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Band Splittings in *trans*-Diacidobisethylenediamine Complexes of Chromium(III)

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The spectra of several complexes of the general type *trans*-$[Cr(en)_2X_2]^{n+}$ have been carefully examined. Splitting of the spectral bands was observed which allowed assignment of the crystal field parameters Dt and Ds. The splittings were also used to calculate empirical molecular orbital parameters, $\delta\sigma$ and $\delta\pi$, as developed by McClure. It is concluded that the degree of splitting and the relative order of the excited states are not always predictable from a simple consideration of octahedral Dq values.

Introduction

The splitting of the first two spin-allowed bands in Co(III) and Cr(III) complexes that occurs upon the lowering of the symmetry from O_h to D_{4h}, C_{4v}, or C_{2v} has prompted many investigations, both theoretical and experimental.[1] Predictions and explanations of the splittings using a crystal model have been given by Moffitt and Ballhausen[2] and Yamatara,[3] while McClure[4] and also Yamatera[3] have used approaches based on a molecular orbital model.

Regardless of the model used, however, interpretation of experimental results is hampered by the fact that the splitting of both bands is needed to evaluate the parameters which arise from the theories. In general, the splitting of one band is readily observed, but to our knowledge, there is only one published example,[5] this being $[Cr(en)_2Cl_2]^+$, where the splitting of both bands can be seen in the published spectra. This inability to evaluate all of the parameters has of necessity led to empirical methods for correlating band splittings with various properties of the ligands. The most recent and successful effort is that of Wentworth and Piper,[1] who used a crystal field model.

We have carefully examined the spectra of a number of *trans*-bis(ethylenediamine) complexes of Cr(III) and have been able to detect the splitting of both bands. To be sure, the splitting of one band is always small and generally shows up only as an ill-defined shoulder. Nonetheless, we believe that its position can be estimated closely enough so that, using the data obtained, reasonable correlation of the results can be realized using either the crystal field theory or the molecular orbital method of McClure.[4]

Theory

The Crystal Field Theory.—The crystal field theory for D_{4h} complexes of Cr(III) has been given by Ballhausen.[6] The ground state of octahedral Cr(III) is $^4A_{2g}$ with the first two excited states being $^4T_{2g}$ and $^4T_{1g}$. Lowering the symmetry to D_{4h} splits the excited states in the following way

$$^4T_{2g} \longrightarrow {}^4B_{2g} + {}^4E_g{}^a$$

$$^4T_{1g} \longrightarrow {}^4A_{2g} + {}^4E_g{}^b$$

Following Wentworth and Piper, we will designate the lower E states as E^a and the higher as E^b. The splittings of the excited states are expressed in terms of two parameters, Ds and Dt. Calling the energy of the ground $^4B_{1g}$ state zero, the energies of the excited states are, to the first order

$$E(^4B_{2g}) = 10Dq \tag{1a}$$

$$E(^4E_g{}^a) = 10Dq - 35/4Dt \tag{1b}$$

$$E(^4A_{2g}) = 10Dq + 12B - 4Ds + 5Dt \tag{1c}$$

$$E(^4E_g{}^b) = 10Dq + 12B + 2Ds - 25/4Dt \tag{1d}$$

Thus the splitting of the first band is $35/4Dt$, while that of the second is $6Ds - 5/4Dt$. For the *cis* isomer, the splittings are just one-half of the *trans*. In the event that both components of each state can be observed, then Dt and Ds can be evaluated directly without making any assumptions about their relative magnitudes. There is no *a priori* restriction imposed by the theory on the sign of Ds and Dt, and the ordering of the split components is dependent upon the sign of Dt for the first band and the signs and relative magnitude of Ds and Dt for the second. Ballhausen[6] also gives the one-electron orbital energies, and since those will be of interest with respect to our later discussion, we give them below.

$$E(x^2 - y^2) = 6Dq + 2Ds - Dt \tag{2a}$$

$$E(z^2) = 6Dq - 2Ds - 6Dt \tag{2b}$$

$$E(xy) = -4Dq + 2Ds - Dt \tag{2c}$$

$$E(xz,yz) = -4Dq - Ds + 4Dt \tag{2d}$$

McClure's Molecular Orbital Model.—We have chosen the molecular orbital model of McClure[4] to apply to our data because the model is simple yet yields results which can be interpreted in such a way as to be chemically meaningful. Furthermore, one

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[1] For a very complete set of references, see R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 709 (1965).

