Polarized Electronic Spectra of Quadrate Chromium(III) Complexes*

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Polarized electronic spectra of single crystals of mixed trans-diacidobis(ethylenediamine)chromium(III) complexes, where the diacido groups are aquohydroxy, aquofluoro, aquochloro, aquobromo, and bromochloro, have been measured at liquid nitrogen temperature. On the basis of polarization characteristics, the observed quartet bands have been given definite quadrate assignments. The band maxima have been fitted with the theoretical energy equations of d^3 configuration immersed in tetragonal ligand field including full configuration interaction but neglecting spin-orbit perturbation. The Dq, Dt, x parameters of the ligand field and the B parameter of the electron correlation have been evaluated by such a fitting and compared with those obtained earlier by us and others for the other trans-diacido systems. A rich doublet structure was uncovered in the 14,000-16,000 cm^{-1} region for the aquofluoro complex and in the 21,000 cm^{-1} region for the aquobromo complex. The doublet bands in the 21,000 cm^{-1} region have been uncovered for the other systems also.

Introduction

The only tetragonal chromium(III) systems on which polarized electronic spectral data have been reported are three acidopentammines[1] and four trans diacidobisethylenediamines.[2-5] The acidopentammines are $[Cr(NH_3)_5Cl]SiF_6$, $[Cr(NH_3)_5Br]SiF_6$, and $[Cr(NH_3)_5F](ClO_4)_2$. The trans diacido systems include the dichloro $([Cr(en)_2Cl_2]Cl . HCl . 2H_2O,$[2] $[Cr(en)_2Cl_2]ClO_4$,[4,5]), difluoro $[Cr(en)_2F_2]ClO_4$,[3] dibromo $([Cr(en)_2Br_2]ClO_4$,[4] $[Cr(en)_2Br_2]Br . H_2O$[5]), and the diaquo $([Cr(en)_2(H_2O)_2]Cl_3 . H_2O,$[4] $[Cr(en)_2H_2O)]Br_3 .$ $. H_2O$[5]). The data on the dichloro system, $[Cr(en)_2Cl_2]ClO_4$, obtained by Dubicki and Day[4] and independently by Klein[5] agree perfectly. However, the spectra of $[Cr(en)_2Br_2]ClO_4$ measured at 4.2°K[4] show distinct resolution as compared with the liquid nitrogen

spectra of $[Cr(en)_2Br_2]Br . H_2O$.[5] Although no better resolution had been achieved in the spectra of $[Cr(en)_2(H_2O)_2]Cl_3 . H_2O$ at 4.2°K,[4] the bands are sharper and the shifts definitive, particularly in the case of the quadrate components of the second cubic band, than that in the spectra of $[Cr(en)_2(H_2O)_2]Br_3 . H_2O$ measured at liquid N_2 temperature.[5] Because of the broad nature of the quadrate components of the second cubic band in the spectra of the diaquo complex at liquid N_2 temperature, the splitting was not well discernible and it was concluded[5] that x, which is the Ds/Dt ratio, for this system is about 0.3 or almost close to zero. On the other hand the sharply defined nature of these same bands attained at 4.2°K gave rise to a definitive estimate of the band maxima[4] which were fitted by a value of −0.80 for x. This seeming discrepancy points to a warning that one has to be careful in estimating the band maxima and assigning the bands on the basis of shifts and intensity changes alone in the polarized spectra of complexes.

It should be noted that the polarized spectral measurements on most of these systems have been made without the use of complete structural data. Although the knowledge of complete crystal structure data is necessary to make definitive assignments of the observed bands in the polarized spectra, it is still possible to obtain meaningful polarized spectral data, provided the molecular orientation in the crystal is favorable, by measuring the spectra along the extinction directions of the single crystal. The trans difluoro complex, $[Cr(en)_2F_2]ClO_4$, studied by Dubicki *et al*[3] is an excellent example of such a posibility. We now report such studies on five mixed trans diacido systems which include the aquohydroxy, aquofluoro aquochloro, aquobromo, and bromochloro complexes.

