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POLARIZED
CRYSTAL SPECTRA OF OPTICALLY
ACTIVE IONS

II. Cobalt tris ethylenediamine ion

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Synopsis

The polarized absorption spectra of $d,1\text{Coen}_3\text{Cl}_3 \cdot 3\text{H}_2\text{O}$, $d,1[\text{Coen}_3\text{Cl}_3]_2 \cdot \text{NaCl} \cdot 6\text{H}_2\text{O}$ and $D[\text{Coen}_3\text{Cl}_3]_2 \cdot \text{NaCl} \cdot 6\text{H}_2\text{O}$ and the deuterated species have been recorded at liquid helium temperatures. Using all of the transitions $(t_{2g})^6 \rightarrow (t_{2g})^5(e_g)$ we get $C = 3,925 \text{ cm}^{-1}$ and $10Dq = 25,275 \text{ cm}^{-1}$. At 4.2°K a discrete vibrational structure is found in the axial, π and σ components of the ${}^1A_{1g} \rightarrow {}^1T_{1g}(O_h)$ transition. Since the axial and σ transverse spectra match, the transition intensity is derived via an electric dipole mechanism. The lowest line in the axial, π and σ spectrum falls at $18,960 \pm 2 \text{ cm}^{-1}$. At the origin the non-cubic potential field in these complexes is estimated to be $0 \pm 4 \text{ cm}^{-1}$, while at the Franck-Condon maximum extrapolation of the symmetric progression leads to a value of the "trigonal" splitting of about 10 cm^{-1} . Furthermore 10–15% of the total intensity in $\text{Co}(\text{en})_3^{+++}$ arises from electronic processes and the remainder from vibronic couplings. A discussion of these features leads to the result that the measured circular dichroism of a solution of optically active $\text{Co}(\text{en})_3^{+++}$ ions is most likely to be explained by assuming two conformers to be present in solution as originally suggested by Woldbye.

Introduction

Recently, a number of investigations that deal with the crystal absorption spectrum⁽¹⁾⁽²⁾⁽³⁾ and the circular dichroism spectrum (C.D.)⁽²⁾ of the tris-ethylenediamine Cobalt(III) ion, $\text{Co}(\text{en})_3^{+3}$, have been reported. In these papers the results were analyzed assuming an effective molecular D_3 point group symmetry.

The solution absorption spectrum⁽⁴⁾ corresponds to that expected on the basis of a simple octahedral O_h crystal field model⁽⁵⁾ viz:

$${}^1A_{1g} \rightarrow {}^1T_{1g} \quad \text{found at } \sim 21,000 \text{ cm}^{-1}$$

$${}^1A_{1g} \rightarrow {}^1T_{2g} \quad \text{found at } \sim 29,000 \text{ cm}^{-1}$$

The broad, weak absorption at $10,000\text{--}16,000 \text{ cm}^{-1}$ has further been associated⁽⁶⁾ with the spin forbidden transition,

$${}^1A_{1g} \rightarrow {}^3T_{1g}.$$

In the main those features were also found in the crystal spectra⁽¹⁾ of $\text{Co}(\text{en})_3^{+3}$. In particular the axial spectra, reported for pure⁽²⁾⁽⁸⁾ and for dilute⁽³⁾ crystals, predicted a ${}^1E(D_3)$ state in the region of the ${}^1T_{1g}(O_h)$ absorption. However, the almost octahedral environment made the evaluation of trigonal field parameters⁽³⁾ rather hazardous. In fact, and this aspect has been largely ignored, these spectra do not give conclusive evidence that trigonal field, D_3 selection rules are adhered to in this compound. Furthermore, recent investigations of the analogous nickel (II) tris-ethylenediamine complex⁽⁷⁾ have shown that the D_3 selection rules are not particularly well obeyed.

Much of the interest of these studies has been to characterize the trigonal field parameters, to establish the distribution of the absorption bands intensities and to elucidate the source of this spectral intensity. In some studies⁽²⁾⁽³⁾⁽⁸⁾ the results have then been compared with the C.D. measurements for this ion in solution and in axial crystals.

Because the absorption bands and the C.D. curves are broad, and because the empirical parameters to be estimated are small, much un-

certainly exists with regard to some of the more fundamental quantities necessary for a successful treatment of the problem. As a result, we have undertaken a study of the spectra in oriented crystals at 4.2 °K in the hope that sufficient resolution of the absorption bands will obtain and that more precise information may become available. A preliminary report of this work⁽⁹⁾ has shown this to be the case.

Experimental

Polarized crystal spectra have been taken at ~ 300°, 80° and 4.2 °K. A Cary 14 spectrophotometer has been used except in cases where increased resolution has been desired and then a Zeiss 2-metre grating spectrograph (dispersion ~ 3 Å/mm in the region of interest) has been used. A microcrystal technique⁽¹⁰⁾ has been used to record the total region of absorption of thin crystals (i. e. 5000–33,000 cm⁻¹). In the 4.2 °K spectra thicker crystals were used so that the weaker regions of absorption, which are of more concern in these spectra, show up more clearly.

Extinction coefficients in the crystal are defined as

$$\epsilon = \frac{[\text{O.D.}][\text{M.W.}]}{t \cdot d \cdot 1000} \quad \text{where}$$

O.D. = optical density
M.W. = molecular weight
t = crystal thickness in cm
d = density in g/cc

Spectra are reported for pure single crystals, oriented and identified by means of X-ray techniques.

Crystal structures

d,l Co en₃Cl₃·3H₂O (here after I): Trigonal⁽¹¹⁾, space group P_{3c1}-D_{3d}⁴

$a = 11.50 \text{ \AA}$ molecular symmetry D₃
 $c = 15.52 \text{ \AA}$ cobalt site symmetry C₃
 $z = 4$

These crystals are hexagonal plates with (0001) well developed or thick hexagonal needles with {1120} well developed. Axial spectra have been

taken on (0001). The unique C_3 axis of the unit cell corresponds to the C_3 axis of the molecule and both are normal to this face. Transverse spectra, with the electric vector parallel (π) or perpendicular (σ) to the C_3 axis were taken on $\{11\bar{2}0\}$ and $\{10\bar{1}0\}$.

The crystal of the other complexes studied grow in similar habits to those described above and spectra were observed in an analogous manner.

d,l [Co en ₃ Cl ₃] ₂ .NaCl.6H ₂ O (II):	Trigonal ⁽¹²⁾ , space group $P_{3Cl} - D_{3d}^2$
$a = 11.45 \text{ \AA}$	molecular symmetry D_3
$c = 15.68 \text{ \AA}$	cobalt site symmetry C_3
$z = 2$	

Axial spectra were taken on (0001); transverse on $(11\bar{2}0)$

D[Co en ₃ Cl ₃] ₂ .NaCl.6H ₂ O (III):	Trigonal ⁽¹³⁾ , space group $P_3 - C_3^1$
$a = 11.47 \text{ \AA}$	molecular symmetry D_3
$c = 8.06 \text{ \AA}$	cobalt site symmetry C_3
$z = 1$	

Axial spectra were taken on (0001); transverse on $\{11\bar{2}0\}$.

