shifts for (FeTPP)$_2$O and (FeTpMPP)$_2$O by a nonlinear least-squares process, as a function of A and J. The results are shown in Table II.

TABLE II

TEMPERATURE DEPENDENCE OF KNIGHT SHIFT OF PYRROLE PROTONS AND COMPUTED SHIFTS FROM BEST-FIT LEAST-SQUARES PARAMETERS

(FeTPP)$_2$O			(FeTpMPP)$_2$O		
	ΔH, cps			ΔH, cps	
Temp, °K	Calcd[a]	Exptl	Temp, °K	Calcd[a]	Exptl
323.2	−480	−481	323.2	−480	−477
313.2	−475	−474	313.2	−474	−473
303.2	−469	−470	303.2	−467	−470
293.2	−463	−464	293.2	−459	−455
283.2	−456	−454	283.2	−452	−455
273.2	−448	−446	273.2	−443	−448
263.2	−440	−440	263.2	−434	−434
253.2	−431	−433	253.2	−423	−419

[a] Calculated from best-fit least-squares parameters: (FeTPP)$_2$O, $A = 1.29 \times 10^5$ cps, $J = -309$ cm^{-1}; (FeTpMPP)$_2$O, $A = 1.44 \times 10^5$ cps, $J = -335$ cm^{-1}.

Table II which outlines the temperature dependence of the Knight shift of pyrrole protons leads to a value of $J = -309$ and -335 cm^{-1} for (Fe^{III}TPP)$_2$O and (Fe^{III}TpMPP)$_2$O, respectively. These values are somewhat larger than those obtained from magnetic susceptibility data of similar chelates in the solid state. The errors involved in measurement could account for some of the disparity between the two sets of results. The errors in the J values determined here are of the order ±50 cm^{-1}. The increase in the value of J noted when the systems are in a solution phase could lie in a slight variation of the bond angle in the relevant Fe^{III}–O–Fe^{III} system, with the tendency to become more linear resulting in a higher J value. A reason for considering an increase in bond angle arises from a consideration of the interaction between the two porphyrin rings which could be influenced by packing in the solid state. It is envisaged that the process of solution could aleviate constraints imposed by packing considerations leading to a widening of the Fe^{III}–O–Fe^{III} bond angle. It must be pointed out that a factor neglected in the treatment of the data here, and which is a problem specific to the porphyrins, is the possibility of a shielding effect due to ring current effects on the protons in the other porphyrin ring. However, it is felt that such effects would be small.[10]

It has been noted by Cohen[3] that it is difficult to obtain preparations of the binuclear iron(III) porphyrins that do not contain small amounts of high-spin impurities. This fact, together with the large diamagnetic corrections for the porphine macrocycle make bulk susceptibility measurements on such systems difficult. The advantage of the nmr method lies in the fact that, even if small amounts of high-spin impurity are present, direct observations on the low-spin binuclear complex can be made to obtain the important magnetic parameters.

(10) D. A. Doughty and C. W. Dwiggins, *J. Phys. Chem.*, **73**, 423 (1969).

CONTRIBUTION FROM THE INORGANIC CHEMISTRY LABORATORY,
OXFORD UNIVERSITY, OXFORD, ENGLAND

The Electronic Spectra of Tetragonal Chromium(III) Complexes

BY L. DUBICKI* AND P. DAY

Received November 24, 1970

The polarized electronic spectra of *trans*-[Cr(en)$_2$X$_2$]ClO$_4$, X = Br and Cl, and *trans*-[Cr(en)$_2$(H$_2$O)$_2$]Cl·H$_2$O are reported and the quartet ligand field bands are assigned. The tetragonal ligand field parameter κ $(=Ds/Dt)$ is found to be +0.8, +0.33, and −0.8 for X = Br, Cl, and H$_2$O, respectively. The intensities of the ligand field bands are vibronic in origin and the temperature dependence of the intensity of the $^4E_g(^4T_{2g})$ band follows the coth law. The nature of the odd-parity states which give intensity to the ligand field transitions is discussed.

I. Introduction

It has been shown[1] that the magnitude of the tetragonal ligand field parameter, κ $(=Ds/Dt)$, can be rationalized by expressing κ in terms of the empirical molecular orbital parameters $\delta\sigma$ and $\delta\pi$[2,3] whose signs can often be predicted from the knowledge of the bonding capabilities of the ligands. This simple model failed in many cases to predict the sign of κ as this required the knowledge of the magnitude of $\delta\sigma$ relative to that of $\delta\pi$. The present work was carried out to establish the signs of these tetragonal parameters. In addition a more penetrating experimental study of the vibronic mechanism seemed possible with the available range of complexes. Quantitative work on the temperature dependence of the intensity of ligand field transitions has been limited to the broad bands in hexaaquo complexes[4] and certain sharp absorptions in [(CH$_3$)$_4$N]$_2$UCl$_6$.[5]

Previous work[6,7] has established that the intensities of the ligand field transitions in *trans*-Co(en)$_2$X$_2$$^+$ and *trans*-Cr(en)$_2$F$_2$$^+$ are predominantly vibronic in origin and that the electronic spectra can be interpreted using the effective point group D_{4h}. According to the vibronic selection rules only the $^4B_{1g} \rightarrow {}^4B_{2g}$, $^4A_{2g}$ transitions are forbidden, both in z polarization. Provided

---

* To whom correspondence should be addressed at the Chemistry Department, Monash University, Clayton, Victoria 3168, Australia.

(1) L. Dubicki and R. L. Martin, *Aust. J. Chem.*, **22**, 839 (1969).

(2) H. Yamatera, *Bull. Chem. Soc. Jap.*, **31**, 95 (1958).

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

(4) O. G. Holmes and D. S. McClure, *J. Chem. Phys.*, **26**, 1686 (1957).

(5) R. A. Satten and E. Y. Wong, *ibid.*, **43**, 3025 (1965).

(6) R. Dingle, *ibid.*, **46**, 1 (1967).

(7) L. Dubicki, M. A. Hitchman, and P. Day, *Inorg. Chem.*, **9**, 188 (1970).