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

[3] H. Yamatera, *Bull. Chem. Soc. Japan*, **31**, 95 (1958).

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

[5] M. Linhard and M. Weigel, *Z. Physik. Chem.* (Frankfurt), **5**, 20 (1955).

[6] C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 101.

can use chemical reasoning to predict, at least for most cases, the signs of the splitting parameters.

The splitting parameters in the McClure model are $\delta\sigma$ and $\delta\pi$ where $\delta\sigma$ (or $\delta\pi$) is a measure of the difference between the σ (or π) antibonding ability of the axial and in-plane ligands. The parameter is considered positive if the axial ligand has the greater antibonding power. From a simple consideration of the symmetry of the orbital involved, the splittings for Cr(III) are then given[4] as

$$\Delta E(^4T_{2g}) = E(^4B_{2g}) - E(^4E_g{}^a) = -2\delta\sigma + 2\delta\pi \quad (3a)$$

$$\Delta E(^4T_{1g}) = E(^4A_{2g}) - E(^4E_g{}^b) = 2\delta\sigma + 2\delta\pi \quad (3b)$$

Thus the splitting is considered positive if the nondegenerate component falls at higher energy than the E component. Again, this method allows for either positive or negative splittings as defined above. The relative displacements of the one-electron orbital energies are then

$$E(x^2 - y^2) = 0 \quad (4a)$$

$$E(z^2) = +(8/3)\delta\sigma \quad (4b)$$

$$E(xy) = 0 \quad (4c)$$

$$E(xz,yz) = -2\delta\pi \quad (4d)$$

The ordering of the levels then depends only upon the sign of $\delta\sigma$ and $\delta\pi$. This approach also predicts the splittings for the *cis* isomer to be one-half that of the *trans*.

Experimental Section

The complexes studied have all been previously reported in the literature, and the procedures used for preparation followed without essential modification those given.

***trans*-[Cr(en)$_2$Cl$_2$]Cl·H$_2$O.**—This was prepared by the method given by Pfeiffer.[7] *Anal.* Calcd for $C_4H_{16}N_4Cl_3Cr\cdot H_2O$: C, 16.70; H, 6.12; N, 18.89. Found: C, 16.14; H, 6.81; N, 19.20.

***trans*-[Cr(en)$_2$Br$_2$]Br·H$_2$O.**—The preparation of this complex also followed a method given by Pfeiffer.[8] *Anal.* Calcd for $C_4H_{16}N_4Br_3Cr\cdot H_2O$: C, 11.18; H, 4.22; N, 13.04. Found: C, 11.18; H, 4.60; N, 12.92.

***trans*-[Cr(en)$_2$(H$_2$O)(OH)]Br$_2$.**—This was prepared according to the direction given by Woldbye.[9] *Anal.* Calcd for $C_4H_{19}N_4Br_2CrO_2$: C, 13.09; H, 5.22; N, 15.27. Found: C, 13.24; H, 5.77; N, 15.15.

***trans*-[Cr(en)$_2$(OH)$_2$]$^+$ and *trans*-[Cr(en)$_2$(H$_2$O)$_2$]$^{3+}$.**—These ions were generated in solution from the aquo–hydroxo complex by control of the pH as described by Woldbye.[9] Salts of the complex ions were not isolated from solution.

***trans*-[Cr(en)$_2$(SCN)$_2$]SCN.**—The preparation used was that due to Rollinson and Bailar.[10] *Anal.* Calcd for $C_7H_{16}N_7S_3Cr$: C, 24.26; H, 4.66; N, 28.30. Found: C, 24.54; H, 4.76; N, 28.40.