The deuterated species of the latter two compounds, IV and V respectively, grow in the same manner and are considered to be isomorphous and isostructural with the parent protonated species.

Results

300 °K spectra:

In the regions where the studies overlap, these spectra are in qualitative agreement with those reported earlier^{(1) (2) (3)}. Since the spectra for I-V are so similar, we report details for one compound only. (II, Table 1, Figure 1).

Some care has been taken in measuring the π spectrum in the region 25,000-33,000 cm^{-1} and in all cases we confirm the earlier report⁽¹⁾ concerning the appearance of an absorption band in this region.

In the region 10,000-15,000 cm^{-1} there is a broad weak absorption (Figure 2), similar to that seen in solutions of Co en_3^{3+} . The absorption is not anisotropic in the crystal.

TABLE 1. Crystal Spectral Results for $d,12[\text{Co en}_3\text{Cl}_3].\text{NaCl}.6\text{H}_2\text{O}$ at various temperatures.

300 °K	$\nu_{\text{max}} \text{ cm}^{-1}$	$\epsilon_{\text{max}} \pm 10\%$	$\Delta\nu_{\text{max}}(\sigma-\pi)$	$\epsilon_{\pi}/\epsilon_{\sigma}$	D ₃ assignment	C ₃ assignment
axial	21400	100	—	—	1E _a	1E _b
	29200	130	—	—	1E _b	1E _b
	~14000	1	—	—	triplet	triplet
π	21285	130	+ 140	1.30	1A ₂	1A
	29650	60	- 450	0.46	1E _b × ϵ or 1A ₁ × α_2	1A
	~14000	~1	—	~1.0	triplet	triplet
σ	21425	100	+ 140	1.30	1E _a	1E _a
	29200	130	- 450	0.46	1E _b	1E _b
	~14000	~1	—	~1.0	triplet	triplet
80 °K*						
axial, π , σ	13500	~0.5	—	1.0	3T _{1g} (O _h)	—
	17750	~2.0	—	1.0	3T _{2g} (O _h)	—

* For spin-allowed transitions add $\sim 300 \text{ cm}^{-1}$ to each ν_{max} and reduce each ϵ_{max} by about 10—15 % to generate 80 °K results. The spectrum at 4.2 °K is very little altered to that at 80 °K if the vibrational finestructure (Table 2) is ignored.

80 °K spectra:

Compared to the above spectra these measurements show an overall shift of ν_{max} values to higher energies, a reduction in the intensity of the

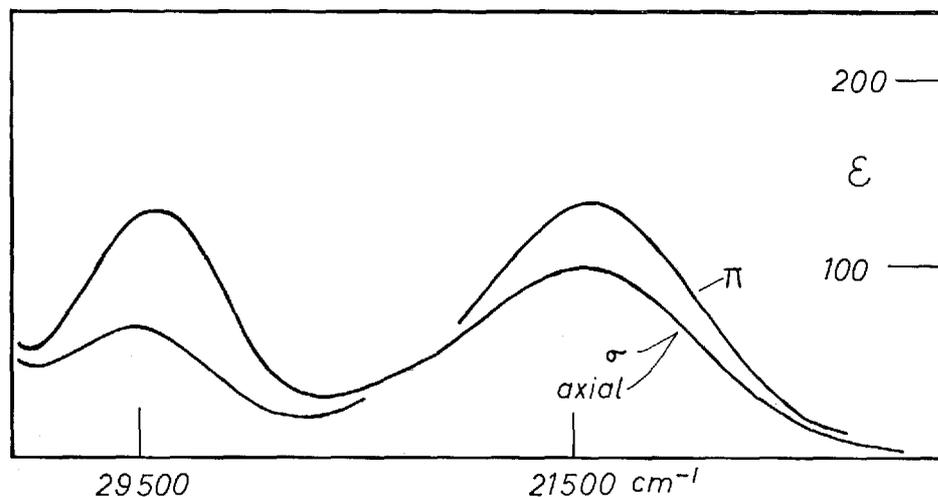


Fig. 1. The room temperature crystal spectrum of $d,12[\text{Co en}_3\text{Cl}_3].\text{NaCl}.6\text{H}_2\text{O}$.

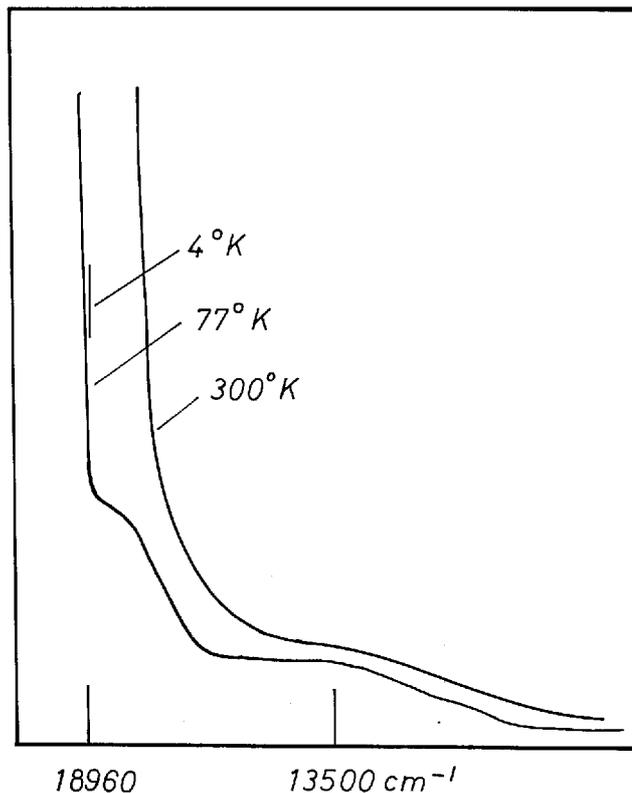


Fig. 2. The effect of temperature on the spectrum of $d,1 [Co en_3Cl_3].NaCl.6H_2O$ in the region of the spin forbidden transitions to ${}^3T_{1g}$ and ${}^3T_{2g}$.

$21,500\text{ cm}^{-1}$ and $29,500\text{ cm}^{-1}$ absorption bands and the resolution of two weak absorption bands on the low energy side of $21,500\text{ cm}^{-1}$ (Figure 2).

