nakahara, Y. Shimura, and R. Tsuchida, *Bull. Chem. Soc. Japan*, **28**, 222 (1955).

(9) F. Basolo, C. J. Ballhausen, and J. Bjerrum, *Acta Chem. Scand.*, **9**, 810 (1955).

(10) F. Basolo, *J. Am. Chem. Soc.*, **72**, 4393 (1950).

(11) J. Fujita and Y. Shimura, *Bull. Chem. Soc. Japan*, **36**, 1281 (1963).

(12) T. Yasui and Y. Shimura, *ibid.*, **36**, 1286 (1963).

(13) W. Moffitt and C. J. Ballhausen, *J. Inorg. Nucl. Chem.*, **3**, 178 (1956).

(14) J. S. Griffith and L. E. Orgel, *J. Chem. Soc.*, 4981 (1956).

(15) H. Yamatera, *Bull. Chem. Soc. Japan*, **31**, 95 (1958).

scheme involving σ and π empirical parameters. However, his crystal field calculation suffered from an attempt to use Slater free ion radial wave functions and ligand dipole moments. It is now well known that this approach fails and that a more profitable path is to regard the crystal field radial parameters as empirical. McClure¹⁶ has also contributed an empirical molecular orbital approach which considers the tetragonal splittings of the excited states in terms of the σ - and π -antibonding energies of the d orbitals, and is equivalent to the method of Yamatera.

In this paper we report an exploration of the crystal field model using empirical radial parameters in order to test their reliability and value in interpreting the observed spectral splittings.

Experimental Observations

The spectrum of the parent octahedral complex, $\text{Co}(\text{NH}_3)_6^{3+}$, is characterized by two bands in the visible and near-ultraviolet which can be assigned unequivocally to ${}^1\text{T}_1$ and ${}^1\text{T}_2$ states, respectively. In the spectra of related monoacidopentaammine or *trans*-diacidotetraammine complexes, splitting of the low-energy band can be observed if the axial ligand is well-separated from ammonia in the spectrochemical series. In the notation of Linhard and Weigel, the bands are labeled IA, IB, and II in order of increasing energy. If, however, the separation is not very large, only a band shift or broadening is observed. In no instance has splitting of the high energy band been observed, although it may well be masked by the onset of charge-transfer transitions.

Some of the more interesting and pertinent observations are those of Linhard and Weigel.^{2,4} From a study of a series of complexes of the types $\text{Co}(\text{NH}_3)_5\text{L}$ and *trans*- $\text{Co}(\text{NH}_3)_4\text{L}_2$, they have shown that the band IB has approximately the same energy as the first spin-allowed band in the parent compound $\text{Co}(\text{NH}_3)_6^{3+}$. Further, the splitting of IA and IB is approximately twice as large in the *trans*-diacidotetraammine complexes as in the monoacidopentaammines, and the wave number of the IA band maximum increases monotonically for the uninegative ligands in the order I, N_3 , Br, Cl, F, NCS, and NO_2 , *i.e.*, the standard spectrochemical series.

The Crystal Field Parameters

Within the formalism of crystal field theory, the energies of the lowest-lying singlet and triplet states above the ground state (Figure 1) for a d^6 ion in a strong octahedral field are

$$E({}^1\text{T}_2) - E({}^1\text{A}_1) = 10Dq + 16B - C \quad (1a)$$

$$E({}^1\text{T}_1) - E({}^1\text{A}_1) = 10Dq - C \quad (1b)$$

$$E({}^3\text{T}_2) - E({}^1\text{A}_1) = 10Dq + 8B - 3C \quad (1c)$$

$$E({}^3\text{T}_1) - E({}^1\text{A}_1) = 10Dq - 3C \quad (1d)$$

where B and C are the electronic mutual repulsion

(16) D. S. McClure, "Advances in the Chemistry of Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, p. 498.