Since the color, visible spectra, and general appearance of the product of this preparation are essentially identical with those for the substance reported to be the *cis* isomer,[7] it is worthwhile mentioning the criteria used to confirm the structures. The *cis* compound was prepared according to the method given by Pfeiffer.[6] *Anal.* Calcd for $C_7H_{16}N_7S_3Cr$: C, 24.26; H, 4.66; N, 28.30. Found: C, 24.31; H, 4.80; N, 27.79. First, the X-ray powder patterns of the two compounds are distinctly different. Second, the infrared spectra of the two show significant differences. The region between 2000 and 2100 cm^{-1}, which is the area of C–N absorption in the thiocyanate ion, shows, after replacement of the noncoordinated thiocyanate by perchlorate ion, only one band for the presumed *trans* isomer but two for the *cis*. Also, the empirical rule developed by McLean, Schreiner, and Laethem[11] for distinguishing between *cis*- and *trans*-bis(ethylenediamine) complexes on the basis of the spectra between 1500 and 1700 cm^{-1} agrees with the structural assignments.

The infrared spectra did not allow an assignment of the coordinated atom in the SCN$^-$ group. The C–N stretching frequency in the *trans* isomer falls at 2080 cm^{-1}. This is in the region of overlaps between N-bonded and S-bonded ranges. Cursory attempts to assign the C–S band were unsuccessful, as is often the case.

***trans*-[Cr(bipy)$_2$Cl$_2$]Cl·2H$_2$O.**—This compound was prepared as previously described.[12] The assignment of the structure as *trans* is based on the infrared spectrum in the 700–800 cm^{-1} region, where *trans*-bis(bipyridyl) complexes show two bands due to C–H bending while the *cis* isomers show three or four.[13]

***cis*-[Cr(en)$_2$Cl$_2$]Cl·H$_2$O.**—This complex was prepared by the method of Rollinson and Bailar.[10] *Anal.* Calcd for $C_4N_4H_{16}Cl_3Cr\cdot H_2O$: C, 16.20; H, 6.12; N, 18.89. Found: C, 16.20; H, 6.29; N, 18.49.

***cis*-[Cr(en)$_2$(N$_3$)$_2$]N$_3$.**—The azide was obtained using the method of Linhard and Weigel.[14] *Anal.* Calcd for $C_4H_{16}N_{13}Cr$: C, 16.10; H, 5.41; N, 61.05. Found: C, 15.89; H, 5.34; N, 60.25.

***cis*-[Cr(en)$_2$(OH)(H$_2$O)]I$_2$.**—This preparation followed that given by Woldbye.[9] *Anal.* Calcd for $C_4H_{19}N_4I_2CrO_2$: C, 10.42; H, 4.15; N, 12.15. Found: C, 10.70; H, 4.19; N, 11.93.

***cis*-[Cr(en)$_2$(OH)$_2$]$^+$ and *cis*-[Cr(en)$_2$(H$_2$O)$_2$]$^{3+}$.**—These were prepared from the aquo–hydroxo complex in solution by the procedures given by Woldbye.[9]

***trans*-[Cr(en)$_2$I$_2$]I.**—Attempts to prepare the pure *trans*-iodide by the method used for the bromide[8] were unsuccessful in that removal of the HgI$_2$ used in the reaction by treating with H$_2$S led to decomposition of the complex. Reflectance spectra were therefore taken on the material, presumed to be [Cr(en)$_2$I$_2$]I·HgI$_2$ with excess HgI$_2$ present, without attempting the removal of HgI$_2$.

Spectra.—Electronic spectra were obtained using a Perkin-Elmer Model 4000A spectrometer. All spectra were taken in 50–50 Spectroquality methanol and distilled water. The time lapse between the solution of the sample and the recording of the spectra varied between 30 and 120 sec. Study of the spectra over a period of time showed that only the *trans*-bromide reacted fast enough to make the observed band position uncertain. The band position for this compound was therefore studied over a short period of time and then extrapolated back to $t = 0$. The concentrations of the solution were varied in order to obtain the best spectra. The instrument was also modified to allow expansion and contraction of the wavelength coordinate so that the best possible resolution of the bands and the greatest emphasis of the shoulders could be realized.