4.2 °K spectra:

With one major exception these spectra are, in general similar to those obtained at $80\text{ }^\circ K$. The low frequency side of the $21,500\text{ cm}^{-1}$ bands develops well resolved vibrational structure, the shape and resolution of which is dependent on the particular crystal lattice under investigation. Crystals I and II are almost indistinguishable with the latter the better resolved (Figure 3). The structure in III is less obvious than in II and is also altered somewhat from that seen in Figure 3. Finally the deuterated species IV and V show frequency shifts that may be correlated with changes in zero point

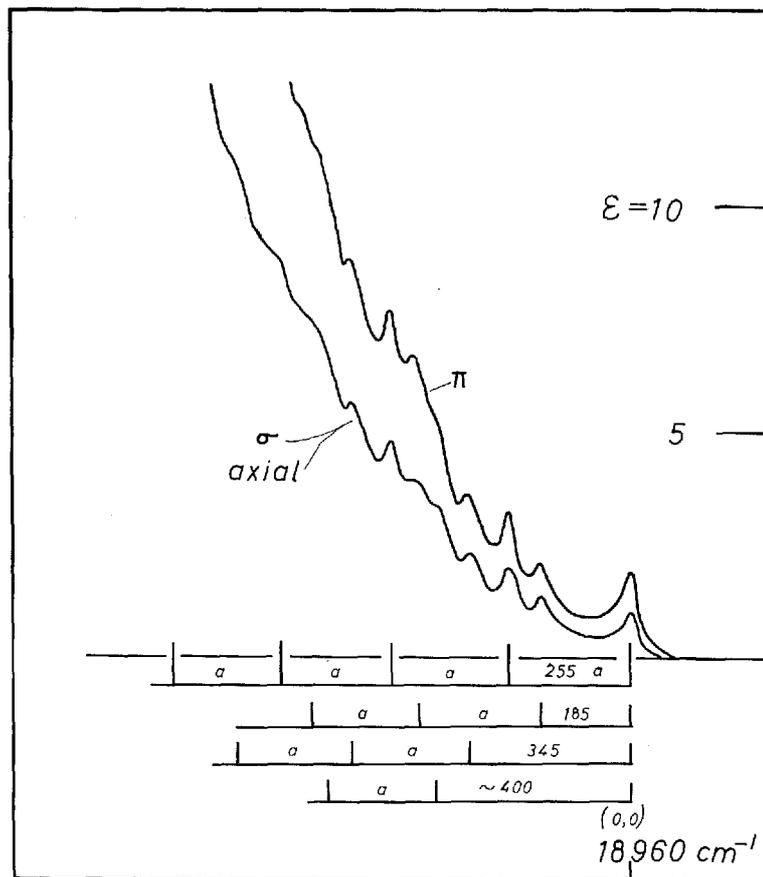


Fig. 3. Vibrational structure in the π , σ and axial spectra of $d,1 \ 2[\text{Co en}_3\text{Cl}_3] \cdot \text{NaCl} \cdot 6\text{H}_2\text{O}$ in the region of the ${}^1T_{1g}(\text{O}_h)$ excited state.

energy and very minor vibrational effects that must arise from mass alterations in the vibrating systems.

For these $4.2 \text{ }^\circ\text{K}$ spectra the absolute frequencies are thought to be good to $\pm 5 \text{ cm}^{-1}$ and the reproducibility to better than $\pm 2 \text{ cm}^{-1}$. Spectral differences greater than 3 cm^{-1} are expected to be meaningful although band width considerations apply differently to various spectra.

Assignment of spectra

(1) Ligand Field Parameters:

At 80 °K, the spectra show four absorption bands that may be confidently associated with singlet/triplet (13,500 cm⁻¹, 17,750 cm⁻¹) and singlet/singlet (21,500 cm⁻¹, 29,500 cm⁻¹) excitations within the *d* orbitals of the cobalt ion. Ignoring the splitting, that is apparent from polarization measurements, it is possible to calculate Dq, B and C. This is done using diagonal energy matrices and since only intensities and average energies are used the spectra are designated with O_h symbols.

${}^1A_{1g} \rightarrow {}^3T_{1g}$	$10 Dq - 3C$	$13500 \pm 50 \text{ cm}^{-1}$
${}^3T_{2g}$	$10 Dq + 8B - 3C$	$17750 \pm 50 \text{ cm}^{-1}$
${}^1T_{1g}$	$10 Dq - C$	$21350 \pm 100 \text{ cm}^{-1}$
${}^1T_{2g}$	$10 Dq + 16B - C$	$29400 \pm 100 \text{ cm}^{-1}$
B_{singlets}	$= 503 \text{ cm}^{-1}$	
B_{triplets}	$= 530 \text{ cm}^{-1}$	
$C_{{}^3T_{1g}/{}^1T_{1g}}$	$= 3925 \text{ cm}^{-1}$	
$C_{{}^3T_{2g}/{}^1T_{2g}}$	$= 3815 \text{ cm}^{-1}$	
$10 Dq$	$= 25,275 \text{ cm}^{-1}$ when $C = 3925 \text{ cm}^{-1}$	

These data should be quite precise as a consequence of the narrowing of the bands and the observation of all four *d-d* absorptions.

(2) 300 °K Spectra:

From the similarity, between Co en₃³⁺ in solutions and in crystals and Co(NH₃)₆³⁺, it has been suggested⁽¹⁴⁾ that the former is "almost" octahedral and that the absorption band intensity is controlled by a similar mechanism in both complexes. This is tantamount to predicting a vibronic intensity gaining mechanism and small trigonal field distortions in the former complex.

The correspondence between axial and σ spectra confirms an electric dipole mechanism in the singlet/singlet systems although no such distinction can be made for the more vulnerable singlet/triplets because the absorptions are isotropic. This is also true at lower temperatures so that no decision can be made between electric and magnetic dipole processes in these weak bands.

Assignment of the spectrum is possible in D₃ or in C₃. (Assignments Table 1). The π component at $\sim 29,650 \text{ cm}^{-1}$ deserves some comment.

Firstly, it is weaker than the other singlet/singlet transitions, thus reflecting a more forbidden character. Secondly, it falls at slightly higher energy than its σ component (1E_b in D_3 or C_3) and finally, it should be absent if D_3 electronic selection rules are rigorously obeyed.

Thus, in D_3 , a vibronic contribution is necessary to describe the absorption. It may be via either of the following mechanisms,

$$\begin{aligned} {}^1A_1 \rightarrow {}^1E_b \times \varepsilon & \quad xy(\sigma) \text{ and } z(\pi) \text{ polarized} \\ {}^1A_1 \rightarrow {}^1A_2 \times \alpha_2 & \quad z(\pi) \text{ polarized.} \end{aligned}$$

If the site symmetry is included, the π intensity follows as a natural consequence of the transformational properties of the electric dipole moment operator in that symmetry

$$\text{i. e. } {}^1A \rightarrow {}^1A \quad z(\pi) \text{ polarized.}$$

From the present results alone it is seen that D_3 vibronic or C_3 electronic selection rules can give a satisfactory description of the broad band spectra. On the basis of a previous paper⁽⁷⁾ and from the temperature dependence of the absorption band intensities (See below) it seems probable that the vibronic D_3 description is likely to dominate the spectrum. In a later section (p. 14) however, it appears that site influences are not entirely negligible.