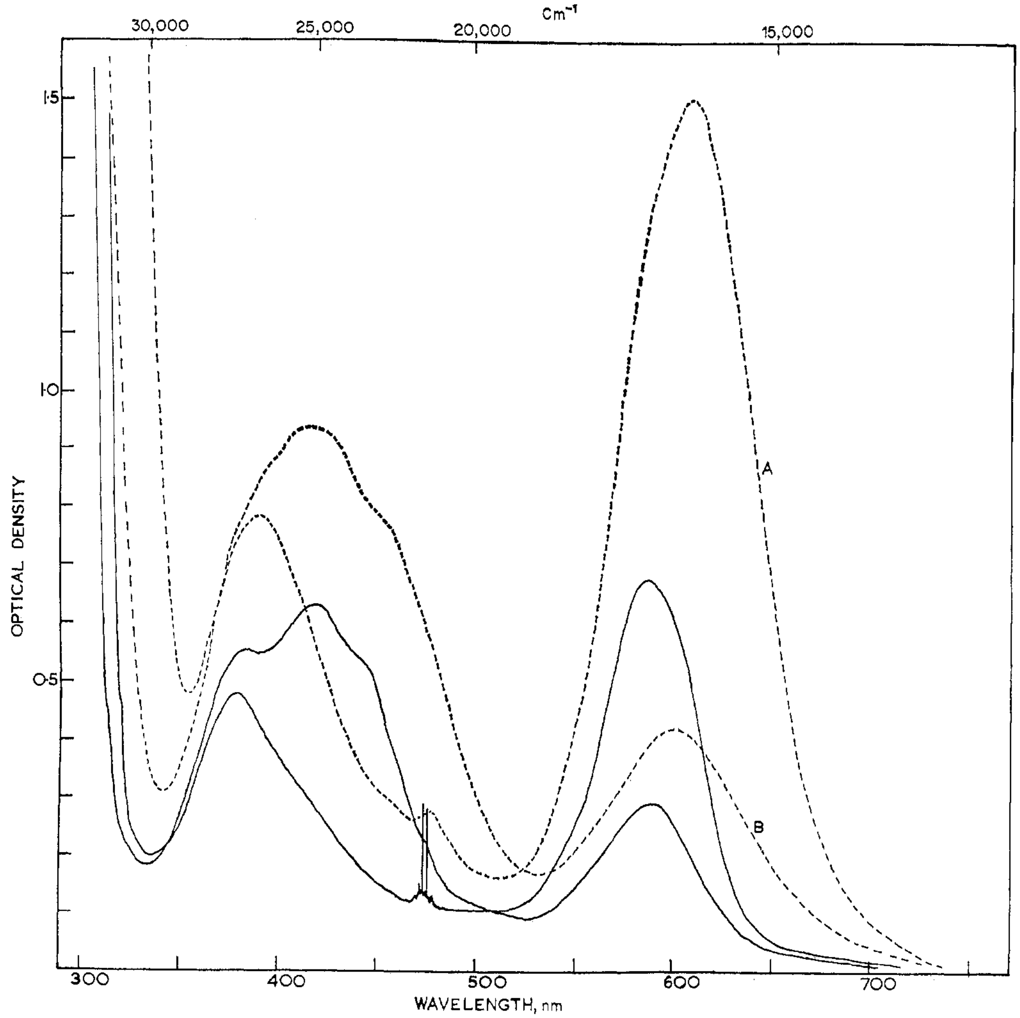

Figure 1.—The electronic spectrum of *trans*-$[Cr(en)_2Br_2]ClO_4$: broken line, 290°K; solid line, 4.2°K. Spectra A are nearly completely *z* polarized while spectra B are predominantly *xy* polarized (*cf.* discussion in section III(a)). Crystal thickness in 0.085 mm.

the orientation of the molecules in the crystal is favorable it should be possible to determine which of the observed polarized spectra are mainly *xy* or *z* polarized even though the crystal structures are not known. A good example of such a favorable orientation is found in the fluoro complex.[7]

II. Experimental Section

Thin plates of *trans*-$[Cr(en)_2X_2]ClO_4$, X = Cl and Br, were obtained by dissolving the perchlorate salts in dimethylformamide, adding a few drops of water, and allowing the solutions to evaporate for several hours. Thin plates of *trans*-$[Cr(en)_2(H_2O)_2]Cl \cdot H_2O$ were obtained by dissolving *trans*-$[Cr(en)_2(OH)(H_2O)](ClO_4)_2 \cdot H_2O$ in dilute HCl and adding a few drops of acetone. The terminal ligands are somewhat labile and it is necessary to have a moderate rate of evaporation. The preparation of a large series of *trans*-$Cr(en)_2XY$ complexes is described in ref 8.

The electronic spectra were recorded on a Cary 14 spectrophotometer. Polarized spectra were obtained by placing a Glan Thompson prism before the sample pinhole. The cryostat has been described elsewhere.[9] The spectral areas were measured by weighing the chart paper. Only the intensity of the well-resolved $^4E_g(^4T_{2g})$ band in the chloro and bromo complexes was quantitatively examined. The base line was chosen as the straight line connecting the point of zero absorption at 700 nm and the point of minimum absorption at ~500 nm, at 4.2°K. The increase in the latter absorption with temperature was taken into account.

III. Results

(a) **Electronic Spectra.**—The electronic spectra of the complexes studied are shown in Figures 1–3. The measurements of the intensity of the $^4E_g(^4T_{2g})$ band (*cf.* section III(b)) indicate that within experimental error the intensities are completely vibronic in origin and hence the vibronic selection rules given in Table VI can be used. The assignment of the spectra is simplified by noting that in all cases *Dt* is negative and the lowest energy quartet state is $^4E_g(^4T_{2g})$.[10] Since only the $^4B_{1g} \rightarrow {}^4E_g$ transitions are allowed in *z* polarization, the observation of two bands in the A spectra of the dibromo and dichloro complexes suggests that A polarization corresponds very closely to the molecular *z* polarization. This interpretation is confirmed by the identification of the effective odd-parity vibration (*cf.* section III(b)). Since all bands are observed in the B spectra, B polarization contains both *z* and *xy* components but the large dichroism suggests that the B spectrum is predominantly *xy* polarized. For the diaquo complex the A and B spectra contain both *z* and *xy* components but since the $^4B_{1g} \rightarrow {}^4B_{2g}$, $^4A_{2g}$ transitions are allowed only in *xy* polarization, spectrum B has more of the *xy* component and the assignment of the spectrum is again straightforward.