Infrared spectra were obtained with a Perkin-Elmer Model 521 spectrophotometer.

Microanalyses.—Analyses for C, H, and N were performed by Schwarzkopf Microanalytical Laboratories and Galbraith Laboratories.

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(7) P. Pfeiffer, P. Koch, G. Lando, and A. Trieschmann, *Ber.*, **37**, 4268 (1904).

(8) P. Pfeiffer, *Z. Anorg. Chem.*, **56**, 261 (1907).

(9) F. Woldbye, *Acta Chem. Scand.*, **12**, 1079 (1958).

(10) C. L. Rollinson and J. C. Bailar, Jr., *Inorg. Syn.*, **2**, 20 (1946).

(11) J. A. McLean, Jr., A. F. Schreiner, and A. F. Laethem, *J. Inorg. Nucl. Chem.*, **26**, 1245 (1964).

(12) W. A. Baker, Jr., and M. G. Phillips, *Inorg. Chem.*, **4**, 915 (1965).

(13) W. R. McWhinnie, *J. Inorg. Nucl. Chem.*, **26**, 15 (1964).

(14) M. Linhard and M. Weigel, *Z. Anorg. Chem.*, **271**, 131 (1952).

Results and Discussion

Spectra.—The spectra of the ions to be considered are shown in Figures 1–7. The splitting of one of the bands is usually quite evident; that of the second is much less so, showing up mainly as an asymmetric broadening of the band. Splitting was not assumed just on the basis of this broadening, however; in all of the spectra presented, definite if faint breaks in the experimental curves can be seen where bands are assigned. The dotted lines in Figures 1–5 represent the approximate resolution of the spectra into Gaussian bands.[15] The bands are those that reproduce the experimental spectra in the region of interest and may therefore be slightly asymmetric.

The band assignments for the spectra are given in Table I. The assignment of the components of the second band, E_g^b lower than A_{2g}, is straightforward if one uses relative intensities as the criterion for the assignments. In all cases reported here, the higher energy component of the second band is the less intense and is therefore assigned as $^4A_{2g}$. Such an assignment leads to reasonable and consistent results. The case of the first band is not so simple, unfortunately. It has generally been assumed that the E_g component will lie lower than the B_{2g}.[1,3,5] This is equivalent to saying that *Dt* should be positive. It is also expected, however, that the intensity of the E_g band will be greater than that of the B_{2g}.[4,16] It can be seen that for the aquo, hydroxo, and aquo–hydroxo complexes the two assumptions are incompatible. If it were not for the fact that the data presented here require it for consistency, we would not have arbitrarily assigned the E_g component as the lower energy band (*i.e.*, assigned *Dt* as positive). We have done so, in spite of the lower intensity of the first band in certain cases, since reversing the assignment (that is, always assigning the more intense as E_g) would lead to $\delta\sigma$ and $\delta\pi$ values that are intuitively unreasonable. For example, such an assignment would lead to the conclusion that OH^- is the most weakly σ-bonding group considered while H_2O is the most weakly π bonding, even less than ethylenediamine. It would also lead to crystal field parameters which are inconsistent with those obtained for the other complexes. It should perhaps be emphasized that the spectral assignments are by no means certain and the problem of the intensities is somewhat bothersome. The question can be conclusively resolved, however, only by looking at single crystal spectra. For $[Cr(bipy)_2Cl_2]^+$ intensities of the higher bands were impossible to obtain because of the presence of ligand bands. The same assignments were therefore made for it as for the others.