In Table 1 ε_{\max} values, ν_{\max} values, $\Delta\nu_{\max}$ values and polarization ratios are listed. It should be noted that these parameters are determined by vibronic contributions, by the shape of the potential surfaces of the upper states, by their relative disposition with regard to the ground state and by the associated Franck-Condon factors $|(\psi''_0|\psi'_1)|^2$ occurring in the expression for the band intensity I:

$$I \propto |(\psi''_0|\psi'_1)|^2 \cdot |(\psi''_{e1}|R_e|\psi'_{e1})|^2.$$

This implies that discussions relating to electronic perturbations are not necessarily valid when parameters derived from ε_{\max} and $\Delta\nu_{\max}$ values are utilized.

(3) 80 °K Spectra:

The weak bands at $<18,000 \text{ cm}^{-1}$ may reasonably be assigned as transitions to ${}^3T_{1g}$ and ${}^3T_{2g}$ (O_h). The broad room temperature absorption in this region is now accounted for. This area is further complicated by what appear to be third and fourth overtones of N-H and C-H stretching vibrations

that have almost comparable intensities to those of the singlet/triplet electronic transitions.

The intensity shifts observed by going to lower temperatures give evidence of considerable vibrational hot band contribution to the intensity of ${}^1T_{1g}$ and ${}^1T_{2g}$ of O_h . The ${}^1T_{1g}$ absorption edge moves 1500 cm^{-1} to higher energy on cooling to this temperature (Figure 2) and is very little affected on further cooling. Allowing for some increase in Dq on cooling this shift still corresponds to the freezing out 3 or 4 quanta of a $250\text{--}300\text{ cm}^{-1}$ ground state vibration. The intensity gaining efficiency of the higher members of these ground state vibrations must be strongly restricted by thermal population considerations at $300\text{ }^\circ\text{K}$ although it is likely that these excited ground state levels are intrinsically more potent at intensity stealing because of anharmonicity and vibrational amplitude considerations. The fact that the overall intensity decreases on cooling certainly supports this point of view as well as it does the argument that a large part of the absorption band intensity arises from vibronic processes.

(4) $4.2\text{ }^\circ\text{K}$ Spectra:

The important feature in these spectra is the development of discrete vibrational structure in all axial, π and σ components of the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ (O_h) transition. Using II as model, it is possible to derive the following information (Table 2, Figure 3).

(i) The axial and σ transverse spectra correspond both in measured intensity and in quantitative matching of the vibrational structure. As a consequence the transition intensity is derived via the electric dipole mechanism (The vibronic bands in this region have $\epsilon \sim 1\text{--}10$ so that magnetic dipole processes could have contributed considerable intensity).

(ii) The lowest line in the axial, π and σ spectrum falls at $18960 \pm 2\text{ cm}^{-1}$. Originally it was considered⁽⁹⁾ that axial, π and σ could not be distinguished although measurements on a large number of crystals suggest that the axial and σ line lies at slightly lower frequency than does the π line. This difference, however, is still within the uncertainty of the measurement. In the present analysis these lines represent the (0,0) transition of the D_3 (or C_3) induced electronic* absorption system.

Thus it is possible to give a precise value for the splitting Δ of the elec-

* In this article the term "electronic" is reserved for the symmetry allowed (0,0) bands plus any associated totally symmetric vibrational progression built upon (0,0). 'Vibronic' refers to intensity arising from non-totally symmetric vibrations and their associated progressions, superimposed upon the (0,0) band.

TABLE 2. Description and Assignment of the vibrational finestructure seen in crystals II and III at 4.2 °K.

Crystal II.			
axial, σ	π	$\varepsilon_{\pi}/\varepsilon_{\sigma}$	assignment
18960 \pm 2 cm^{-1}	18960	2.0	(0,0)
19146	19146	1.3-1.5	+ 185
19218	19218	2.0	+ 255
19305	19306	1.3-1.5	+ 345
\sim 19370	?	< 1.5	\sim + 400
19405	19410	\sim 1.4	+ 185 + 255
19470	19465	2.0	+ 2 \times 255
19555	19550	1.3-1.6	345 + 255
19630	?	< 1.5	+ 400 + 255
19665	\sim 19670	< 2.0	+ 185 + 2 \times 255
19730	19740	\sim 2.0	+ 3 \times 255
\sim 19800	—	< 2.0	+ 345 + 2 \times 255
\sim 20000	20000	\sim 2.0	+ 4 \times 255
Crystal III.			
axial, σ	π	$\varepsilon_{\pi}/\varepsilon_{\sigma}$	assignment
(18915)	(18915)	—	(0,0)
19100 \pm 5 cm^{-1}	19100 \pm 5 cm^{-1}	> 1	+ 185
19158	19158	> 1	+ 255
?	?	—	—
?	?	—	—
19345	19345	> 1	+ 185 + 255
19395	19395	> 1	+ 2 \times 255
19500	19500	> 1	+ 345 + 255 ?
—	—	—	—
\sim 19600	\sim 19600	—	+ 185 + 2 \times 255
\sim 19660	\sim 19660	—	3 \times 255
19750	19750	—	+ 345 + 2 \times 255
—	—	—	—

These assignments are not unique, see text.

tronic energy level by the non-cubic potential field in these complexes; i. e. $\Delta = 0 \pm 4 \text{ cm}^{-1}$ and if the axial and σ spectra really are below the π band, $\Delta \sim 1-3 \text{ cm}^{-1}$.

The intensity of these (0,0) bands is $\varepsilon \sim 1-2$ and in all cases the ratio between components is $\varepsilon_{\pi}/\varepsilon_{\sigma} = 2.0 \pm 10 \%$.

3) A vibrational analysis of the first 12–15 lines (Figure 3) provides the following information,

(i) A progression, involving a symmetrical vibration with frequency $255 \pm 5 \text{ cm}^{-1}$ in the excited state and based on (0,0), extends some 5 or 6 numbers before it is lost in the continuous absorption that builds up very rapidly as the frequency increases. After approximate background corrections the ratio $\varepsilon_{\pi}/\varepsilon_{\sigma}$ remains near that found for (0,0). This is expected for a totally symmetrical vibration superimposed upon the (0,0) band.

(ii) A vibration of $185 \pm 5 \text{ cm}^{-1}$ adds one quantum to (0,0) and is then followed by 2 or 3 quanta of the symmetrical $255 \pm 5 \text{ cm}^{-1}$ vibration. The intensity ratio $\varepsilon_{\pi}/\varepsilon_{\sigma}$ for each member is in the range 1.3–1.6. The appearance of only one quantum of $185 \pm 5 \text{ cm}^{-1}$ plus the change in polarization ratio from that shown by (0,0) indicates that this vibration is non totally symmetrical.