---

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

(9) B. D. Bird, P. Day, and E. A. Grant, *ibid.*, 100 (1970).

(10) J. R. Perumareddi, *J. Phys. Chem.*, **71**, 3155 (1967).

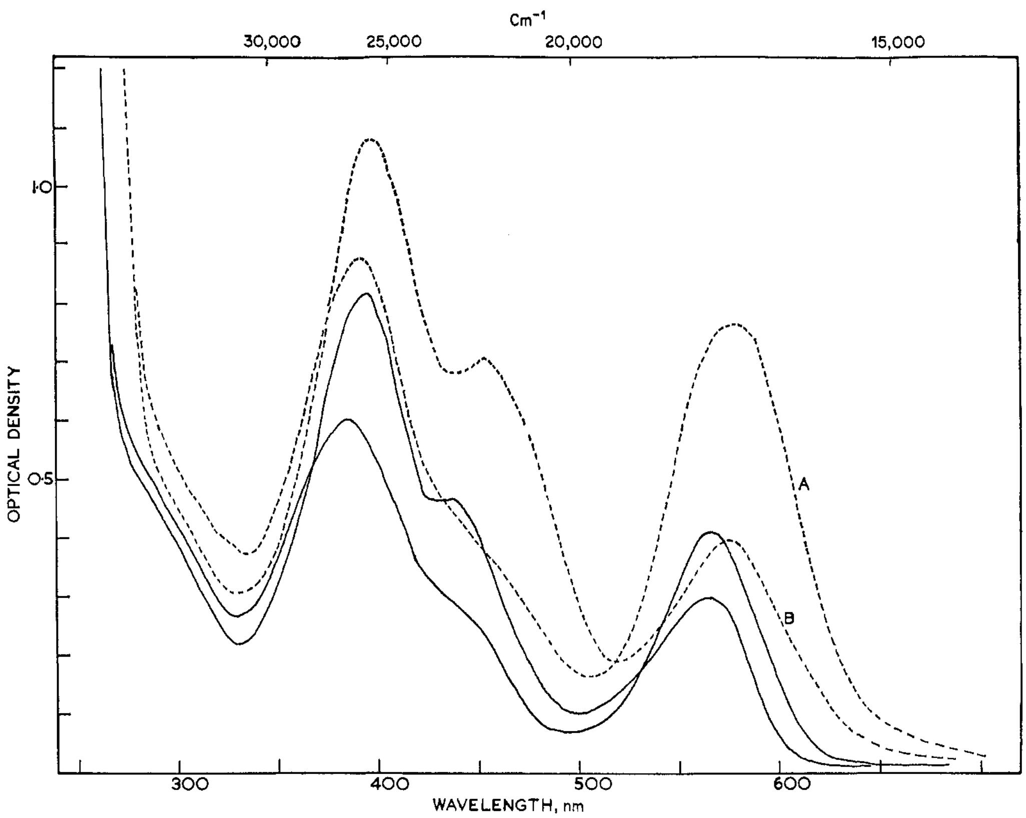

Figure 2.—The electronic spectrum of *trans*-$[Cr(en)_2Cl_2]ClO_4$: broken line, 290°K; solid line, 4.2°K. Spectra A are nearly completely z polarized while spectra B are predominantly xy polarized. Crystal thickness is 0.068 mm.

The fitting of the band maxima with the ligand field matrices of Perumareddi[10] is given in Tables I–III.

TABLE I

SPECTRAL DATA OF *trans*-$[Cr(en)_2Br_2]ClO_4$[a]

Freq, cm⁻¹			Freq, cm⁻¹		
Calcd[c]	Obsd	Assignment	Calcd	Obsd	Assignment
16,970	17,000 (A)[b]	${}^4E_g({}^4T_{2g})$	22,500	22,500 (B)	${}^4B_{2g}({}^4T_{2g})$
19,930	20,945 (A)	${}^3B_{2g}({}^2T_{2g})$	23,860	23,900 (B)	${}^4A_{2g}({}^4T_{1g})$
20,300	21,040 (A)	${}^2E_g({}^2T_{2g})$	26,340	26,300 (A)	${}^4E_g({}^4T_{1g})$

[a] Data in Tables I–III taken at 4.2°K. [b] The observed frequency is taken from the polarized spectrum in which the particular band is more intense. [c] Calculated using the matrices of Perumareddi[10] for $Dq = 2250$ cm^{-1}, $Dt = -580$ cm^{-1}, $B = 575$ cm^{-1}, $C/B = 5.0$, and $\kappa = +0.8$.

TABLE II

SPECTRAL DATA OF *trans*-$[Cr(en)_2Cl_2]ClO_4$

Freq, cm⁻¹			Freq, cm⁻¹		
Calcd[a]	Obsd	Assignment	Calcd[a]	Obsd	Assignment
17,710	17,700 (A)	${}^4E_g({}^4T_{2g})$	25,470	25,400 (B)	${}^4A_{2g}({}^4T_{1g})$
22,500	22,800 (B)	${}^4B_{2g}({}^4T_{2g})$	26,190	26,000 (A)	${}^4E_g({}^4T_{1g})$

[a] Calculated using the matrices of Perumareddi[10] for $Dq = 2250$ cm^{-1}, $Dt = -520$ cm^{-1}, $B = 600$ cm^{-1}, $C/B = 5.0$, and $\kappa = +0.33$.

TABLE III

SPECTRAL DATA OF *trans*-$[Cr(en)_2(H_2O)_2]Cl \cdot H_2O$

Freq, cm⁻¹			Freq, cm⁻¹		
Calcd[a]	Obsd	Assignment	Calcd[a]	Obsd	Assignment
20,160	20,000 (A)	${}^4E_g({}^4T_{2g})$	23,500	23,500 (B)	${}^4B_{2g}({}^4T_{2g})$
21,860		${}^2B_{2g}({}^2T_{2g})$	27,250	27,500 (A)	${}^4E_g({}^4T_{1g})$
22,625	22,285 (A)	${}^2E_g({}^2T_{2g})$	29,260	29,300 (B)	${}^4A_{2g}({}^4T_{1g})$

[a] Calculated using the matrices of Perumareddi[10] for $Dq = 2350$ cm^{-1}, $Dt = -380$ cm^{-1}, $B = 625$ cm^{-1}, $C/B = 5.0$, and $\kappa = -0.8$.