Crystal Field and Molecular Orbital Parameters.—The parameters obtained from the data of Table I are given in Tables II and III. It can be seen that the values derived from both models are quite consistent. The order of the values of 10*Dq* as obtained from the crystal field treatment is $OH^- < I^- < Br^- < Cl^- < H_2O$ and en < bipy, an arrangement in agreement with that normally listed,[17] except for the low position of OH^- which is normally positioned between Cl^- and H_2O. In view of the recent work of Hatfield,[18] one might expect the 10*Dq* values for the aquo and hydroxo complexes to be very nearly the same. The relative nephe-

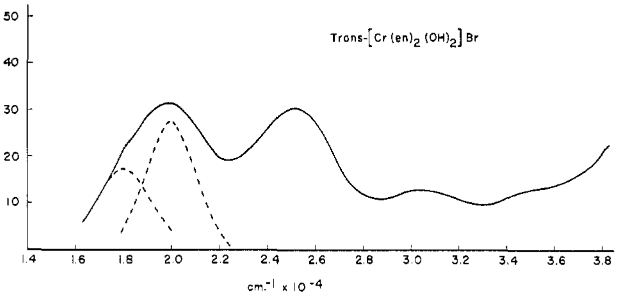

Figure 1.—Absorption spectrum of *trans*-$[Cr(en)_2(OH)_2]^+$.

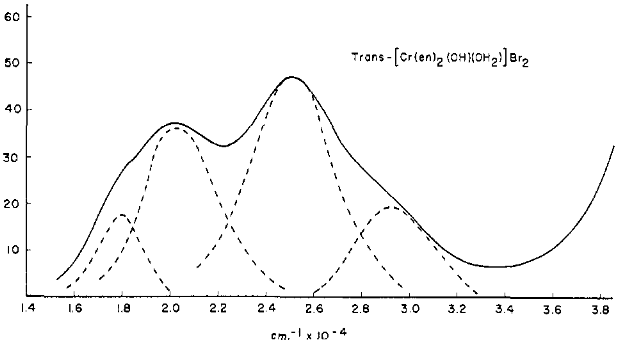

Figure 2.—Absorption spectrum of *trans*-$[Cr(en)_2(OH)(H_2O)]^{2+}$.

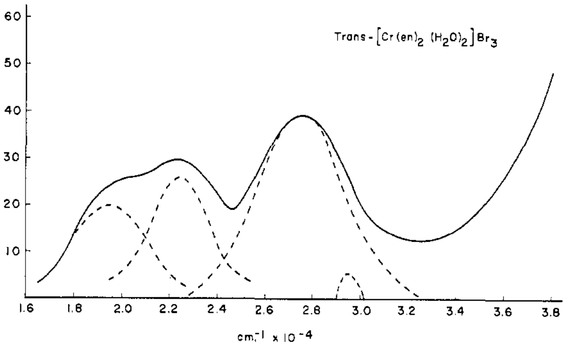

Figure 3.—Absorption spectrum of *trans*-$[Cr(en)_2(H_2O)_2]^{3+}$.

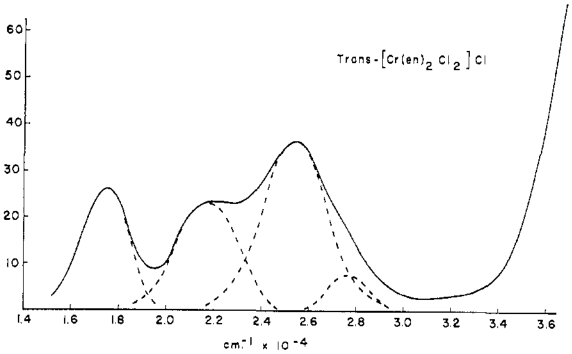

Figure 4.—Absorption spectrum of *trans*-$[Cr(en)_3Cl_2]^+$.

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[15] C. K. Jørgensen, *Acta Chem. Scand.*, **8**, 1495 (1954).

[16] L. E. Orgel, *J. Chem. Phys.*, **23**, 1004 (1955),

[17] C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press Ltd., London, 1962, p 109.

[18] W. E. Hatfield, J. F. Anders, and L. J. Rivela, *Inorg. Chem.*, **4**, 1088 (1965).