Experimental Section

Preparations of Compounds. The *trans*-$[Cr(en)_2(H_2O)F](ClO_4)_2 . H_2O$ was prepared exactly according to the procedure described in the literature.[6]

The preparation of *trans*-$[Cr(en)_2(H_2O)(OH)]Br_2 . H_2O$ was carried out by a slightly modified procedu-

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(**) Taken, in part, from the M.S. theses of R.L. Klein, Jr. (Florida Atlantic University, 1971) and N.C. Miller (Florida Atlantic University, 1973).
(1) J.A. Stanko, Ph. D. Thesis, University of Illinois, 1966.
(2) S. Yamada, *Coordin. Chem. Rev.*, 2, 83(1967).
(3) L. Dubicki, M. A. Hitchman, and P. Day, *Inorg. Chem.*, 9, 188(1970).
(4) L. Dubicki and P. Day, *Inorg. Chem.*, 10, 2043(1971).
(5) R. L. Klein, Jr., M.S. Thesis, Florida Atlantic University, August 1971.

(6) J. W. Vaughn, O. J. Stvan, and V. E. Magnuson, *Inorg. Chem.* 7, 736(1968).
(7) F. Woldbye, *Acta Chem. Scand.*, 12, 1079(1958).

re from that used by Woldbye.[7] The starting material in our case was trans-[Cr(en)₂F₂]ClO₄. The difluoro complex was converted to trans-[Cr(en)₂Br₂]Br . H₂O which was then allowed to aquate. From this point on the procedure was same as Woldbye's. A sample preparation was as follows. Twelve grams of the dibromo complex was added to 40 ml of 1:1 (by volume) 47 per cent HBr and H₂O. The mixture was warmed on a steam bath until solution was complete and then allowed to aquate in dark for 36 hours at *ca.* 22°C. The aquated solution was saturated with KBr and 20 ml of pyridine was added. The precipitate, formed on cooling in ice, was filtered and washed with first 50% ethanol to remove most of the KBr, then with acetone, and air dried leaving trans-[Cr(en)₂(H₂O)(OH)]Br₂, light orange in color. The yield was 4.6 g. The product was slightly contaminated with KBr as shown by somewhat lower values of extinction coefficients in its solution spectrum.

The preparations of trans-[Cr(en)₂(H₂O)Cl]Cl₂, [Cr(en)₂(H₂O)Br]Br₂, and [Cr(en)₂BrCl]Cl were carried out according to the procedures reported in the literature.[8]

Growth of Single Crystals. Crystals of trans-[Cr(en)₂(H₂O)(OH)]Br₂ . H₂O were obtained directly from the mother liquor of the preparation. The dichroism of these orange crystals was almost indistinguishable.

Single crystals of trans-[Cr(en)₂(H₂O)F](ClO₄)₂ . H₂O were grown by dissolving the complex in water and cooling slowly. This slow cooling was achieved by using a styroform container filled with water to a level slightly higher than the level of the complex solution in a small flask which rested inside the container. The styroform container was then placed in a refrigerator. These crystals showed pink-orange to red-orange dichroism.

The procedure for growing single crystals of trans-[Cr(en)₂(H₂O)Br]Br₂ was as follows. A 3 ml portion of ice cold 2 *M* HClO₄ was saturated with the complex bromide, filtered, and placed in a large test tube. Ice cold acetone was carefully poured into the test tube so as to form a layer above the complex solution. The tube was then stoppered, placed in a refrigerator. After 24 hours when the two layers diffused, several large crystals which appeared to be tetrahedral in habit had formed near the original interface between the two layers. Sections taken parallel to the faces showed a strong pink to green dichroism.

Crystals of trans-[Cr(en)₂(H₂O)Cl]I₂ were prepared by saturating a concentrated solution of NaI with the complex chloride at room temperature, filtering the solution, and cooling slowly in a refrigerator. Crystals which appeared as stout terminated prisms with two predominant parallel faces grew on the bottom of the container. Sections taken parallel to these faces showed dichroism identical to that of aquobromo complex.

Crysals of trans-[Cr(en)₂BrCl]ClO₄ were grown by the method of Stanko.[1] A filtered, saturated aqueous solution of the complex chloride was placed in a 10

ml beaker filling it almost to the top. The 10 ml beaker was placed inside a 50 ml beaker into which was added water until it reached almost to the top of the smaller beaker. Ten ml of saturated aqueous NaClO₄ were then carefully pipetted into the bottom of the larger beaker and the entire setup placed in a refrigerator until diffusion was complete in 18-24 hours. The thin rhomb shaped crystals appeared on the edge of the smaller beaker. They exhibited a pink-green to olive-green dichroism.