(iii) A non totally symmetrical vibration with frequency $345 \pm 5 \text{ cm}^{-1}$ appears ($\varepsilon_{\pi}/\varepsilon_{\sigma} \sim 1.3-1.5$) and has several quanta of $255 \pm 5 \text{ cm}^{-1}$ built on it.

(iv) Finally the axial and σ spectra show a weakly resolved band at (0,0) + $\sim 400 \text{ cm}^{-1}$ followed by one or more quanta of $255 \pm 5 \text{ cm}^{-1}$. This vibration is not totally symmetrical.

No reliable infrared or Raman analysis is available for the Co en_3^{3+} ion. The IR spectrum shows a strong band at $\sim 250 \text{ cm}^{-1}$ and medium absorptions at $350-370 \text{ cm}^{-1}$, $440-470 \text{ cm}^{-1}$ and above. It is not unreasonable to associate these values with those found in the electronic spectrum and they are quite likely to be associated with components of the $2t_{1u}$ and t_{2u} vibrations of the CoN_6 octahedron. Because of the influence of the site it is not possible to get any more information about the parentage of these vibrations.

If the D_3 assignment is preferred, these electronic transitions must be

$${}^1A_1 \rightarrow {}^1A_2 \quad \pi \text{ spectrum}$$

and ${}^1A_1 \rightarrow {}^1E_a \quad \text{axial and } \sigma \text{ spectrum}$

t_{1u} of O_h transforms like $a_2 + e$ and t_{2u} like $a_1 + e$ in D_3 so that if each vibration is equally efficient at gaining intensity, any vibronic contribution arising from a nearly degenerate pair a_2/e or a_1/e , will give rise, in the first quantum, to bands with composite polarizations $\varepsilon_{\pi}/\varepsilon_{\sigma} \sim 0.7$ in the former and $\varepsilon_{\pi}/\varepsilon_{\sigma} \sim 1.3$ in the latter instances. If the site symmetry is included the ratio is ~ 1.3 both cases.

The discussion of a transition $(t_{2g})^6 \rightarrow (t_{2g})^5(e_g)^1$, should admit the possibility of observing a dynamic Jahn-Teller effect in the upper states.

In the present case, if the transitions may be classified in D_3 or C_3 , the π spectrum is associated with a transition ${}^1A \rightarrow {}^1A$, and the σ spectrum with ${}^1A \rightarrow {}^1E_a$. The former transition should then be able to experience a pseudo Jahn-Teller effect, the latter a genuine one. The close correspondence, between the σ and π absorption in the vibrational structure as well as the position of the (0,0) band, makes it impossible to evaluate any Jahn-Teller parameters. Anyhow, the states behave as if no such effect is active.^{(31) (32)}

Minor differences in the structure, seen in this region for other crystals, must be due to alterations in molecular and or crystal environment by crystal packing forces. Certainly, distortions of the ligand framework have been observed⁽³⁾ although the molecular units still maintain D_3 symmetry and, in the cases of interest, the cobalts still occupy a site with C_3 symmetry. Because of the nature of the spectra it has not been possible to separate these various influences and the differences are loosely termed crystal effects. Even more to the point, it is still not possible to unambiguously distinguish the contributions from a vibronic D_3 mechanism and from C_3 site.

Crystal III shows some difference from II in this region. As seen earlier, the space group is altered and the packing is slightly different with small variations in the metal/chelate angles. These effects must be responsible for the changes in the details of the crystal spectrum.

Comparing with II, the spectrum of III shows an overall shift of 50–60 cm^{-1} towards lower energy, the intensity of the $255 \pm 5 \text{ cm}^{-1}$ progression is greatly reduced (including that of the origin) and the $345 \pm 5 \text{ cm}^{-1}$ progression is not clearly seen at low frequencies. When these changes are taken into account it is possible to discuss the spectrum of III in the same way as for II. The final conclusions (for III) are,

- (i) The (0,0) band is very weak and is not resolved from the background.
- (ii) The $255 \pm 10 \text{ cm}^{-1}$ vibration is identified and appears in several progressions, thereby confirming the previous analysis in II.
- (iii) (0,0) lies at lower energy than in II and the trigonal field splitting is again very slight and less than the un-certainty of the measurements.
- (iv) The correspondence between axial and σ spectra again supports the electric dipole mechanism for the intensities which, in total, are very similar to the values found in II.

The assignment of these lines (Table 2) is not unique. For instance the whole pattern could be moved 140 cm^{-1} to lower energies when the (0,0) band in II and the lowest resolved band in III would coincide. This would introduce new problems in the vibrational analysis so that the present arrangement is preferred.

The deuteration of II to give IV results in the following changes in the spectrum. The only region that appears to be affected is the low energy side of ${}^1T_{1g}(O_h)$. Here, the (0,0) band moves $105 \pm 5 \text{ cm}^{-1}$ to higher energy although relative intensities, within the band system, remain unaltered. This is quite in accord with similar studies on, for instance, naphthalene⁽¹⁵⁾, benzene⁽¹⁶⁾, acetylene⁽¹⁷⁾ and the nickel (II) tris ethylenediamine ion⁽⁷⁾.

The observed vibrational frequencies of the upper state do not seem to be influenced by the deuteration. In particular, the totally symmetrical mode, $\nu = 255 \pm 5 \text{ cm}^{-1}$ is not altered by as much the error of the measurements. The axial, π and σ spectra still have the same relationship to each other.

The shift in the (0,0) band position can be rationalized in terms of changes in zero point energies in the ground and excited states of the two complexes⁽¹⁶⁾. The invariance of the vibrational frequencies upon deuteration indicates very little movement of the exchanged protons in the normal modes corresponding to these frequencies.

The compounds III and V behave in an analogous manner and they will not be considered further.

(5) Intensities:

The intensities reported in this and some earlier investigations are in good agreement (Table 1).

One of the major problems, in earlier works, has been to separate the electronic intensity, f_{e1} from the vibronic intensity f_{vib} . From the present measurements, especially in II, it has been possible to get reliable expressions for these two contributions.