TABLE IV

TETRAGONAL SYMMETRY PARAMETERS FOR *trans*-$Cr(en)_2X_2$

X	Dt,[a] cm⁻¹	κ[a]	$\delta\sigma$,[b] cm⁻¹	$\delta\pi$,[b] cm⁻¹
F[c]	−320	−2.5	+600	+2000
H_2O	−380	−0.8	−260	+1410
Cl	−520	+0.33	−1240	+1040
Br	−580	+0.8	−1780	+750

[a] Obtained by fitting the observed band energies with the ligand field matrices of Perumareddi.[10] [b] Obtained from the equations given in section III(a). [c] Taken from ref 7.

The parameters κ and Dt, treated as symmetry parameters, can be transformed into the empirical molecular orbital parameters by the relationships[1]

$$\delta\sigma = \frac{3Dt}{2}(\kappa + {}^5/_4) = -{}^3/_8\Delta(\mathrm{e})$$

$$\delta\pi = \frac{3Dt}{2}(\kappa - {}^5/_3) = -{}^1/_2\Delta(\mathrm{t}_2)$$

where $\Delta(\mathrm{e})$ is the one-electron energy difference $\epsilon(x^2 - y^2) - \epsilon(z^2)$ and $\Delta(\mathrm{t}_2) = \epsilon(xy) - \epsilon(xz, yz)$.[11] The tetragonal symmetry parameters are listed in Table IV. The splitting of the e_g orbitals, $\Delta(\mathrm{e})$, is found to be +4.8, +3.3, +0.72, and −1.6 kK for X = Br, Cl, H_2O, and F, respectively. These results confirm the work of Glerup and Schäffer,[11] who derived the values of $\Delta(\mathrm{e})$ and $\Delta(\mathrm{t}_2)$ for *trans*-$Cr(NH_3)_4X_2$ (X = Br, Cl, F, H_2O, OH) from a systematic study of their solution spectra.

$\delta\sigma$ and $\delta\pi$ are essentially symmetry parameters which contain both covalent and electrostatic contributions. The two contributions may be resolved by estimating the electrostatic component in the manner described by Yamatera.[2] Unfortunately the molecular dimensions

---

(11) J. Glerup and C. E. Schäffer, "Progress in Co-ordination Chemistry," M. Cais, Ed., Elsevier, Amsterdam, 1968, p 500.

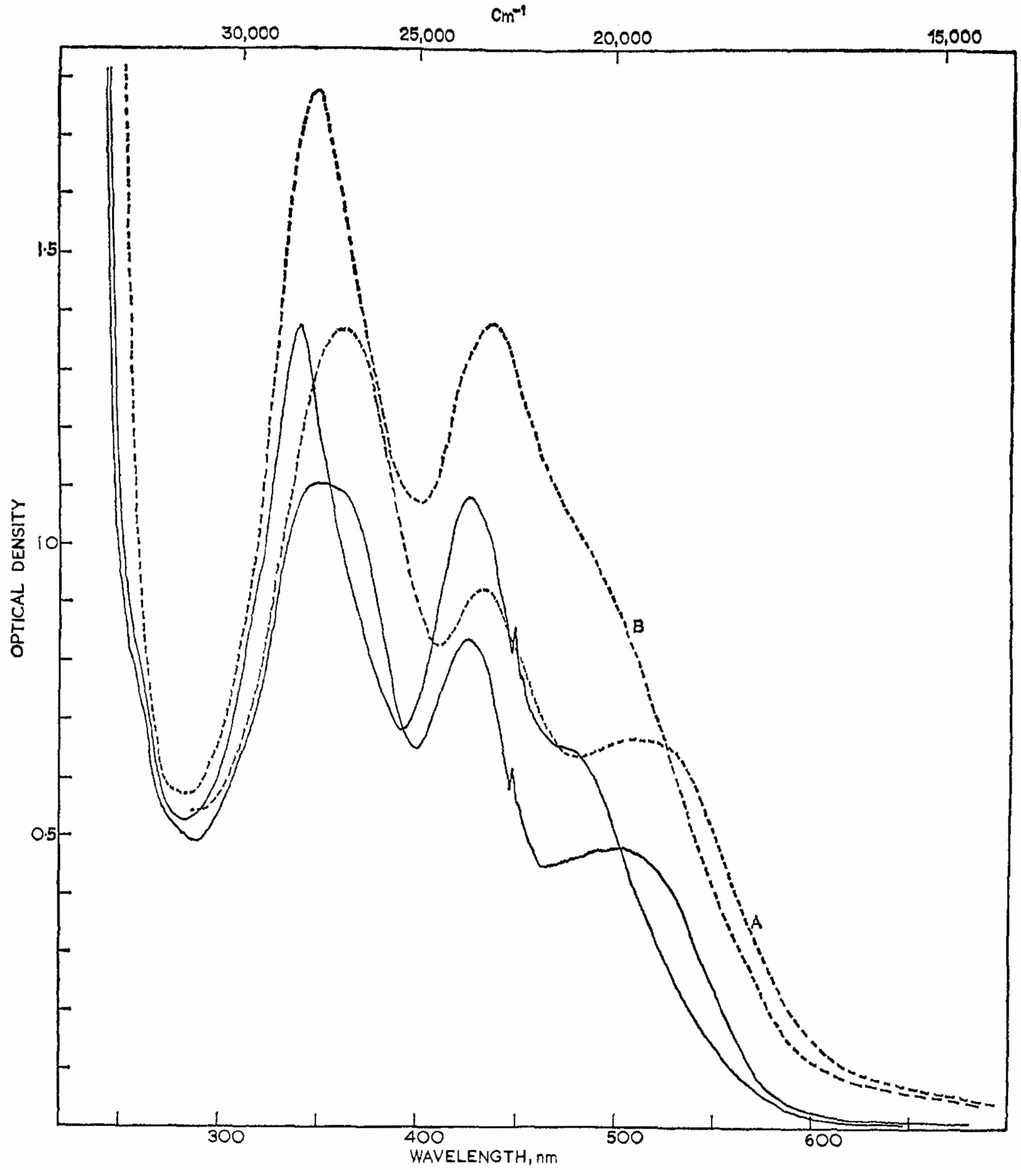

Figure 3.—The electronic spectrum of *trans*-$[Cr(en)_2(H_2O)_2]Cl \cdot H_2O$: broken line, 290°K; solid line, 4.2°K. Spectrum B has more of the *xy* component. Crystal thickness is 0.17 mm.