parameters. The wave numbers of the strong singlet bands are generally used to solve for Dq with the assumption that the ratio B/C has the free-ion value. In the calculations of succeeding sections we will use rather the wave numbers of the ${}^1\text{T}_1$ and ${}^3\text{T}_1$ bands to obtain Dq . Lowering the symmetry to tetragonal acentric (C_{4v}) or tetragonal centric (D_{4h}) will partially lift the degeneracy of these excited states as shown in Figure 1.¹⁷ The energies of the singlets above the ground state are then to a first-order approximation

$$E({}^1\text{E}^b) - E({}^1\text{A}_1) = 10Dq + 2Ds - 25/4Dt + 16B - C \quad (2a)$$

$$E({}^1\text{B}_2) - E({}^1\text{A}_1) = 10Dq - 4Ds - 5Dt + 16B - C \quad (2b)$$

$$E({}^1\text{A}_2) - E({}^1\text{A}_1) = 10Dq - C \quad (2c)$$

$$E({}^1\text{E}^a) - E({}^1\text{A}_1) = 10Dq - 35/4Dt - C \quad (2d)$$

For the sake of completeness, we also give the matrix element

$$\langle {}^1\text{E}^a | V_{\text{T}} | {}^1\text{E}^b \rangle = -\sqrt{3}(Ds - 5/4Dt)$$

although we shall not need it in much of the development that follows.

We define Dq as $1/6\rho_4^{xy}$,¹⁸ and take the radial parameters ρ_n as empirical. Note that Dq depends only on the in-plane field strength. We see, then, that $Dq(\text{O}_h) = Dq(\text{C}_{4v} \text{ or } \text{D}_{4h})$ when comparing the field strengths of $\text{Co}(\text{NH}_3)_6^{3+}$ and $\text{Co}(\text{NH}_3)_5\text{L}$ or *trans*- $\text{Co}(\text{NH}_3)_4\text{L}_2$. The parameters Ds and Dt have been previously defined in the tetragonal centric field¹⁹ as

$$Ds = 2/7(\rho_2^{xy} - \rho_2^z)$$

$$Dt = 2/21(\rho_4^{xy} - \rho_4^z)$$

and in the acentric field as²⁰

$$Ds = 1/7(2\rho_2^{xy} - \rho_2^{z+} - \rho_2^{z-})$$

$$Dt = 1/21(2\rho_4^{xy} - \rho_4^{z+} - \rho_4^{z-})$$

Note that for the monoacidopentaammines, where the symmetry is C_{4v} , $\rho_n^{xy} \approx \rho_n^{z-}$ and the expressions reduce to

$$Ds = 1/7(\rho_2^{xy} - \rho_2^{z+})$$

$$Dt = 1/21(\rho_4^{xy} - \rho_4^{z+})$$

We now have the relationships

$$Ds(\text{D}_{4h}) = 2Ds(\text{C}_{4v}) \quad (3a)$$

$$Dt(\text{D}_{4h}) = 2Dt(\text{C}_{4v}) \quad (3b)$$

(17) Throughout the text we have, for simplicity, neglected the customary group theoretical notation g which is affixed as a subscript to the irreducible representation in the centric point groups O_h and D_{4h} .

(18) In this and subsequent definitions, recall that

$$\rho_n^{xy \text{ or } z} = eq(r^n/R^{n+1})_{av}$$

where e and r are the electronic charge and radius, while q and R are the effective ligand charge and distance from the metal, respectively. The superscripts refer to the coordinate axes on which the ligands are placed. The acido ligands are always placed on the z axis.

(19) T. S. Piper and R. L. Carlin, *J. Chem. Phys.*, **33**, 1208 (1960).

(20) R. A. D. Wentworth and T. S. Piper, *ibid.*, **41**, 3884 (1964).