Measurement of Spectra. All the spectra were measured on a Cary-14 recording spectrophotometer. The crystal spectra were obtained at liquid nitrogen temperature by using a cold finger dewar specially constructed to fit on to the sample compartment of the spectrophotometer. The crystal was placed with its predominating face lying over the hole of the copper sample plate and fixed by thin strands of Apiezon Regd Grease *N*. The sample plate was then secured to the cold finger of the dewar. The dewar was then assembled and liquid nitrogen poured into the inner component. The dewar placed under vacuum was set on to the sample compartment. In the reference compartment, a copper plate having the same size hole as the sample plate was mounted in the reference beam. The reference beam was attenuated as needed by neutral density filters placed in the reference cell compartment. The light was polarized by a Glans Taylor polarizing prism which was secured to a disc and dial vernier and positioned in the entrance window of the sample compartment. Extinction angles (measured by a Bausch and Lomb Research Petrographic Microscope, Model R) were set by rotating the dial to the desired angles. The dewar was aligned with the sample beam at a particular wave length by adjusting for maximum transmittance. A base line was determined under the same conditions without the crystal and subtracted from the measured spectrum.

Because of the high intensity of the spin allowed bands (extinction coefficients ∼30 cm⁻¹ *M*⁻¹), the crystals were thinned to the desired thickness by wiping the predominant faces with a paint brush dipped in water and polished on a dampened sheet of bond paper. Original crystals were used without thinning for obtaining the low intensity spin-forbidden bands.

Results

The unpolarized single crystal spectra as well as the absorption spectra of solutions of crystals of all compounds have also been measured in this work. Solution spectral data have been reported[9,10] on all the compounds except the bromochloro complex. Our data on the band maxima and extinction coefficients in all the solution spectra agree with those published. The solution spectrum of trans-[Cr(en)₂BrCl] in H₂O shows band maxima at 592, 449, and 396 nm with extinction coefficients 24.1 19.3, and 26.6 cm⁻¹ *M*⁻¹, respectively. The unpolarized crystal spectra are si-

(8) W. W. Fee, J. N. MacB. Harrowfield, and W. G. Jackson, *J. Chem. Soc.*, A, 2612(1970).

(9) C. S. Garner and D. A. House in "Transition Metal Chemistry," Vol. 6, R. L. Carlin Ed., Marcel Dekker, Inc., New York, 1970.
(10) J. R. Perumareddi, *Coordin. Chem. Rev.*, 4, 73(1969).

Table I. Observed Band Maxima in the Doublet Regions of the Spectra of Single Crystals of trans-Diacidobis(ethylenediamine)-chromium(III) Complexes.

Complex	Band Maxima [a] in cm^{-1}
$[Cr(en)_2(H_2O)(OH)]Br_2 \cdot H_2O$	22,400
$[Cr(en)_2(H_2O)F](ClO_4)_2 \cdot H_2O$	14,780; 14,960; 15,050; (15,240); 15,360; (15,440); (15,500); 15,710; (15,810); 15,840; (15,870); 16,250; (16,390); 16,470)
$[Cr(en)_2(H_2O)Cl]I_2$	21,322; 21,413
$[Cr(en)_2(H_2O)Br]Br_2$	20,973; (21,008); 21,119; 21,209; 21,268; 21,381
$[Cr(en)_2BrCl]ClO_4$	20,790; 20,877
$[Cr(en)_2Cl_2]ClO_4$ [b]	14,605; 14,770; 14,875; (14,910); (15,030); 15,080; 15,150; (15,250); 15,290; (15,340); 15,430; 15,550; (15,630); (15,730); 21,340; 21,490; (21,550),
$[Cr(en)_2Br_2]Br \cdot H_2O$ [b,c]	20,960; 21,090; 21,260
$[Cr(en)_2(H_2O)_2]Br_3 \cdot H_2O$ [b,d]	22,080
$[Cr(en)_2F_2]ClO_4$ [b]	(16,000)

[a] Values in parentheses are shoulders; [b] Ref. 5; [c] Similar doublet structure had been uncovered[4] in trans-$[Cr(en)_2Br_2]ClO_4$; [d] A similar band appears in the polarized spectrum[4] of trans-$[Cr(en)_2(H_2O)_2]Cl_3 \cdot H_2O$.

milar to the solution spectra except the band maxima are usually shifted to higher energies in crystal spectra by a few hundred wavenumbers and in some cases as much as thousand wavenumbers. In addition, bands appearing as shoulders in solution spectra are better resolved in crystal spectra.