are not known. Nevertheless for a hard acid like the Cr(III) ion one may expect the trend in covalency to be $F^- > H_2O > Cl^- > Br^-$ for both σ and π bonding, which would be similar to the observed trend in $\delta\sigma$ to $\delta\pi$. The high position of the fluoride ion in this two-dimensional spectrochemical series applies only to the Cr(III) complex. In *trans*-$Co(en)_2F_2^+$, $|\delta\sigma|$ and $\delta\pi$ are smaller since the second ligand field band ($^1T_{2g}$) exhibits no discernible splitting in the solution spectrum. This difference has been attributed to the partially filled t_{2g} subshell in Cr(III) where ligand to metal π interaction should stabilize the complex.[1]

(b) **Effective Odd-Parity Vibrations.**—The intensity of a vibronically allowed transition should follow the relationship[12] $f(T) = f(0) \coth (h\nu/2kT)$ where $f(0)$ is the oscillator strength at 0°K and ν is the frequency of the odd-parity vibration. Lohr[13] has shown that the coth law depends only on the assumption that the ground state is a harmonic oscillator. It is independent of the form of the excited-state potential which only determines the distribution of the intensity. Figure 4 illustrates the applicability of the coth law to broad electronic transitions.

In Table V the vibrational frequencies derived from

TABLE V

ODD-PARITY VIBRATIONAL MODES (CM^{-1})

	trans-$Co(NH_3)_4X_2$[a]		*trans*-$Cr(en)_2X_2$[b]		
	X = Br	X = Cl	X = Br	X = Cl	X = F[c]
$\epsilon_u\delta$(NMX), MX bend	140	178	130[d]	170[e]	~250
$\epsilon_u\delta$(NMN)	295	290			
$\epsilon_u\nu$(MN)	486	501			
$\alpha_{2u}\delta$(NMX), o.p. def	228	290[g]	200[f]	320[f]	>400
$\alpha_{2u}\nu$(MX)	318	353[g]			

[a] Taken from the infrared data given in ref 14. [b] Taken from the temperature dependence of the electronic spectra. [c] Taken from ref 7. [d] Experimental error 5 cm^{-1}. [e] Experimental error 10 cm^{-1}. [f] Experimental error 30 cm^{-1}. [g] Recent laser Raman studies suggest that the two α_{2u} assignments should be interchanged: T. M. Loehr, J. Zinich, and T. V. Long, II, *Chem. Phys. Lett.*, **7**, 183 (1970).

(12) A. D. Liehr and C. J. Ballhausen, *Phys. Rev.*, **106**, 1161 (1957).

(13) L. L. Lohr, Jr., *J. Chem. Phys.*, **50**, 4596 (1969).

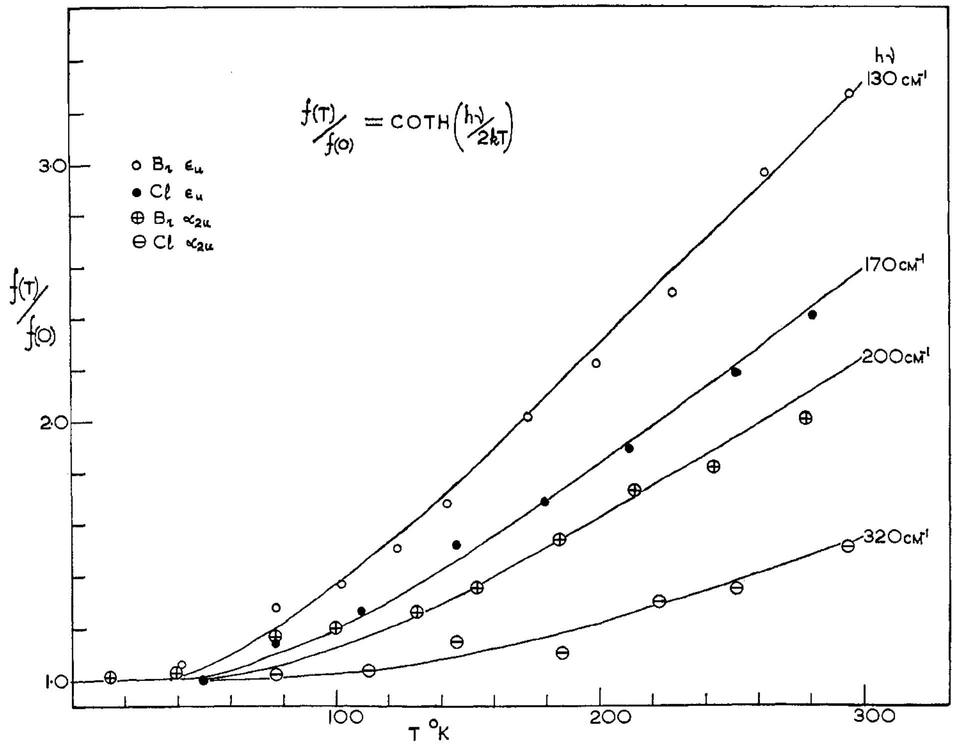

Figure 4.—The temperature dependence of the ${}^4E_g({}^4T_{2g})$ band intensity for *trans*-[Cr(en)$_2$X$_2$]ClO$_4$, X = Cl and Br, in both A and B spectra. The effective vibration in B polarization is assumed to be α_{2u}. For vibronic selection rules see Table VI.

the coth plots are compared with the infrared data for *trans*-Co(NH$_3$)$_4$X$_2$.[14] The normal-coordinate analysis on the cobalt complex[14] indicates that the skeletal α_{2u} and ϵ_u vibrations are of fairly pure mode as labeled in Table V. The very close correspondence between the effective ϵ_u and $\epsilon_u\delta$(NMX),MX bend energies clearly demonstrates that of the three ϵ_u vibrations only the $\epsilon_u\delta$(NCrX),CrX bend is active, at least for the ${}^4E_g({}^4T_{2g})$ band. The data are not sufficiently accurate to distinguish between the two α_{2u} vibrations and the infrared-inactive β_{2u} vibration. These problems are examined in section IV(b).