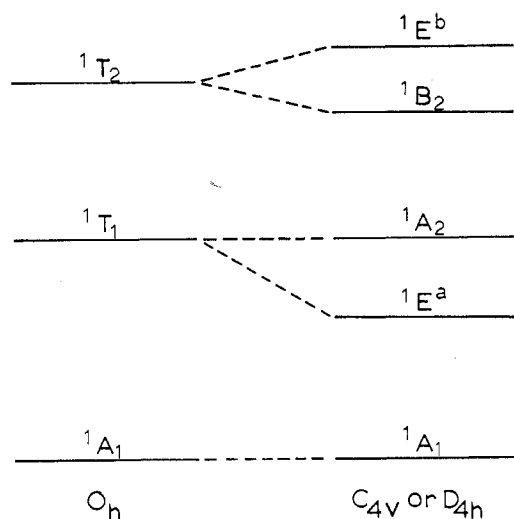


Figure 1.—Tetragonal splitting of the excited states of cobalt(III). The relative ordering of the tetragonal components is explained within the text.

which can be used to compare spectral properties of $\text{Co}(\text{NH}_3)_5\text{L}$ and *trans*- $\text{Co}(\text{NH}_3)_4\text{L}_2$ complexes.

In order to make further progress we will next assume that the radial crystal field parameters are characteristic of a given ligand irrespective of the particular substituted complex ion in which it is found. Then Dt for our cobalt complexes may be expressed in terms of the Dq values

$$Dt(C_{4v}) = 2/7(Dq^{xy} - Dq^{z^2}) \quad (4a)$$

$$Dt(D_{4h}) = 4/7(Dq^{xy} - Dq^{z^2}) \quad (4b)$$

These equations provide an efficient means of comparing the field strength of a ligand L in the complexes CoA_5L , *trans*- CoA_4L_2 , and CoL_6 .

Now returning to the equations for the d^6 configuration, we can see that the splitting of the 1T_1 state depends upon Dt alone with the approximation that interaction between the ${}^1E^a$ and ${}^1E^b$ levels under the tetragonal field is neglected. These observations suggest that we may define a useful empirical parameter Dt' by the equation

$$Dt' = -4/35[W - (10Dq - C)_{xy}] \quad (5)$$

where W is the energy $E({}^1E^a) - E({}^1A_1)$. The prime is added to indicate that this parameter is an approximation to Dt inasmuch as the off-diagonal tetragonal matrix element is neglected. Furthermore, as we shall see, it will be convenient to take the quantity $(10Dq - C)_{xy}$ from the parent octahedral complex, a procedure which entails the further approximation that C is constant irrespective of substitution of the parent octahedral complex. Finally, values of Dq calculated from Dt' and eq. 4 will also be indicated to be approximate with a prime as Dq' .

For the d^3 ion chromium(III) the splitting of the excited 4T_2 state is just that of the 1T_1 state of cobalt(III): $35/4Dt$. However, $10Dq$ may be taken directly from the wave number of the transition ${}^4A_2 \rightarrow {}^4T_2$.

The IA and IB Bands

We are now in a position to explain theoretically the observations of Linhard and Weigel. Note that the energy of the 1A_2 state is exactly that of its parent state in O_h symmetry. The parameter C is expected to change slightly, but it will be shown that this change will not significantly alter our results. In Table I (see next section) it can be seen that the energy of the IB band does not differ markedly from that of the first spin-allowed band in the parent compounds. Thus, we can confidently assign the IB band to the transition ${}^1A_1 \rightarrow {}^1A_2$ in the cases where the IA and IB bands are resolved. Furthermore, when the field strength of the axial ligand is less than that of the in-plane ligands, the energy of the ${}^1E^a$ state is less than that of the 1A_2 state. Therefore, the IA band is assigned to the transition ${}^1A_1 \rightarrow {}^1E^a$. These assignments are in full accord with the earlier ones.¹³⁻¹⁶ Since the splitting of the ${}^1E^a$ and 1A_2 states depends only on Dt in a first-order approximation, the energy separation of these states in *trans*-diacidotetraammines should be twice that in the monoacidopentaammines, in agreement with the experimental observation. In the cases where no splitting is observed, the shift of the band maximum from that in the parent compound is indicative of the relative position of the ${}^1E^a$ component. Support for this contention was provided in a recent study of the circular dichroism of the *trans* complex ions, $\text{Co}(l\text{-pn})_2\text{Cl}_2^+$ and $\text{Co}(l\text{-pn})_2(\text{NO}_2)_2^+$.²¹

Results

The experimental data on the IA, IB, and II bands of cobalt(III) complexes are given in Table I and those of chromium(III) are given in Table II.