If f_{e1} arises only from (0,0) + $n\nu$, where $\nu = 255 \text{ cm}^{-1}$ (a lower limit to f_{e1}) then in ${}^1A_1 \rightarrow {}^1A_2$; 1E_a , where the total band width is 7000 cm^{-1} , $n = 28$. The (0,0) bands have $\Delta\nu_{1/2} \simeq 30 \text{ cm}^{-1}$ so assuming overall $\Delta\nu_{1/2} \simeq 100 \text{ cm}^{-1}$ and taking a mirror image about the band centre the intensity expression reduces to

$$f_{e1} \simeq 4.6 \times 10^{-9} \sum_{n=1}^{28} \epsilon_{\max} \Delta\nu_{1/2} = 9.2 \times 10^{-7} \sum_{n=1}^{14} \epsilon_{\max}$$

For the ${}^1A_1 \rightarrow {}^1E_a$ transition $\epsilon_{(0,0)} = 1 \pm 10\%$ and assuming each line increases by one ϵ unit/line [reasonable, at least for $n < 5$] this leads to

$$f_{e1}^E = 1.1 \times 10^{-4}; \quad f_{\text{total}}^E = 1.84 \times 10^{-3}$$

e1 + vib

Thus

$$f_{e1}^E / f_{\text{total}}^E \simeq 6 \times 10^{-2}$$

and

$$f_{\text{el}}^{\text{A}_2}/f_{\text{total}}^{\text{A}_2} = 10 \times 10^{-2} \quad \text{since} \quad \begin{aligned} f_{\text{el}}^{\text{A}_2} &= 2.2 \times 10^{-4} \\ f_{\text{total}}^{\text{A}_2} &= 2.18 \times 10^{-3}. \end{aligned}$$

These estimates are probably better than order of magnitude since the lower limit is given by the bands we actually observe and this accounts for better than 10 % of the total f_{el} . Thus it is very reasonable to conclude that 10–15 % of the total intensity arises from electronic processes and the remainder from vibronic coupling.

Comparison between the solution oscillator strengths for Co en_3^{3+} and $\text{Co}(\text{NH}_3)_6^{3+}$ lends support to this supposition. In solution the difference between the intensity in this band is

$$\Delta f_{\text{total}} \simeq 4 \times 10^{-4}$$

whereas in the crystal the electronic intensity for

$${}^1\text{A}_1 \rightarrow {}^1\text{A}_2 + {}^1\text{E}_g \quad \text{is} \quad f_{\text{el}}^{\text{A}_2, \text{E}_g} \simeq \frac{1}{3} f_{\text{el}}^{\text{A}_2} + \frac{2}{3} f_{\text{el}}^{\text{E}_g} = 1.5 \times 10^{-4}.$$

In the same way, if the π component at $\sim 29,650 \text{ cm}^{-1}$ is entirely vibronic, and controlled by D_3 selection rules as opposed to C_3 site symmetry rules, then again it would indicate considerably vibronic intensity. Unfortunately, quantitative estimates based upon this absorption system are not likely to be very useful.

In III the (0,0) band is not clearly resolved and the structure is less clear than in II. Nevertheless, the correlations made in the previous section allow an estimate of f_{el} to be made. The intensity arising from (0,0) + $n\nu$ where $\nu \simeq 250 \text{ cm}^{-1}$ is estimated to be in the region $f_{\text{el}} \simeq 1 \times 10^{-5}$. The concomitant decrease in $f_{\text{el}}^{\text{A}_2, \text{E}_g}$ may account for the fact that, for a number of crystals, the total intensity, $f_{\text{total}}^{\text{E}_g}$ for component III seems to be 5–10 % less than that for compound II. Measured intensities in our crystals carry $\pm 10 \%$ error so that this apparent difference may not be real.

(6) Distribution of intensity:

The ${}^1\text{A}_{1g} \rightarrow {}^1\text{T}_{1g}(\text{O}_h)$ absorption of II is the best example to discuss. Ignoring the differences in structure and in the distribution $f_{\text{el}}/f_{\text{vibronic}}$, the same remarks apply to the equivalent transition in III.

The (0,0) band shows $\varepsilon_{\text{A}_2}/\varepsilon_{\text{E}_g} = 2.0$ whereas the value measured at the ν_{max} position is $\varepsilon_{\text{A}_2}/\varepsilon_{\text{E}_g} = 1.3$.

This variation must arise from differing vibronic contributions in A_2 and E_a because totally symmetrical vibrations would be expected to follow the ratio given at (0,0) and there does not seem to be any reason why totally symmetrical vibrations associated with one transition should not appear in the other. Assuming that the active vibrational modes of the octahedral CoN_6 ($2t_{1u} + t_{2u}$) are equally adept at gaining intensity it is seen, that when D_3 selection rules persist and the electronic contribution arising from $(\psi_{e1} | R_e | \psi_{e1}'')$ is taken into account (assumed to be 2.0 in this case in favour of 1A_2), the expected ratio is

$$\varepsilon_{II}/\varepsilon_I = 0.9 \quad (\text{obs. } 1.3).$$

If the site influence is included, this becomes

$$\varepsilon_{II}/\varepsilon_I = 1.3.$$

Short of actually attempting calculations of vibronic coupling intensities, these arguments are not very conclusive as concerns the D_3/C_3 symmetry question although, the predominance of polarized vibronic contributions can be rationalized in this manner.

The theoretical elucidation of the electronic intensity distribution is as usual a rather delicate matter. Compare for instance the two point groups D_3 (Symmetry elements E, $2C_3$ and $3C_2$) and C_{3v} (Symmetry elements E, $2C_3$ and $3\sigma_v$). These two groups look very similar indeed, but a cobalt (III) complex will have quite a different intensity distribution if it belongs to the one or the other point group. The levels T_{1g} (O_h) and T_{2g} (O_h) will in *both* of the lower symmetries transform as A_2 , E (T_{1g}) and A_1 , E (T_{2g}). However, the electric dipole vectors transform as (A_2 , E) representations in D_3 and as (A_1 , E) representations in C_{3v} . Hence the 21,000 cm^{-1} band is expected to be seen in σ polarization for a D_3 molecular group and be forbidden in σ polarization assuming a C_{3v} point group, whereas the reverse is true for the 29,000 cm^{-1} band.

These general predictions are of course born out by actual calculations. Indicating the angular parts of the *molecular orbitals* in C_3 quantization, we have⁽¹⁸⁾ for the pertinent molecular orbitals

$$t^+ = \sqrt{\frac{2}{3}} \psi_{x^2-y^2} - \sqrt{\frac{1}{3}} \psi_{xz}$$

$$t^- = \sqrt{\frac{2}{3}} \psi_{xy} + \sqrt{\frac{1}{3}} \psi_{yz}$$

$$\begin{aligned}
t^{\circ} &= \psi_z, \\
e^+ &= \sqrt{\frac{1}{3}} \psi_{x^2-y^2} + \sqrt{\frac{2}{3}} \psi_{xz} \\
e^- &= \sqrt{\frac{1}{3}} \psi_{xy} - \sqrt{\frac{2}{3}} \psi_{yz}
\end{aligned}$$