IV. Discussion

(a) Nature of the Odd-Parity States.—The mathematic formulation of the vibronic mechanism has been described by many authors.[12,15–17] Following Englman,[16] the admixture of the odd-parity states C and D in the even-parity ground and excited ligand field states A and B is given by

$$|A'\rangle = |A\rangle + \sum_C |C\rangle\langle C|H_v|A\rangle/(E_A - E_C) \qquad (1)$$

$$|B'\rangle = |B\rangle + \sum_D |D\rangle\langle D|H_v|B\rangle/(E_B - E_D) \qquad (2)$$

where H_v is the part of the vibrational Hamiltonian which is odd in the electronic coordinates. The dipole moment matrix element for the transition A′ → B′ is given by

$$\langle A'|P|B'\rangle = \sum_D \frac{\langle A|P|D\rangle\langle D|H_v|B\rangle}{E_B - E_D} + \sum_C \frac{\langle B|P|C\rangle\langle C|H_v|A\rangle}{E_A - E_C} \qquad (3)$$

where the dependence on the vibrational quantum numbers is ignored. From (3) it is apparent that three factors determine the extent to which a particular *ungerade* state contributes to the intensity. For *trans*-M(en)$_2$X$_2$ complexes which have electron-donor ligands the most important odd-parity states are believed to be those derived from the ligand-to-metal charge-transfer transitions πe_u, $\sigma a_{2u}(px)$, $\sigma e_u \rightarrow 3d$ (*cf.* Figure 5).[17] The transitions $3d \rightarrow \pi^*\sigma^*e_u$, σ^*a_{2u} are ex-

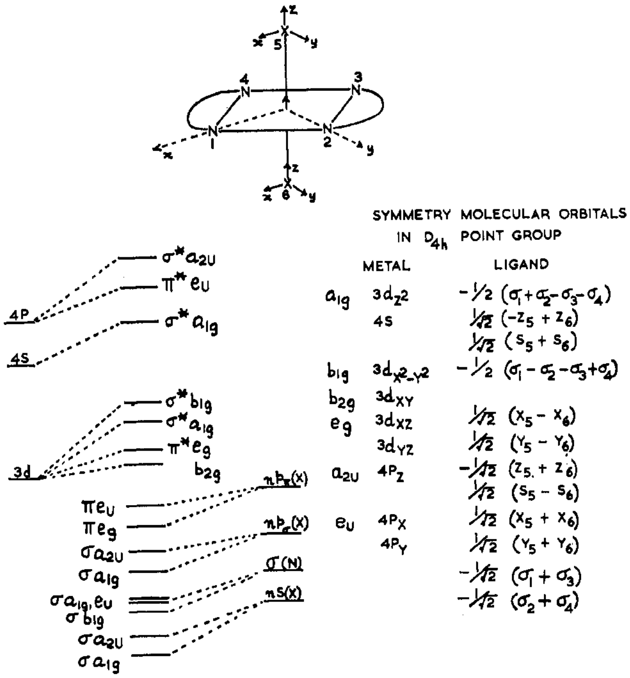

Figure 5.—Qualitative one-electron energy diagram for *trans*-M(en)$_2$X$_2$. The orientation of the axes at the nitrogen atoms is the same as at the metal atom.

---

(14) I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, **22**, 759 (1966).

(15) S. Koide and M. H. L. Pryce, *Phil. Mag.*, **3**, 607 (1958).

(16) R. Englman, *Mol. Phys.*, **3**, 48 (1960).

(17) R. Fenske, *J. Amer. Chem. Soc.*, **89**, 252 (1967).

pected to occur at even higher energy than $\sigma e_u \rightarrow 3d$ although it is probable that the metal 4p orbitals are involved to some extent in the lower energy charge-transfer transitions.

Fenske[17] has shown that since P and H_v are one-electron operators, the determinantal wave functions for C and D must not differ from the determinantal wave functions of both A and B by more than one spin orbital. Consequently only the charge-transfer transitions to the mainly metal b_{1g} ($3d_{x^2-y^2}$) and a_{1g} ($3d_{z^2}$) orbitals are important. The odd-parity states which satisfy this one-electron approximation and also the vibronic symmetry requirements are listed in Table VI.

TABLE VI

VIBRONIC SELECTION RULES AND THE *UNGERADE* STATES VIBRONICALLY ADMIXED IN THE GROUND AND EXCITED LIGAND FIELD STATES FOR *trans*-$Cr(en)_2X_2$ COMPLEXES WITH EFFECTIVE POINT GROUP D_{4h}[a]

	Excited state		Ground state
		xy Polarization	
$^4B_{1g} \rightarrow {}^4B_{2g}(xy \rightarrow x^2 - y^2)$	ϵ_u	$^4E_u(\sigma e_u, \pi e_u \rightarrow x^2 - y^2)$	^4E_u
$^4A_{2g}(xy \rightarrow z^2)$	ϵ_u	$^4E_u(\sigma e_u, \pi e_u \rightarrow z^2)$	^4E_u
$^4E_g(A)(xz \rightarrow z^2)$	α_{2u}	$^4E_u(\sigma e_u, \pi e_u \rightarrow z^2)$	$^4B_{2u}$
$^4E_g(B)(xz \rightarrow x^2 - y^2)$	α_{2u}	$^4E_u(\sigma e_u, \pi e_u \rightarrow x^2 - y^2)$	. . .
$^4E_g(A)(xz \rightarrow z^2)$	β_{2u}	$^4E_u(\sigma e_u \rightarrow z^2)$	. . .
$^4E_g(B)(xz \rightarrow x^2 - y^2)$	β_{2u}	$^4E_u(\sigma e_u \rightarrow x^2 - y^2)$	$^4A_{2u}$
		z Polarization	
$^4B_{ag} \rightarrow {}^4E_g(A)(xz \rightarrow z^2)$	ϵ_u	$^4B_{2u}(\sigma a_{2u}(px) \rightarrow z^2)$	^4E_u
$^4E_g(B)(xz \rightarrow x^2 - y^2)$	ϵ_u	. . .	^4E_u

[a] The *ungerade* states are derived from πe_u, σa_{2u}, $\sigma e_u \rightarrow 3d$ transitions and satisfy the one-electron approximation discussed in section IV(a). The transitions $3d \rightarrow \pi^*\sigma^*e_u$, σ^*a_{2u} are neglected. The constraint imposed by the vibrational matrix elements is discussed in section IV(b).