The values of Dt' were calculated from the wave numbers of the maximum of band IA where it is resolved while the wave number of the transition ${}^1A_1 \rightarrow {}^1A_2$ was taken from that of the ${}^1A_1 \rightarrow {}^1T_1$ band of the parent hexaammine or analogous compound.

In order to extend the calculation to those cases in which the IA and IB bands are not resolved, an analysis of the intensity must be made. Two simple approximations are possible. In the first, which we have adopted in the calculations recorded in Tables I and II, the observed band maximum can be taken to be the average of the energy of the 1T_1 band of the parent compound and that of the ${}^1E^a$ state above the ground state. In the second approximation, the energy of the ${}^1A_1 \rightarrow {}^1E^a$ transition may be taken directly from the maximum of the unresolved band. The first approximation in effect assumes that the intensities of transitions to 1A_2 and ${}^1E^a$ states are equal. The second assumes that only the ${}^1E^a$ transition has appreciable intensity. The second approximation is supported for monoacido derivatives by the selection rules in C_{4v} , ${}^1A_1 \rightarrow {}^1E$ and ${}^1A_1 \rightarrow {}^1A_2$, which are valid only in the absence of a vibronic contribution to the intensity. Furthermore, these selection rules would not be expected to hold for a lower symmetry case

(21) R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 202 (1965).

TABLE I
ABSORPTION SPECTRA, SPLITTING PARAMETERS, AND VALUES OF Dq' FOR MONOACIDOPENTAAMMINE AND *trans*-DIACIDOTETRAAMMINE COMPLEXES OF COBALT(III)

Complex	Band maxima, $\text{cm.}^{-1} \times 10^3$			Ref.	Dt' , cm.^{-1}	Dq' , cm.^{-1} ^a
	IA	IB	II			
$\text{Co}(\text{NH}_3)_6^{3+}$		21.05	29.50	3	...	2490 (NH_3)
$\text{Co}(\text{NH}_3)_5\text{F}^{2+}$	19.45	21.47 ^g	28.27	3	183	1849 (F)
$\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$	18.72	21.35 ^g	27.50	3	266	1559 (Cl)
$\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$	18.23	21.95 ^g	Masked	3	321	1366 (Br)
$\text{Co}(\text{NH}_3)_5\text{I}^{2+}$	17.25	Masked	Masked	3	434	971 (I)
$\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$		20.3	30.3	3	172	1888 (H_2O)
$\text{Co}(\text{NH}_3)_5\text{NO}_2^{3+}$		21.84	30.80 ^g	4	-180	3120 (NO_2)
$\text{Co}(\text{NH}_3)_5\text{N}_3^{2+}$		19.28	27.0 ^g	5	404	1076 (N_3)
$\text{Co}(\text{NH}_3)_5\text{O}_2\text{C}_3\text{H}_5^{2+b}$	19.88	<i>c</i>	28.39	2	134	2021 ($\text{O}_2\text{C}_3\text{H}_5$)
$\text{Co}(\text{NH}_3)_5\text{CN}^{2+}$		22.70	30.56	<i>d</i>	-382	3817 (CN)
$\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$		20.7	27.0 ^g	5	80	2210 (NCS)
$\text{Co}(\text{NH}_3)_4\text{Cl}_2^+$	15.90	21.00	24.94	6	588	1461 (Cl)
$\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2^+$		22.72	28.82 ^g	4	-382	3152 (NO_2)
$\text{Co}(\text{NH}_3)_4(\text{N}_3)_2^+$		17.61	25.0 ^g	5	786	1114 (N_3)
$\text{Co}(\text{NH}_3)_4(\text{O}_2\text{C}_3\text{H}_5)_2^{2+b}$	18.12	21.80	27.36	2	335	1904 ($\text{O}_2\text{C}_3\text{H}_5$)
$\text{Co}(\text{en})_3^{3+}$		21.47	29.50	6	...	2530 (en)
$\text{Co}(\text{en})_2\text{F}_2^+$	17.20	22.62	27.60	6	488	1676 (F)
$\text{Co}(\text{en})_2\text{Cl}_2^+$	16.12	22.49 ^g	25.92 ^g	6	612	1459 (Cl)
$\text{Co}(\text{en})_2\text{Br}_2^+$	15.21	21.68 ^g	Masked	6	716	1277 (Br)
$\text{Co}(\text{en})_2(\text{H}_2\text{O})_2^{3+}$	18.2	22.5	29.0 ^g	<i>e</i>	374	1875 (H_2O)
$\text{Co}(\text{en})_2(\text{NCS})\text{Cl}^+$	17.8	22.4	Masked	6	419	2050 (NCS) ^f
$\text{Co}(\text{en})_2(\text{NO}_2)_2^+$		23.3	Masked	11	-418	3262 (NO_2)
$\text{Co}(\text{CN})_6^{3-}$		32.3	39.0	11	...	3600 (CN)