Using thick crystals, we were able to uncover a rich doublet structure in the unpolarized spectra of some of the complexes. The observed spin-forbidden band maxima are given in Table I which also includes data on other diacido systems obtained earlier by us. The doublet bands of aquochloro, aquobromo, bromochloro, and dibromo complexes appear in their polarized spectra also. In the case of aquohydroxy complex, one spin-forbidden band exclusively appears in the ⊥ polarized spectrum. Complete analysis of these bands will be presented in another communication. Our main concern in this report is with the spin-allowed bands.

The polarized spectra of all the systems obtained at liquid N$_2$ temperature are presented in Figures 1 through 5. The spectra of each compound had been reproduced by making the measurements on different crystals of a preparation and also on crystals grown from a second preparation. The size of the crystal in these figures is stated as being greater than the size of the hole over which it is mounted. Although the polarizations are marked ∥ and ⊥, they are not meant to be taken strictly in the sense that the electric vec-

tor having been polarized parallel (z) and perpendicular (x, y) to the molecular tetragonal axis. As pointed above, the spectra were obtained along the extinction directions measured on a well defined face of the crystal and only if the molecular alignment in the crystal is such that the extinction directions correspond to being parallel and perpendicular to the molecular tetragonal axis do we have the correspondingly polarized spectra. In the absence of crystal structure data these directions should perhaps be read as, say, A and B polarizations. However, the polarizations
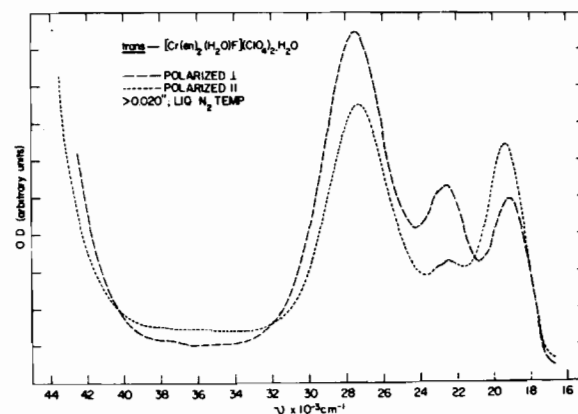

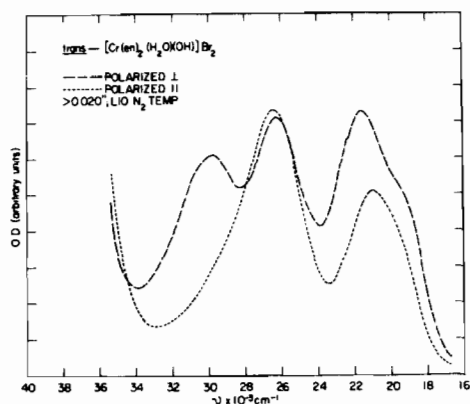Figure 2. Polarized Electronic Spectra of trans-$[Cr(en)_2(H_2O)F](ClO_4)_2 \cdot H_2O$.

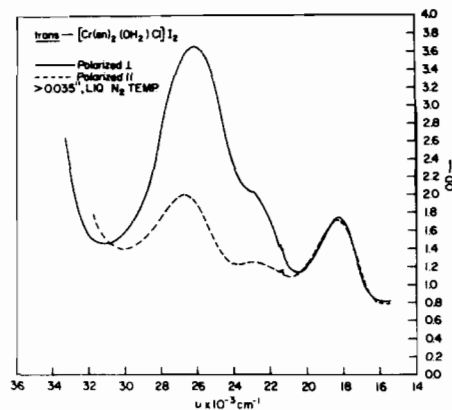Figure 1. Polarized Electronic Spectra of trans-$[Cr(en)_2(H_2O)(OH)]Br_2 \cdot H_2O$.