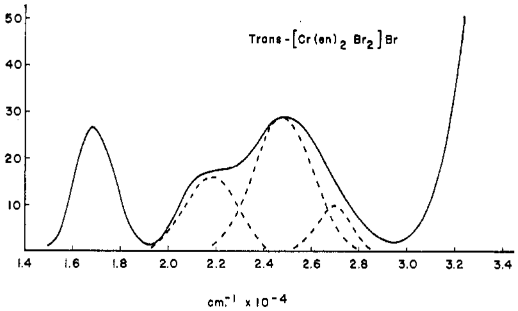

Figure 5.—Absorption spectrum of *trans*-$[Cr(en)_2Br_2]^+$.

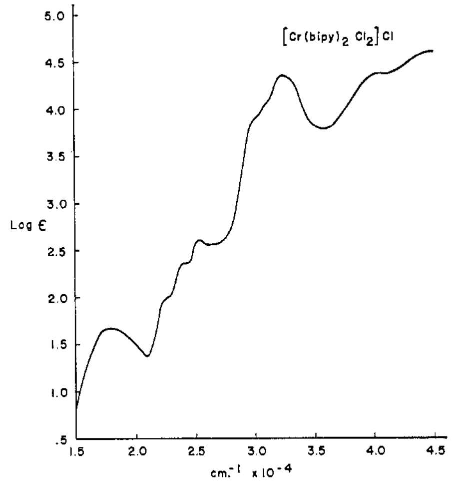

Figure 6.—Absorption spectrum of *trans*-$[Cr(bipy)_2Cl_2]^+$.

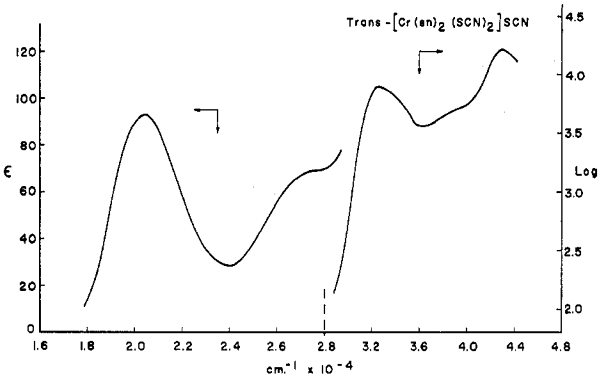

Figure 7.—Absorption spectrum of *trans*-$[Cr(en)_2(SCN)_2]^+$.

TABLE I

ABSORPTION SPECTRA AND BAND ASSIGNMENT OF *trans*-$[CrA_4B_2]^{n+}$ COMPLEXES

	Band maxima, $cm^{-1} \times 10^{-3}$	E_{max}	Assignment
$[Cr(en)_2(OH)_2]^+$	18.25	13	E_g (T_{2g})
	19.92	27	B_{2g}
	25.19	30	E_g (T_{1g})
	30.30	13	A_{2g}
$[Cr(en)_2(OH)(H_2O)]^{2+}$	18.02	18	E_g (T_{2g})
	20.20	36	B_{2g}
	25.16	47	E_g (T_{1g})
	29.41	19	A_{2g}
$[Cr(en)_2(H_2O)_2]^{3+}$	19.68	20	E_g (T_{2g})
	22.47	36	B_{2g}
	27.47	39	E_g (T_{1g})
	29.67	6	A_{2g}
$[Cr(en)_2(Cl_2)]^+$	17.54	26	E_g (T_{2g})
	21.88	23	B_{2g}
	25.38	36	E_g (T_{1g})
	27.70	8	A_{2g}
$[Cr(en)_2Br_2]^+$	16.78	26	E_g (T_{1g})
	21.79	16	B_{2g}
	24.81	29	E_g (T_{1g})
	26.95	10	A_{2g}
$[Cr(en)_2I_2]^+$	16.35[a]	...	E_g (T_{2g})
	21.00	...	B_{2g}
$[Cr(bipy)_2Cl_2]^+$	18.02	46	E_2 (T_{2g})
	22.47	?	B_{2g}
	24.10	?	E_2 (T_{1g})
	25.51	?	A_{2g}
$[Cr(en)_2(SCN)_2]^+$	20.70	93	$^4T_{2g}$
	27.47	67	$^4T_{1g}$

[a] Only two bands are observable owing to the onset of a high-intensity band at ~22,000 cm^{-1}.