^a Values of Dq' were computed for the ligands indicated in parentheses (for octahedral complexes we list in this column Dq values).
^b $\text{O}_2\text{C}_3\text{H}_5$ = propionate. ^c Band maximum not given, although visually appears close to 21,000 cm.^{-1} . ^d H. Siebert, *Z. anorg. allgem. Chem.*, **327**, 63 (1964). ^e J. Bjerrum and S. E. Rasmussen, *Acta Chem. Scand.*, **6**, 1265 (1952). ^f Computed using $Dq'(\text{Cl}) = 1459$ cm.^{-1} and $Dq'(\text{en}) = 2530$ cm.^{-1} . ^g Shoulder.

TABLE II
ABSORPTION SPECTRA, SPLITTING PARAMETERS, AND VALUES OF Dq' FOR MONOACIDOPENTAAMMINE AND *trans*-DIACIDOTETRAAMMINE COMPLEXES OF CHROMIUM(III)^a

Complex	Band maxima, $\text{cm.}^{-1} \times 10^3$			Dt' , cm.^{-1}	Dq' , cm.^{-1} ^b
	IA	IB	II		
$\text{Cr}(\text{NH}_3)_6^{3+}$		21.5	28.49	...	2150 (NH_3)
$\text{Cr}(\text{NH}_3)_5\text{Cl}^{2+}$	19.4	22.1 ^c	26.6	240	1310 (Cl)
$\text{Cr}(\text{NH}_3)_5\text{NCS}^{2+}$		20.37	27.0 ^c	129	1700 (NCS)
$\text{Cr}(\text{en})_3^{3+}$		21.88	28.50	...	2188 (en)
$\text{Cr}(\text{en})_2\text{Cl}_2^+$	17.29	22.00	25.30	525	1272 (Cl)
$\text{Cr}(\text{en})_2(\text{H}_2\text{O})_2^+$	19.7	22.6	27.7	227	1790 (H_2O)
CrCl_6^{3-d}		13.18	18.70	...	1318 (Cl)
$\text{Cr}(\text{NCS})_6^{3-}$		17.7	23.6	...	1770 (NCS)
$\text{Cr}(\text{H}_2\text{O})_6^{3+}$		17.5	24.5	...	1750 (H_2O)

^a Except where indicated all spectral data taken from C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, London, 1962, p. 110. ^b Values of Dq' are for ligands indicated in parentheses. ^c Shoulder. ^d W. E. Hatfield, R. C. Fay, C. E. Pfluger, and T. S. Piper, *J. Am. Chem. Soc.*, **85**, 265 (1963).

such as $\text{Co}(\text{NH}_3)_5\text{NO}_2^{2+}$. Our analysis of the empirical data shows that internally consistent values of Dt' and Dq' are obtained only when the first approximation is used. Evidently vibronic contributions to the intensity are important. The values of Dq' calculated in this approximation are recorded in the tables.

For the parent octahedral compounds, Dq and C can be computed from eq. 1b and 1d providing the wave number of the 3T_1 band is known. For $\text{Co}(\text{NH}_3)_6^{3+}$, $\text{Co}(\text{en})_3^{3+}$, and $\text{Co}(\text{CN})_6^{3-}$, these are 13,400, 13,800, and 25,000²² cm.^{-1} , respectively. Furthermore, B can be computed from eq. 1a and 1b. Calculated values of Dq can be found in Table I under the column Dq' , while the values of B and C were found to be 528, 3825; 502, 3835; and 418, 3650 cm.^{-1} , respectively.