Figure 3. Polarized Electronic Spectra of trans-$[Cr(en)_2(H_2O)Cl]I_2$.

are labelled || and ⊥ in the figures to indicate that they are predominently the spectra obtained in parallel and perpendicular polarizations, although it is quite possible that each of these may have the other component mixed in it to a certain extent. The correspondence of the measured spectra with the predominantly || and ⊥ polarized spectra had been inferred by a consideration of the source of intensity of the observed bands and the predicted polarization patterns.

In all the systems studied, we observed the split components of only the first two cubic bands, $^4T_{2g}$ and $^4T_{1g}$, which give rise to the tetragonal components $^4B_{2g}$, ^4E_g, and $^4A_{2g}$, ^4E_g, respectively. Neither of the two components of the third cubic band $^4T_{1g}$ had been uncovered in any of the systems. Hence, we shall confine our attention to these transitions only. There is no doubt that the transitions in consideration are of electric dipole in origin. The question is the source of intensity of the observed bands. Neglecting the ring portions of the ethylenediamine ligands, the polarized spectra of trans diacido systems in which the axial ligands are of the same kind have been satisfactorily interpreted using D_{4h} as the effective symmetry with vibronic intensity mechanism.[3-5] Extendin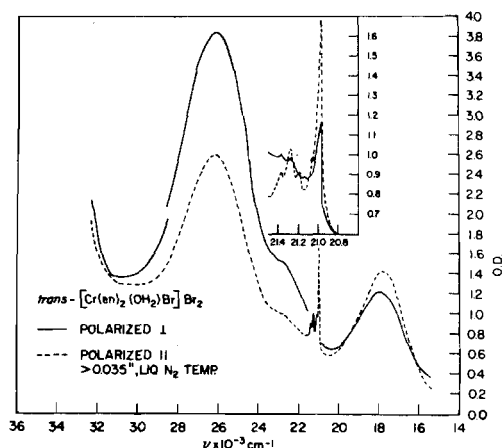g this assumption, the effective symmetry of the mixed trans diacido systems in which the axial ligands are of a different kind can be approximated to C_{4v} point group. There are then three possibilities for the bands in the spectra of these systems to acquire intensity. 1) The noncentrosymmetric nature of the effective symmetry alone may be responsible for the observed intensity of the bands. 2) Vibronic intensity mechanism with C_{4v} as the effective symmetry may be operating. 3) If the trans ligand pair can be viewed as an averaged ligand pair, the effective symmetry may further be approximated to D_{4h}. Even otherwise, this case applies to the aquohydroxy complex, since its pseudo symmetry can be considered as D_{4h} if only the coordinating atoms of the ligands are taken into account. If the symmetry is taken as D_{4h}, vibronic mechanism has to be responsible for the source of intensity.

The selection rules based on the static C_{4v} symmetry alone predict that only the two ^4E components are allowed in the perpendicular polarization and none at all in the parallel polarization. This case can be ruled out for the present systems because, firstly, the intensities of the bands in the spectra of these mixed systems (C_{4v}) are about the same as those of the D_{4h} systems and secondly, the observed polarization pattern is completely different from the predicted. The other two cases which are applicable in the present study are summarized in Table II. The effec-

Figure 4. Polarized Electronic Spectra of trans-[Cr(en)₂(H₂O)Br]Br₂.
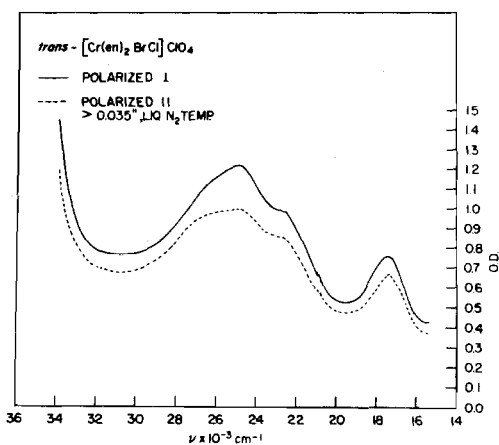
Figure 5. Polarized Electronic Spectra of trans-[Cr(en)₂BrCl]ClO₄.

Table II. Vibronic Selection Rules in C_{4v} and D_{4h} Symmetric for d³ Complexes (vibrational modes allowing the electronic transitions are given in parentheses).