It has been suggested[17] that the odd-parity admixture in B is the more important quantity because the denominator in (2) is smaller and $\langle A|P|D\rangle$ is expected to be greater than $\langle B|P|C\rangle$. The latter assumption is based on Jørgensen's[18] observations that in hexahalide complexes the charge-transfer transitions to metal e_g orbitals are more intense than those to the t_{2g} orbital. It is also necessary to consider the relative magnitudes of $\langle D|H_v|B\rangle$ and $\langle C|H_v|A\rangle$. However the neglect of the odd-parity admixture in A simplifies the analysis and in the present qualitative discussion this approximation will be used.

It should be noted that the states $^4E_g(A)$ and $^4E_g(B)$ interact to produce the ligand field states $^4E_g(^4T_{2g})$ and $^4E_g(^4T_{1g})$. The $^4E_g(^4T_{2g})$ state has more $^4E_g(A)$ character as can be seen from the strong-axial, strong-field matrices given in ref 19. Electron repulsion also mixes $^4E_u(\pi e_u \rightarrow z^2)$ and $^4E_u(\pi e_u \rightarrow x^2 - y^2)$.

(b) **Odd-Parity Vibrations.**—Nakagawa and Shimanouchi[14] have shown that the skeletal α_{2u} and ϵ_u (and presumably β_{2u}) vibrations are of fairly pure mode and hence they can be represented by the Hamiltonians

$$\epsilon_u\delta(\text{NMX}) \quad {}^1/_2(x_5 + x_6 - 2x_0)\frac{\partial}{\partial x}(V_5 + V_6)$$

$$\epsilon_u\delta(\text{NMN}) \quad {}^1/_2(x_2 + x_4 - 2x_0)\frac{\partial}{\partial x}(V_2 + V_4)$$

$$\epsilon_u\nu(\text{MN}) \quad {}^1/_2(x_1 + x_3 - 2x_0)\frac{\partial}{\partial x}(V_1 + V_3)$$

$$\alpha_{2u}\delta(\text{NMX}) \quad {}^1/_4(z_1 + z_2 + z_3 + z_4 - 4z_0)\frac{\partial}{\partial z}(V_1 + V_2 + V_3 + V_4)$$

$$\alpha_{2u}\nu(\text{MX}) \quad {}^1/_2(z_5 + z_6 - 2z_0)\frac{\partial}{\partial z}(V_5 + V_6)$$

$$\beta_{2u}\delta(\text{NMN}) \quad {}^1/_4(z_1 - z_2 + z_3 - z_4)\frac{\partial}{\partial z}(V_1 - V_2 + V_3 - V_4)$$

The observation that only the $\epsilon_u\delta(\text{NMX})$ vibration is active in z polarization is not surprising for the following reasons. The two $^4B_{2u}$ states that mix with $^4E_g(A)$ are derived from the one-electron excitations $np_\sigma x$, $nsx \rightarrow (z^2)$. The matrix element which gives a measure of the effectiveness of the odd-parity vibration is $\langle ^4E_g(A)|H_v(\epsilon_u)|^4B_{2u}\rangle$. The wave functions for $^4B_{2u}$ and for one component of $^4E_g(A)$ are

$$|^4B_{2u}\rangle = \frac{1}{\sqrt{2}}\{|{----}(\overset{+}{a}_{2u})(\overset{-}{z}{}^2){-----}(x\overset{+}{y})x\overset{+}{z})(y\overset{+}{z})| - |{-----}(\overset{-}{a}_{2u})(\overset{+}{z}{}^2){-----}|\}$$

and

$$|^4E_g(A)\rangle = |{-----}(\overset{+}{x}y)(\overset{+}{z}{}^2)(y\overset{+}{z})|$$

we have

$$\langle ^4E_g(A)|H_v(\epsilon_u)|^4B_{2u}\rangle = -\frac{1}{\sqrt{2}}\langle (xz)|H_v(\epsilon_u)|\sigma a_{2u}\rangle$$

where (z^2) and (xz) are the mainly metal a_{1g} and e_g orbitals, respectively, and

$$(xz) = C_M^*(3d_{xz}) - C_L^*\frac{1}{\sqrt{2}}(x_5 - x_6)$$

$$\sigma a_{2u} = C_L[-\frac{1}{\sqrt{2}}(z_5 + z_6)] + C_M(4p_z) + \ldots$$ [20]

It is evident that the dominant term in the expansion of the vibronic matrix element is

$$C_M^*C_L\left\langle 3d_{xz}\middle|\frac{\partial}{\partial x}(V_5 + V_6)\middle|-\frac{1}{\sqrt{2}}(z_5 + z_6)\right\rangle$$

which arises from the $\epsilon_u\delta(\text{NMX})$ vibration. In contrast the Hamiltonians for the other two $\epsilon_u\delta(\text{NMN})$ and $\nu(\text{MN})$ vibrations have the potentials centered on the in-plane ligands and for these vibrations the above term becomes a three-center integral of much smaller magnitude.

The situation is more complicated for the ϵ_u vibrations in xy polarization because of the existence of ^4E_u states arising from the charge transfer from $\sigma(N)$ orbitals. The above argument suggests that $\epsilon_u\delta(\text{NMX})$ vibration will mix $^4E_u(\pi e_u)$ while $e_u\delta(\text{NMN})$ and $\nu(\text{MN})$ vibrations will mix $^4E_u(\sigma e_u)$. Although $^4E_u(\sigma e_u)$ lies at higher energy, the matrix element $\langle ^4B_{1g}|P|^4E_u(\sigma e_u)\rangle$ is much larger than $\langle ^4B_{1g}|P|^4E_u(\pi e_u)\rangle$ so that even a very small admixture of $^4E_u(\sigma e_u)$ may be important (*cf.* Appendix). It is therefore possible that

---

(18) C. K. Jørgensen, *Mol. Phys.*, **2**, 309 (1959).

(19) J. R. Perumareddi, *J. Phys. Chem.*, **71**, 3144 (1967).