(22) These values taken from ref. 11.

(Note that C is remarkably constant over a large range of field strength.)

The reliability of the values of Dq' for the tetragonal complexes is best illustrated by an analysis of the errors. The error propagated in Dq' by inaccurate spectral measurement of the position of the ${}^1E^a$ band is obtained from eq. 4a or 4b and eq. 5 with the result

$$\Delta Dq' = 2/5\Delta W(C_{4v})$$

$$\Delta Dq' = 1/5\Delta W(D_{4h})$$

Therefore, the absolute value of Dq' for a given ligand will not be greatly effected by the error in wave numbers of the band maximum. This is important since we have used data from a number of different laboratories.

A more serious source of error could lie in the approximation that the intensities of the ${}^1E^a$ and 1A_2 bands are equal. In the cases where they are resolved, this is roughly true. However, in cases where the band envelopes are not sufficiently separated to permit resolution, more proof is needed. On this point our inchoate investigation of the polarized crystal spectra of monoacidpentaamminecobalt(III) salts has revealed that with $\text{Co}(\text{NH}_3)_5\text{NO}_2^{2+}$, where the bands are not resolved with unpolarized radiation, the 1A_2 band retains considerable intensity in parallel polarization.

Discussion

The constancy of Dq' values for any given ligand in the final column of Tables I and II is remarkably good. It is especially encouraging to note that the cyanide ion Dq value computed for $\text{Co}(\text{CN})_6^{3-}$ agrees within 6% to $Dq'(\text{CN})$ computed for $\text{Co}(\text{NH}_3)_5\text{CN}^{2-}$ and that the calculated values for water agree to within 3% to the value of 1820 cm^{-1} given by Jørgensen²³ for $\text{Co}(\text{H}_2\text{O})_6^{3+}$. Furthermore, when the empirical values of Dq' for chloride ion and ethylenediamine are used, a value for thiocyanate ion can be computed from the spectra of $\text{Co}(\text{en})_2(\text{NCS})\text{Cl}^+$ which agrees within 7% to that computed from $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$. Similar reliability of empirical radial parameters has been found in four-, five-, and six-coordinate chlorocuprates.^{24,25}

It is now evident that these excellent results require that the difference in C in the parent compounds and CoA_5L or $\text{trans-CoA}_4\text{L}_2$ be insignificant. We noted earlier that C is remarkably constant in the parent ammine and cyanide complexes, although these should represent a wide difference in the strength of covalent bonding in a molecular orbital sense. Consequently, one would expect little change in C from the parent ammine complex to $\text{Co}(\text{NH}_3)_5\text{CN}^{2+}$. Indeed, if it is assumed that the mutual repulsion parameter remains isotropic in the low symmetry field and that it can be approximated by averaging over the ligand field exerted on the electrons, then there is less than a 3% difference between the experimental value of C found for $\text{Co}(\text{NH}_3)_6^{3+}$ and one calculated for $\text{Co}(\text{NH}_3)_5\text{CN}^{2+}$.

The values of C for the parent compounds differ markedly from those of Griffith,²⁶ who assumed that C could be computed from the experimental value for B and a C/B ratio of 4.0. However, the experimental energies of the 3T_1 , 1T_1 , and 1T_2 bands make it clear that this approximation is not valid. In fact, the C/B ratio is very close to twice that assumed by Griffith. Where they can be obtained, empirical values for all crystal field parameters are preferable.

A Possible Spectral "trans Effect"

There are some small but undoubtedly significant differences in the Dq' values recorded for a given acidogroup. Comparing the Dq' values for the dihalotetra-

ammine compounds with those of the monohalopentaammine compounds we see that the latter are in every case 6 to 9% larger. We are tempted to attribute this to a "trans effect" and can cite some structural evidence in support. The crystal structure of $\text{Co}(\text{NH}_3)_5\text{Cl}_3^{27}$ indicates that the ammonia group *trans* to the chloro group has a bond distance some 0.06 Å shorter than the average for the *cis* ammonia groups. This difference in bond distance is significant. Shortening and consequent strengthening of the bond *trans* to a more weakly bonding group is to be expected from any simple model.