Point Group	$^4T_{2g}$		$^4T_{1g}$	
	$^4B_2$	^4E	$^4A_2$	^4E
C_{4v}	⊥(4ε)	⊥($4\alpha_1$, $2\beta_1$, β_2) || (4ε)	⊥(4ε)	⊥($4\alpha_1$, $2\beta_1$, β_2) || (4ε)
		|| (β_2)	|| (β_2)	
D_{4h} ᵃ	⊥($3\varepsilon_u$)	⊥($2\alpha_{2u}$, β_{2u}) || ($3\varepsilon_u$)	⊥($3\varepsilon_u$)	⊥($2\alpha_{2u}$, β_{2u}) || ($3\varepsilon_u$)

ᵃ A g subscript should be added to the electronic energy levels in this case.

tiveness of the nondegenerate β_2 vibrational mode in inducing intensity had been questioned[1] in the case of cobalt(III) complexes of C_{4v} symmetry. In any case, in both the mechanisms all four tetragonal bands are predicted to appear in the perpendicular polarization and either only the ^4E transitions(D_{4h}) or the ^4E transitions and the $^4A_2$ with perhaps reduced intensity (C_{4v}) are predicted to appear in the parallel polarization. The relative intensities of the bands in one or both polarizations, of course, depend on the effectiveness of the vibrations which cause the gain in intensity. In addition, it is now clearly established,[11, 10, 3-5] theoretically and experimentally, that in the quadrate chromium(III) systems in which Dt is negative, the $^4B_2$ component of $^4T_{2g}$ (the lowest energy cubic band) is positioned higher in energy than its ^4E component. The labelling of the polarizations

(11) (a) J. R. Perumareddi, *J. Phys. Chem.*, 71, 3144(1967); (b) *Ibid.*, *J. Phys. Chem.*, 71, 3155(1967); (c) R. Krishnamurthy, W. B. Schaap, and J. R. Perumareddi, *Inorg. Chem.*, 6, 1338(1967); (d) R. K. Lowry and J. R.Perumareddi, *J. Phys. Chem.*, 74, 1371(1970).

Table III. Observed Band Maxima (in cm⁻¹) and Their Assignments in the Single Crystal Polarized Spectra of trans-Diacido-bis (ethylenediamine) chromium(III) Complexes (values in parentheses are shoulders).

Complex		$^4B_1 \to {}^4E(^4T_{2g})$	$^4B_1 \to {}^4B_2$	$^4B_1 \to {}^4A_2$	$^4B_1 \to {}^4E(^4T_{1g})$
[Cr(en)₂(H₂O)(OH)]Br₂ . H₂O	⊥	(19,450)	21,570	29,850	26,370
	‖	(19,450)			26,460
[Cr(en)₂(H₂O)F](ClO₄)₂ . H₂O	⊥	19,140	22,530	27,490	
	‖	19,300			27,280
[Cr(en)₂(H₂O)Cl]I₂	⊥	18,215	22,831	26,178	
	‖	18,282			26,667
[Cr(en)₂(H₂O)Br]Br₂	⊥	17,953	22,831	26,110	
	‖	17,794			26,176
[Cr(en)₂BrCl]ClO₄	⊥	17,422	22,624	24,814	
	‖	17,331			(26,800)

Table IV. Comparison of Spectral Parameters Evaluated by Alternate Fittings from the Spectra of Trans Difluoro and Dichloro Complexes.[5]

Parameter	[Cr(en)₂F₂]ClO₄		[Cr(en)₂Cl₂]ClO₄	
	I	II	I	II
Dt, cm⁻¹	—346	—305	—529	—558
Ds, cm⁻¹	747	778	—196	—195
$x = Ds/Dt$	—2.16	—2.55	0.37	0.35
B, cm⁻¹	685	631	598	617

was aided by both these considerations.