TABLE II

CRYSTAL FIELD PARAMETERS FOR *trans*-$[CrA_4B_2]^{n+}$ COMPLEXES

Complex	10*Dq*, $cm^{-1} \times 10^{-3}$	*B*, cm^{-1}	*Dt*, cm^{-1}	*Ds*, cm^{-1}
$[Cr(en)_2(OH)_2]^+$	19.92	675	+191	−812
$[Cr(en)_2(OH)(H_2O)]^{2+}$	20.20	651	+249	−657
$[Cr(en)_2(H_2O)_2]^{3+}$	22.47	632	+319	−300
$[Cr(en)_2Cl_2]^+$	21.88	597	+496	−283
$[Cr(en)_2Br]^{2+}$	21.79	581	+573	−237
$[Cr(en)_2I_2]^+$	21.00	...	531	...
$[Cr(bipy)_2Cl_2]^+$	22.47	422	+509	−128

TABLE III

$\delta\sigma$ AND $\delta\sigma$ VALUES FOR *trans*-$[CrA_4B_2]^{n+}$ COMPLEXES

Complex	$\delta\sigma$, cm^{-1}	$\delta\pi$, cm^{-1}
$[Cr(en)_2(OH)_2]^+$	860	1695
$[Cr(en)_2(OH)(H_2O)]^{2+}$	518	1607
$[Cr(en)_2(H_2O)_2]^{3+}$	−150	1205
$[Cr(en)_2Cl_2]^+$	−505	1665
$[Cr(en)_2Br_2]^+$	−723	1782
$[Cr(bipy)_2Cl_2]^+$	−760	1465

lauxetic effect can also be obtained from the *B* values and is $OH^- < H_2O < Cl^- < Br^-$ and en < bipy, again essentially in agreement with expectation.[17]

The values of $\delta\sigma$ and $\delta\pi$ resulting from the application of McClure's model are also very reasonable. The order of σ-antibonding ability as derived from the data is $OH^- >$ bipy > en $> H_2O > Cl^- > Br^-$ and for the π-antibonding ability it is $Br^- > OH^- > Cl^- > H_2O >$ bipy > en. The orders are about what would be logically expected except that the high σ antibonding of bipyridyl is surprising when one considers pK_a values. Having only one bipyridyl complex obviously makes this value less reliable. It should be noted that the $\delta\pi$ values for OH^-, Br^-, and Cl^- are all very similar and small errors in assigning band maxima might change the order of their values but not the general result. In any event, the signs of $\delta\sigma$ and $\delta\pi$ are certainly logical. It is significant that OH^- is more *strongly* σ antibonding than ethylenediamine in spite of having a weaker ligand field strength. As of course has been suggested,[18,19] an explanation lies in the high π-antibonding ability of OH^-. Similar relationships can be seen between $\delta\sigma$, $\delta\pi$, and the ligand field strengths of the other ligands.

The relative energies of the one-electron orbitals are of interest. As expected, the two theoretical approaches agree on the ordering. It is worth noting that for the two complexes containing hydroxide, the d_{z^2} orbital lies higher than the $d_{x^2-y^2}$, thus reflecting the high σ strength of hydroxide. As would be predicted, d_{xy} lies lower than $d_{xz,yz}$ owing to the π-antibonding character of the axial ligands. Application of eq 2a–d yields d_{z^2}–$d_{x^2-y^2}$ and d_{xy}–$d_{xz,yz}$ separations which agree precisely in magnitude and sign with those predicted by McClure's method ($(8/3)\delta\sigma$ and $2\delta\pi$, respectively), as of course they must since the two different formulations are equivalent.