In our calculations we have assumed that all the ammonia groups have the same field strength. Since for the *trans* ammonia group it is in fact larger, this assumption has the effect of attributing too large a field strength to the halo groups in the pentaammine series.

Alternately one could postulate a polarization of the halide anion which would be larger in the pentaammine series and would also account for the increased field strength. Since both effects could operate simultaneously, it is difficult to assess the importance of either.

The only other crystal structure available to test the possibility of such a *trans* effect is that of $\text{Co}(\text{NH}_3)_5(\text{N}_3)^{28}$ but in this compound all ammonia groups are equidistant from the metal to within experimental error. In consonance with this observation, note the constancy of Dq' for the azido group.

Band II

The splitting of band II has never been observed. We may well ask if this is due to the onset of charge-transfer bands which might obscure the splitting or if it is a result of the ligand field. Let us examine the case of $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$, where the separation of band II and the onset of charge transfer is some 12,000 cm^{-1} .² No splitting is observed. The molecular orbital model of Yamatera¹⁵ suggests that for this case, the splitting of band II should be less than that of band I (2000 cm^{-1}). Unfortunately, the crystal field model makes no ready prediction since this splitting depends on Ds . We do know that the separation of the ${}^1E^b$ and 1B_2 states should be $6Ds = 5/4Dt$, and we also believe that Ds should be positive. Past experience^{19,23} has indicated that $\rho_2 \approx \rho_4$, leading to $Ds \approx 3Dt$. However, if this were the case, the total splitting of band II should be about 3000 cm^{-1} , a value greater than that observed for band I, and in contradiction to experimental observation. Such a choice would also lead to a different ordering of the one-electron xy and xz, yz orbitals than that qualitatively predicted by MO theory (Figure 2). Note, however, that the xy orbital can only lie at higher energy than the degenerate set xz, yz if the condition $3Ds - 5Dt > 0$ is met.¹⁹

In Figure 3 we plot the splitting of the ${}^1E^b$ (neglecting configurational interaction between ${}^1E^a$ and ${}^1E^b$) and

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$\frac{x^2-y^2}{6Dq + 2Ds - Dt}$	$\frac{x^2-y^2}{\quad\quad\quad}$
$\frac{3z^2-r^2}{6Dq - 2Ds - 6Dt}$	$\frac{3z^2-r^2}{\quad\quad\quad}$
$\frac{xy}{-4Dq + 2Ds - Dt}$	$\frac{xz, yz}{\quad\quad\quad}$
$\frac{xz, yz}{-4Dq - Ds + 4Dt}$	$\frac{xy}{\quad\quad\quad}$
(a)	(b)

Figure 2.—Qualitative ordering of the one-electron energy levels for $\text{Co}(\text{NH}_3)_6\text{F}^{2+}$. (a) Crystal field prediction with $3Ds - 5Dt > 0$; this ordering is also predicted by the qualitative argument that the field is greater in the xy plane than along the z axis. (b) Molecular orbital prediction based on the idea that fluoride ion has weaker σ -bonding power but stronger π -bonding power than ammonia.

1B_2 states as a function of D_s and utilizing the value $Dt' = 183 \text{ cm}^{-1}$ found from the splitting of band I. The ordinate is calibrated such that the zero of energy represents the band maximum of band II in $\text{Co}(\text{NH}_3)_6^{3+}$. It is now readily seen that any of a range of values of D_s from -150 to 250 cm^{-1} would probably satisfy the spectral observations. But the crystal field model indicates that we should choose D_s to be positive. Such a choice leads to $D_s < 5/3Dt$ and qualitative agreement with the MO ordering of one-electron orbitals. Furthermore, we can now understand that the decrease in wave numbers of band II from CoA_4 to CoA_5L or *trans*- CoA_4L_2 is caused by the tetragonal perturbation and not unexpectedly large changes in the mutual repulsion parameter B . This fact has not been previously explained.