From the above discussion, the assignments of the observed bands in the spectra of all systems except the bromochloro should be clear. The polarized spectra of the bromochloro complex are similar to those of the diaquo system[4,5] in that the parallel spectrum contains the perpendicular spectrum to a considerable extent. The quadrate assignments of the two components of the second cubic band were arrived at as follows. The band at 24,814 cm⁻¹ in the perpendicualr spectrum has definite asymmetry on its high energy side which becomes clear as a shoulder (26,800 cm⁻¹)in parallel spectrum. The reduction in intensity of the 24,814 cm⁻¹ band is greater than the reduction in intensity of the shoulder from perpendicular to parallel spectrum. Thus, the band at 24,814 cm⁻¹ and the shoulder at 26,800 cm⁻¹, respectively, were assigned the $^4A_2$ and ^4E transitions. It should be noted, that in all the tetragonal Cr³⁺ systems studied so far the aquohydroxy complex is the third case, difluoro and dibromo being the other two, in which a clear cut resolution of the second cubic band had been observed in the perpendicular polarization and the $^4A_2$ component had been found to be completely wiped out as predicted in the parallel polarization. In all the other systems, these components had been discerned on the basis of change in intensity and shifts of the maxima in the two polarizations. The band maxima and their assignments in the spectra studied are presented in Table III.

The observed band maxima can be fitted[11b,d,5] exactly with the quadrate d³ energy equations[10,11a] with full configuration interaction. It should be commented, however, that because of the observed ^4E band maxima being not usually identical in the two polarizations, it is possible to carry out four alternate fittings in general. One method is to fit all the four

band maxima taken from the perpendicular spectrum. The second method is to use the $^4B_2$ and $^4A_2$ band maxima from the perpendicular spectrum and the ^4E maxima from the parallel spectrum. The other two methods, of course, are to use each of the ^4E maxima from the parallel spectrum with the other three maxima taken from the perpendicular spectrum. When the two components of the second cubic band are inferred by a shift, only the second method and one of the latter two methods of fitting are possible. The parameters do vary depending upon the method of fitting used. Table IV shows, for instance, the variation of the parameters for the first two methods of fitting in the case of the difluoro and dichloro systems. This variation should be kept in mind when a comparison of the parameters is made of different systems.

We have carried out all the above methods of fitting for the systems studied. The bands have been fitted to within ± 10cm⁻¹, in most cases ±5cm⁻¹. The parameters evaluated by the second method of fitting are given in Table V. The parameters of the other trans diacido systems obtained by polarized spectral studies earlier are also included in this table for a comparison. The cubic ligand field parameter, Dq, in all these tetragonal derivatives is expected to be same as that of their parent octahedral complex [Cr(en)₃]³⁺, which has been found to be ~ 2240 cm⁻¹ by a measurement of the unpolarized single crystal spectrum of [Cr(en)₃]Cl₃ . 3½H₂O at liquid N₂ temperature, i.e., under the same conditions used for the tetragonal systems. This prediction seems to have been borne out considering that the $^4B_2$ band, which directly gives the Dq value, in most cases is a shoulder. The Dt parameter is directly related to the difference in the octahedral Dq of the equatorial and axial ligands[10,11a] the greater the difference the greater is the absolute magnitude of Dt. This trend is observed in these systems and in addition it should be noted that the Dt value of a mixed diacido system, [Cr(en)₂XY], is approximately the average of the Dt values of the pure diacido systems, [Cr(en)₂X₂] and [Cr(en)₂Y₂]. Unfortunately, the second axial ligand field parameter x (or Ds) does not seem to be amenable to such a simple interpretation as Dt at the present time except that its significance can be understood only in terms of molecular orbital description which is discussed later. It is interesting to note, however, that with the exception of aquofluoro com-

Table V. Spectral Parameters of trans-Diacidobis(ethylenediamine)chromium(III) Complexes.

Complex	Dq, cm⁻¹	Dt, cm⁻¹	x = Ds/Dt	B, cm⁻¹
[Cr(en)₂(H₂O)(OH)]Br₂ . H₂O	2157	—237	—2.68	725
[Cr(en)₂(H₂O)F](ClO₄)₂ . H₂O	2253	—360	0.01	656
[Cr(en)₂(H₂O)Cl]I₂	2283	—497	0.270	610
[Cr(en)₂(H₂O)Br]Br₂	2283	—552	0.118	608
[Cr(en)₂BrCl]ClO₄	2262	—562	0.687	625
[Cr(en)₂(H₂O)₂]Cl₃ . H₂O ᵃ	2350	—398	—0.681	657
[Cr(en)₂F₂]ClO₄ ᵇ	2180	—305	—2.55	631
[Cr(en)₂Cl₂]ClO₄ ᵇ	2262	—558	0.35	617
[Cr(en)₂Br₂]ClO₄ ᵃ	2250	—577	0.782	573