(20) The same results apply to the $\sigma a_{2u}(sx)$ orbital but the corresponding $^4B_{2u}(sx)$ state lies at much higher energy, and since the magnitude of $\langle ^4B_g|P|^4B_{2u}(px)\rangle$ is at least comparable to that of $\langle ^4B_{1g}|P|^4B_{2u}(sx)\rangle$, the $^4B_{2u}(sx)$ state should not be important in the vibronic process.

the effective ϵ_u vibration for the $^4B_{1g} \rightarrow {}^4B_{2g}$, $^4A_{2g}$ transitions would have a value intermediate between that of $\epsilon_u\delta$(NMX) and $\epsilon_u\delta$(NMN), ν(MN) if a single coth function is used in the analysis of the intensity. Unfortunately, the $^4A_{2g}$, $^4E_g(^4T_{1g})$, and $^4B_{2g}$ bands overlap strongly (*cf.* Figures 1 and 2), and the effective frequency cannot be obtained with any accuracy. Even so, the intensities decrease appreciably with decrease in temperature, suggesting that the lower energy $\epsilon_u\delta$(NMX) vibration and hence the $^4E_u(\pi e_u)$ state are more important. The activity of the $\epsilon_u\delta$(NMN) and ν(MN) vibrations could increase along the series X = Br, Cl, F since the energy of the $^4E_u(\pi e_u)$ state will increase and approach that of the $^4E_u(\sigma e_u)$ state.

A similar situation occurs for the $^4B_{1g} \rightarrow {}^4E_g$ transitions in *xy* polarization. The $\alpha_{2u}\nu$(MX) vibration will mix $^4E_u(\pi e_u)$ while $\alpha_{2u}\delta$(NMX) and $\beta_{2u}\delta$(NMN) will mix $^4E_u(\sigma e_u)$. It is possible that the $\alpha_{2u}\nu$(MX) vibration will be more effective for X = Br since $^4E_u(\pi e_u)$ will lie at lower energy for X = Br than for X = Cl. The experimental data are not good enough to establish which of the vibrations is dominant. It would be desirable to have complete and precise infrared and Raman data for the Cr(III) complexes.[21]

There is no doubt that in *z* polarization most of the intensity comes from the $^4B_{2u}(\sigma a_{2u}(px) \rightarrow z^2)$ state. Its energy is intermediate between that of $^4E_u(\pi e_u)$ and $^4E_u(\sigma e_u)$ and the matrix element $\langle ^4B_{1g}|P|^4B_{2u}\rangle$ is large.[22] It is evident from Figures 1 and 2 that for X = Br the $^4E_g(^4T_{2g})$ band is more intense in *z* than in *xy* polarization and that this difference is reduced for X = Cl and possibly reversed for X = F. This trend is consistent with the increasing energy of the $^4B_{2u}(px)$ state and the decreasing one-electron splitting $\epsilon(x^2 - y^2) - \epsilon(z^2)$.

Appendix

The charge-transfer transitions $\sigma e_u \rightarrow a_{1g}$, b_{1g} are much more intense than $\pi e_u \rightarrow a_{1g}$, b_{1g}.

For example,

$$\langle ^4B_{1g}|P|^4E_u(B)(\pi e_u)\rangle = \sqrt{2}\langle \pi e_u|P|(x^2 - y^2)\rangle \quad \text{(i)}$$

$$\langle ^4B_{1g}|P|^4E_u(B)(\sigma e_u)\rangle = \sqrt{2}\langle \sigma e_u|P|(x^2 - y^2)\rangle \quad \text{(ii)}$$

where $x^2 - y^2 = C_M^*(3d_{x^2-y^2}) - C_L^*\frac{1}{\sqrt{2}}(-\sigma_1 + \sigma_2 + \sigma_3 - \sigma_4)$

$$\pi e_u = C_L\frac{1}{\sqrt{2}}(x_5 + x_6) + \ldots$$

$$\sigma e_u = -C_L\frac{1}{\sqrt{2}}(\sigma_1 + \sigma_3) + \ldots$$

The nitrogen σ orbitals are assumed to be simply $2p_x$ and $2p_y$ orbitals and all orbitals are represented by a single Slater function whose radial normalization factor is $N_{nl}^{\mu_{nl}}$ and radial exponent is μ_{nl}. The largest term in (i) is the two-center charge-transfer integral

$$C_M^*C_L\left\langle 3d_{x^2-y^2}|P|\frac{1}{\sqrt{2}}(x_5 + x_6)\right\rangle = C_M^*C_L\sqrt{\frac{2}{5}} \times \frac{N_{np}^{\mu_{np}}}{N_{(n+1)d}^{\mu_{np}}}S(3d_\delta^{\mu_{3d}}, (n + 1)d_\delta^{\mu_{np}})$$

In (ii) there is an added contribution from one-center ligand-ligand integrals

$$\langle \sigma e_u|P|(x^2 - y^2)\rangle = -\frac{C_M^*C_L}{\sqrt{2}}\left\{\frac{N_{2p}^{\mu_{2p}}}{N_{3s}^{\mu_{2p}}}S(3d_\sigma^{\mu_{3d}}, 3s^{\mu_{2p}}) + \frac{N_{2p}^{\mu_{2p}}}{N_{3d}^{\mu_{2p}}}\sqrt{\frac{4}{5}}S(3d_\sigma^{\mu_{3d}}, 3d_\sigma^{\mu_{2p}})\right\} - C_LC_L^*\frac{1}{\sqrt{2}}R_{MN}$$

where R_{MN} is the metal–nitrogen separation.

Acknowledgment.—We are grateful to Drs. W. G. Jackson and J. N. MacB. Harrowfield for providing samples of the chromium(III) complexes. We also thank the Royal Commission for the Exhibition of 1851 for a research scholarship (to L. D.) and the Science Research Council for an equipment grant.

---

[21] M. N. Hughes and W. R. McWhinnie, *J. Chem. Soc. A*, 592 (1967). These authors have measured the infrared spectra of *trans*-Cr(en)$_2$X$_2$ and have assigned the metal–halogen stretching frequencies as ν(CrCl) 351 cm^{-1} and ν(CrBr) 278 cm^{-1}.

[22] This is readily seen by a calculation similar to that given in the Appendix.