Conclusion

Recently, crystal field theory has been freely criticized as devoid of physical reality except, of course, for those aspects which are dependent on symmetry alone. Simple molecular orbital models have been sought. However, these simple theories do not provide any clear-cut prescription for adjusting the required parameters and, hence, they may be used to rationalize widely disparate orderings of the energy levels.²⁹ Furthermore, for an analogous series of compounds, the hexaammines, it has been shown that no single set of rules for obtaining Coulomb and resonance integrals will lead to a uniformly good fit of the $3d$ orbital splitting.³⁰ Another important failure of the simple Hückel theory is its inability to account for splittings due to mutual repulsions of the electrons; for example, in the case of cobalt(III), the 3T_1 , 3T_2 , 1T_1 , and 1T_2 levels are predicted to be degenerate. The empirical molecular orbital models of Yamatera¹⁵ and McClure¹⁶ have promise. Unfortunately, we

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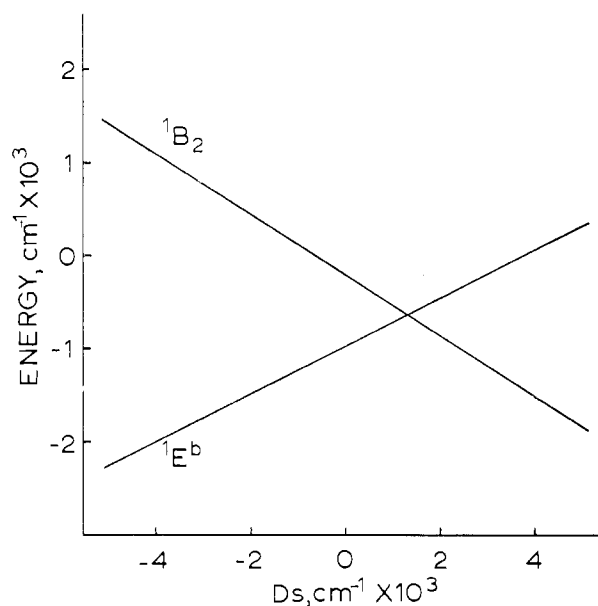


Figure 3.—Tetragonal splitting of the 1T_2 state for $\text{Co}(\text{NH}_3)_6\text{F}^{2+}$ as a function of D_s taking Dt to be 183 cm^{-1} . The zero of energy on the ordinate is the energy of the 1T_2 state for $\text{Co}(\text{NH}_3)_6^{3+}$.

have not been able to obtain reliable values of the σ and π parameters for cobalt(III) complexes because experimental splittings of both 1T_1 and 1T_2 states are required while we have at hand only the splitting of the 1T_1 state.

In view of these manifold difficulties with the available molecular orbital theories, we suggest that the capabilities and limitations of crystal field theory should be further explored.

In this article, we have demonstrated the utility of crystal field theory in analyzing tetragonal splittings of the spectroscopically accessible 1T_1 state of cobalt(III) and the 4T_2 state of chromium(III). We have shown that this splitting depends to an excellent approximation on only the fourth power radial parameter of the axial ligand. Thus, these splittings may be expressed in terms of Dq values of the axial ligands—a result which apparently does not follow directly from current molecular orbital theories. Empirical data on a number of complexes indicate that these values of Dq characteristic of a given ligand may be carried over from compound to compound with an accuracy of better than 10%. At the very least, a consideration of these findings will lead to the correct assignment of excited states.

In conclusion, we believe that crystal field theory will continue to enjoy wide application by chemists interested in the spectroscopy of coordination compounds, since molecular orbital theory is tedious of application and, in its present form, rife with parameters whose adjustment is dubious at best.³¹

(31) NOTE ADDED IN PROOF.—After the submission of this paper we devised an empirical molecular orbital approach which indicates that to a good approximation the splitting of the 1T_1 state depends only on $\delta\Delta$, the difference of octahedral field strengths of the axial and in-plane ligands. For example, we find that in the monoacido compounds $E({}^1E^b) - E({}^1A_2)$ is $5/2(Dq^L - Dq^A)$ or $1/4\delta\Delta$. Details of this method and its implications will be submitted for publication shortly.