Utilizing the symmetry operations of the D_3 group (\hat{i} , \hat{j} , and \hat{k} being the unit vectors) we get

$$\begin{aligned}
(t^{\circ} |r| e^+) &= \alpha \hat{i} + \alpha \hat{j} + \alpha \hat{k} \\
(t^{\circ} |r| e^-) &= \alpha \hat{i} + \alpha \hat{j} + \alpha \hat{k} \\
(t^+ |r| e^+) &= \alpha \hat{i} - \beta \hat{j} + \alpha \hat{k} \\
(t^+ |r| e^-) &= \beta \hat{i} + \alpha \hat{j} + \gamma \hat{k} \\
(t^- |r| e^+) &= \beta \hat{i} + \alpha \hat{j} - \gamma \hat{k} \\
(t^- |r| e^-) &= \alpha \hat{i} + \beta \hat{j} + \alpha \hat{k}
\end{aligned}$$

where the occurring molecular integrals are

$$\begin{aligned}
\alpha &= (t^{\circ} |x| e^-) \\
\beta &= (t^+ |x| e^-) \\
\gamma &= (t^+ |z| e^-)
\end{aligned}$$

The excited states are mainly determined by the cubic field, but are split (at least in principle) by the lower field. The following formular for the electronic dipole matrix elements are then obtained by utilizing the proper excited states functions:

$$\begin{aligned}
({}^1A_1 |R_e| {}^1T_2(A_1)) &= 0 \\
({}^1A_1 |R_e| {}^1T_2(E^A)) &= (\alpha - \sqrt{2}\beta)\hat{i} \\
({}^1A_1 |R_e| {}^1T_2(E^B)) &= (\alpha - \sqrt{2}\beta)\hat{j} \\
({}^1A_1 |R_e| {}^1T_1(A_2)) &= 2\gamma\hat{k} \\
({}^1A_1 |R_e| {}^1T_1(E^A)) &= (-\alpha - \sqrt{2}\beta)\hat{i} \\
({}^1A_1 |R_e| {}^1T_1(E^B)) &= (-\alpha - \sqrt{2}\beta)\hat{j}
\end{aligned}$$

The theoretical polarization ratio in D_3 symmetry is therefore for the "first" (${}^1T_{1g}$) band

$$\frac{I_{\pi}}{I_{\sigma}} = \frac{4\gamma^2}{(\alpha + \sqrt{2}\beta)^2}$$

and for the "second" (${}^1T_{2g}$) band

$$\frac{I_{\pi}}{I_{\sigma}} = \frac{0}{(\alpha - \sqrt{2}\beta)^2}$$

These intensity ratios are completely analogous to those of McCLURE⁽¹⁹⁾ apart of course from the fact that the levels are "reversed" and that the matrix elements α , β , and γ are different from his, due to the different symmetry elements of the group.

The actual evaluation of our matrix elements requires a detailed knowledge of the molecular orbitals, whose angular transformational properties are indicated by t^+ , t^- and etc. Notice in particular that the *signs* of α , β and γ are unknown, and unrelated to each other. Since the actual intensities are rather small, the matrix elements are probably only of the order of magnitude of 10^{-10} Å. In strictly octahedral symmetry they would of course be zero. They owe their non zero value to the participation of the chelate ring orbitals in the bonding, and/or perhaps to "misdirection" of the nitrogen orbitals⁽²⁰⁾. The fact that the σ components of the 1T_1 and 1T_2 bands have nearly the same intensity indicates that either $|\alpha| \ll |\beta|$ or $|\beta| \ll |\alpha|$.

A rather interesting sidelight are thrown upon these considerations if we for a moment consider the less general model proposed by SUGANO and TANABE⁽²¹⁾. Their model considers explicitly the introduction of an "odd" perturbing field of the form

$$V_{\text{odd}}^s = a \sum_i z_i + \text{higher "odd" terms.}$$

If the expansion is broken off after the first term (*assuming* this to be predominant) we get the intensity ratio for the first (${}^1T_{1g}$) band $I_{\pi}/I_{\sigma} = 4/1$, but $I_{\pi}/I_{\sigma} = 0/0$ for the second (${}^1T_{2g}$) band*. The experimental ratio for the "allowed" intensity of the first band is as we have seen, close to two.

(7) The Absorption Spectrum and Circular Dichroism.

The foregoing discussions have clarified some questions as to the splittings of electronic components and the influence of vibronic intensity upon the

* There appears to be a mistake in SUGANO and TANABE⁽²¹⁾; they get a line strength different from zero for I_{σ} in the "second" band.

fine structure and the overall intensity distribution within these components. Pertinent to the question of the origin of the C.D., both in a crystal and in solution, is the ability of non-totally symmetric vibrations to contribute to the rotational power. MOFFITT and MOSCOWITZ⁽²²⁾ have suggested that such contributions should be very small whereas WEIGANG⁽²³⁾, in a series of papers, has developed the concept to the point where non totally symmetric vibrations of the excited state may contribute significantly to the C.D. From WEIGANG's treatment, it would appear that it is nearly impossible to clarify this question from the present work because the spectra are not sufficiently resolved, and the C.D. results are very broad and structureless. Yet even under these circumstances it still seems profitable to consider the more general aspects of this matter.

Absorption band maxima are often used as the measure of an electronic energy. In terms of the Franck-Condon model, and with the crystal near 0 °K, the absorption maximum certainly represents the (n, 0), vertical transition in a case where only one vibration may be excited. In polyatomic molecules, and especially when several vibrations of different symmetry type and of different frequency are excited, the final absorption envelope is made up from the superposition of curves obtained from several sections of what is now a (3n-6) dimensional surface. Each section may have a different potential function and the resultant band envelope, as determined by $(\psi_0''|\psi_i')^2$, may have quite a different character for each section. When the vibrational structure is resolved it is possible to estimate these various contributions. In the present case, the totally symmetric vibration, $\nu = 255 \text{ cm}^{-1}$ and the non totally symmetric, $\nu = 185, 345$ and $\sim 400 \text{ cm}^{-1}$ are seen only at low ν' so that the estimate of their contributions are necessarily approximate. If it is assumed that each section of the P.E. surface has the same shape, it is possible to sum over these contributions by taking (0,0) + n 255 adding it at (0,0) + 185; (0,0) + 345 and (0,0) + 400 cm^{-1} with due account taken of intensities. This is shown in Figure 4. The π set gives each contribution equal intensity and results in $\nu_{\text{max}} = 21650 \text{ cm}^{-1}$, $\epsilon_{\text{max}} = 108$. The σ set halves the contribution from (0,0) + n 255 and provides $\nu_{\text{max}} = 21750 \text{ cm}^{-1}$ and $\epsilon = 94$. In actual fact, the non-totally symmetric contribution in σ should be increased and hence $\Delta\nu_{\text{max}}$ should increase slightly. This procedure demonstrate the origin of the so-called "trigonal field" splitting in ν_{max} . The good agreement with experiment is probably fortuitous although it does again suggest that the major contributors to the absorption band intensity have been identified.