trans-**[Cr(en)$_2$(NCS)$_2$]$^+$.**—The one *trans* complex that we have studied in which absolutely no splitting can be observed is the thiocyanate. Its spectrum is given in Figure 7. On the basis of *Dq* values obtained from octahedral complexes, one would expect the band splittings for the thiocyanate to be about that of the aquo complex, since 10*Dq* for $[Cr(NCS)_6]^{3-}$ is 17,800 cm^{-1} and for $[Cr(H_2O)_6]^{3+}$ it is 17,400 cm^{-1}. Although it is possible that the thiocyanate is S-bonded in the *trans* complex, this would lead to a prediction of an even larger splitting since available data indicate that the ligand field strength of the N-bonded form is appreciably greater than that of the S-bonded form.[17] We thus believe that splittings in lower symmetry complexes cannot necessarily be predicted on the basis of differences in ligand field strengths as represented by *Dq* values for octahedral complexes. This conclusion is reinforced by the observation that the splitting of the first band in the hydroxo complex is less than for the aquo complex. The value of *Dt* then is not necessarily expected to be a simple function of the difference in octahedral *Dq* values for the two ligands.

cis **Isomers.**—The spectra of a number of *cis* complexes have also been studied. A summary of the band positions and the 10*Dq* and *B* values is given in Table IV. No splitting of the bands was observed. The 10*Dq* values were obtained from the observed maximum of the first band and *B* from the difference between the first and second. Since these bands are presumably composed of two unresolved components, a slight error will be introduced by this procedure, but considering the narrowness of the bands, the error cannot be large, except possibly for the aquo–hydroxo complex where appreciable asymmetric broadening on the high-energy side of the second band is observed. It is this broadening that is probably responsible for the anomalously low value of *B* for this complex.

TABLE IV

BAND MAXIMA AND 10*Dq* AND *B* VALUES FOR *cis*-$[Cr(en)_2X_2]^{n+}$ COMPLEXES

X	I	II	*B*
en	21.9	28.5	550
SCN^-	20.6	26.8	516
H_2O	20.5	27.4	575
N_3^-	19.6	25.1	460
$(OH)(H_2O)$	19.5	25.6	508
OH^-	19.0	26.5	625
Cl^-	18.9	24.9	500
Br^- [a]	18.4	24.1	475

[a] Data taken from L. P. Quinn and C. S. Garner, *Inorg. Chem.*, **3**, 1348 (1964).

The order of ligand field strengths based on the spectra of the *cis* isomers is $Br^- < Cl^- < OH^- < N_3^- < H_2O < SCN^- <$ en, and the nephelauxetic effect is $OH^- < H_2O <$ en $< SCN^- < Cl^- < Br^- < N_3^-$. This order for the nephelauxetic effect is the same as that found for the *trans* isomer, although in all comparable cases the *B* value for the *cis* isomer is smaller than that for the *trans*. Correspondingly the 10*Dq* values for the *trans* isomers are greater than those for the *cis* isomers. The explanation for this might lie in a decreased effectiveness of the π-antibonding character of the axial ligands in the *trans* configuration, since only two of the t_{2g} set will be used in the *trans* configuration and all three in the *cis*. Recall that ethylenediamine has no lone pairs of π symmetry and that π bonding of the ligand-to-metal type operates in such a way as to decrease the 10*Dq* value.

It is to be noted that hydroxide has a relatively greater ligand field in the *cis* isomers than in the *trans*. Piper and Wentworth[1] have recently suggested the existence of a "spectral *trans* effect." We feel that the relative weakness of OH^- in the *trans* configuration may be due to such an effect. That is, in this form, the metal–OH band is weakened owing to the *trans* effect of the opposite OH^- and thus is less effective than in the *cis* isomer.

Finally, there is the question of why no splitting is observed in the *cis* isomer. Splittings of 2000–2500 cm^{-1} are predicted for the first band in the chloride and bromide and the second band in the hydroxo and aquo–hydroxo complexes. Splittings of this magnitude should be observed, but except for the aquo–hydroxo complex there is no hint even of splitting. In fact, the bands are in general rather narrow. The question thus remains unanswered.

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(19) F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p 54.