ᵃ The parameters for these systems are obtained by an exact fitting of the data from ref. 4;   ᵇ Ref. 5.

plex, x does average out, within the variation mentioned above, for a mixed [Cr(en)₂XY] system from the pure [Cr(en)₂X₂] and [Cr(en)₂Y₂] systems as Dt does. The large discrepancy between the predicted (—1.60) by this averaging an dthe derived (0.01) x value for the aquofluoro system may be an indication that our estimated transition energies of the two components of the second cubic band by shifts of the broad band maxima in the polarized spectra are probably not accurate. Further resolution of these components should be achieved to resolve this problem. These predictions and observations cannot be tested in the case of aquohydroxy complex because the crystal spectrum of the dihydroxy complex is not known. Our attempts to isolate the solid dihydroxy complex have not been successful so far. From the observed parameters of the aquohydroxy and diaquo complexes, the dihydroxy system is expected to have a large x value —4.7, not observed so far for any quadrate Cr^{3+} complex, and a Dt value of about —80cm⁻¹. Such a low Dt value for the dihydroxy complex implies that the hydroxy ligand should be close to the ethylenediamine ligand (on the low energy side) in the one-dimensional spectrochemical series of ligands, at least in the case of Cr^{3+} complexes. It will be interesting to verify this result. The B value is around 600cm⁻¹ in all the systems except the aquohydroxy, aquofluoro, diaquo, and difluoro in which it is greater. Aquo and fluoro complexes in the case of octahedral systems do have high B values as compared with the chloro and bromo complexes and it is interesting that the B value of a hydroxy complex also comes out to be high. Finally, the averaging principle noted for Dt and x also applies to B.

The derived Dq, Dt, and x parameters of these systems give rise to the one-electron energy level diagram[11a] shown in figure 6. As Yamatera showed[12] in terms of molecular orbital theory the splitting of the cubic t_{2g} orbital is due to the difference in the π-antibonding character of the equatorial ligand(xy) and the axial ligand (zx, yz). Similarly, the splitting of the e_g orbital arises due to the difference in the σ-antibonding character of the equatorial ligand (x^2-y^2) and the axial ligand (z^2). From this figure it follows that in all these systems the axial ligands are more π-antibonding than the equatorial ethylenediamine li-
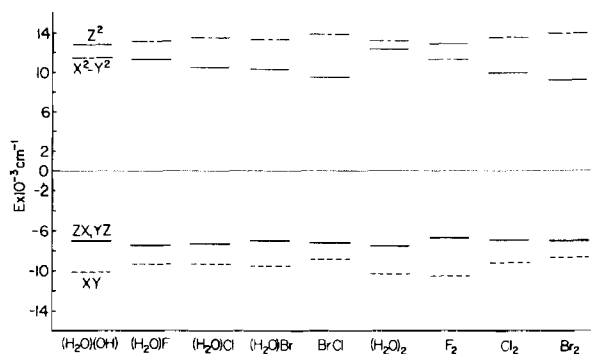

Figure 6. One-Electron Molecular Energy Levels of trans-Diacidobis(ethylenediamine)chromium(III) Complexes.

gand (en) which is expected since en cannot π-bond. Fluoro and hydroxy ligands come out to be more σ-antibonding while H₂O, Cl⁻, and Br⁻ are less σ—antibonding than the en. The relative σ— and π—antibonding properties of ligands can be expressed somewhat on a quantitative basis in terms of molecular orbital parameters into which the ligand field parameters can be easily transformed. Such an analysis has already been carried out[4,5] for the pure diacido systems discussed here. It should be pointed out that the ligand field and molecular orbital parameters have been obtained for several other diacido systems also mainly from solution spectral studies.[13]

(12) (a) H. Yamatera, *Bull. Chem. Soc. Japan*, *31*, 95(1958); see also (b) D. S. McClure in "Advances in the Chemistry of Coordination Compounds," S. Kirschner Ed., The Macmillan Co., New York, N. Y. 1961.
(13) See for instance, W. W. Fee and J. N. MacB. Harrowfield, *Aust. J. Chem.* *23*, 1049(1970) and references cited therein.