As we have demonstrated experimentally for most purposes the (0,0)

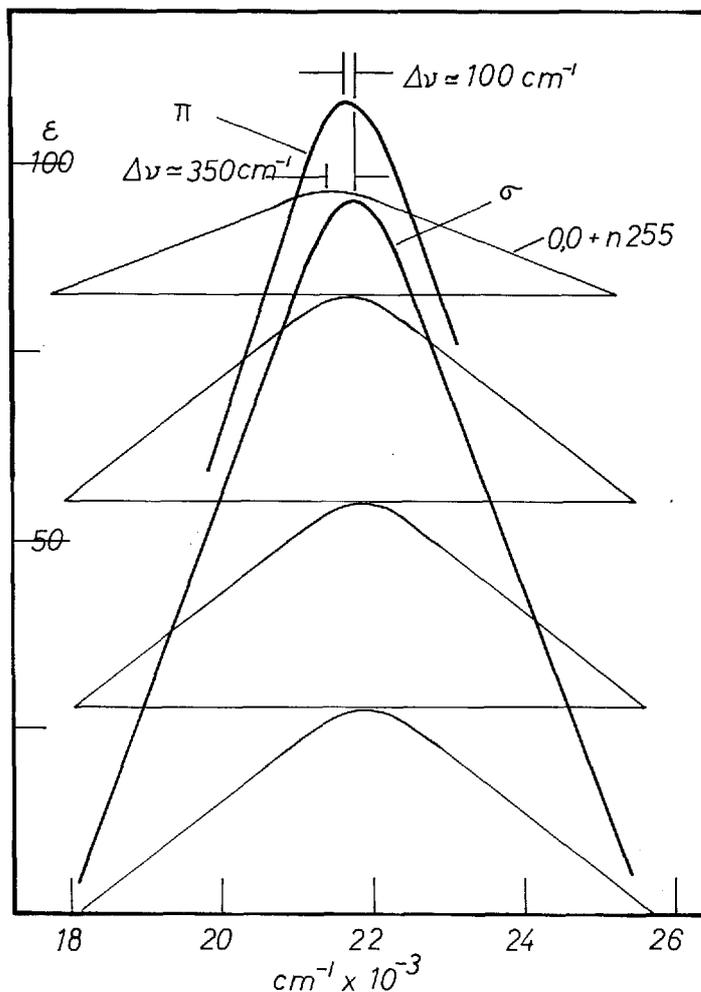


Fig. 4. Computed absorption curves for the ${}^1T_{1g}(O_h)$ components of II. The π and σ curves represent the absorption bands when the electronic and the three vibronic terms contribute intensity. The splitting $\Delta\nu \approx 100 \text{ cm}^{-1}$ should correspond to the measured splitting of the band maxima in absorption. The $\Delta\nu \approx 350 \text{ cm}^{-1}$ is the difference between the σ absorption maxima and the axial crystal C.D. maximum in the case that only electronic intensity contributes to the C.D.

bands in π and σ plus the first five or six members of the totally symmetric vibrational progression must be considered degenerate. Table II. If this means that ${}^1T_{1g}(O_h)$ is almost unaffected by non-cubic potential terms then, barring such influences as the Jahn-Teller effect, the P. E. Surfaces, for π and σ at

least at low ν' , must be almost, if not exactly, degenerate* for each section when the same vibration occurs in both spectra. Thus for the symmetric mode, $\nu = 255 \text{ cm}^{-1}$, the splitting of the Franck-Condon maxima should be very small, and of the order of the experimental uncertainty. We estimate this to be $\pm 10 \text{ cm}^{-1}$, and this should then be the true trigonal field splitting of ${}^1\text{T}_{1g}$.

If the details of the analysis of II are transferred to III then the C.D. may be considered. McCaffery and Mason⁽²⁾ have obtained axial absorption and C.D. corresponding to σ polarization in a crystal of III. The ν_{max} values, $\nu_{\text{max}}^{\text{abs}} = 21400 \text{ cm}^{-1}$ and $\nu_{\text{max}}^{\text{C.D.}} = 21,050 \text{ cm}^{-1}$ agree well with the simple composite curves shown in Figure 4. In the case that only the totally symmetric vibrational progression contributes to the C.D.⁽²²⁾: Calculated** values $\nu_{\text{max } \sigma, \pi}^{0,0+n255} = 21450 \text{ cm}^{-1}$, $\nu_{\text{max } \sigma}^{\text{total}} = 21750 \text{ cm}^{-1}$. This result is suggestive that, for this case the non-totally symmetric vibrations are not very important and certainly there does not appear any change of sign in the axial σ polarized (${}^1\text{E}$) C.D. which would have given support to the vibronic model⁽²³⁾.

The transition ${}^1\text{A}_{1g} \rightarrow {}^1\text{T}_{1g}$ is fully allowed as a magnetic dipole transition. Since the excited state to a good approximation is composed of d -orbitals, we can calculate the matrix elements of the magnetic dipole transition, assuming pure d -orbitals. We get with our chosen orientations:

$$\begin{aligned} \langle {}^1\text{A}_1 | \vec{L} | {}^1\text{T}_1(\text{A}_2) \rangle &= -i\hbar 2\sqrt{2}\hat{k} \\ \langle {}^1\text{A}_1 | \vec{L} | {}^1\text{T}_1(\text{E}^{\text{A}}) \rangle &= i\hbar 2\sqrt{2}\hat{i} \\ \langle {}^1\text{A}_1 | \vec{L} | {}^1\text{T}_1(\text{E}^{\text{B}}) \rangle &= i\hbar 2\sqrt{2}\hat{j} \end{aligned}$$

The value of $2\sqrt{2}\hbar$ should with our approximation be valid to within a few per cent. We get then for the ratio of the Rotatory Strengths $\mathfrak{R} = \langle {}^1\text{A}_1 | \vec{R} | {}^1\text{X} \rangle$ (${}^1\text{X} | \vec{L} | {}^1\text{A}_1$) of the components of ${}^1\text{T}_{1g}$, \mathfrak{R}_π and \mathfrak{R}_σ

$$\frac{\mathfrak{R}_\pi}{\mathfrak{R}_\sigma} = \frac{2\gamma}{\sqrt{2}\beta + \alpha} = \pm \sqrt{\frac{I_\pi}{I_\sigma}} \approx \pm \sqrt{2}$$

* The correspondence between $\nu_{0,0}$ values is necessary but not sufficient since, for some normal coordinate σ , the $\nu_{0,0}$'s may coincide but the surfaces may have minima quite removed from each other. Since ${}^1\text{T}_{1g}(\text{O}_h)$ in $\text{Co}(\text{NH}_3)_6^{3+}$ is at almost the same energy as the resultant π and σ states in Co en_3^{3+} such a possibility can probably be safely neglected here.

** These are taken from 4.2 °K spectra whereas the experimental results in (2) were obtained at $\sim 300 \text{ }^\circ\text{K}$. The 4.2 °K results should have 300–400 cm^{-1} subtracted from them in order to provide a result that may be compared with the results in (2).

where the value $\sqrt{2}$ is taken from our experiments. Hence

$$\Re_{\pi} \approx \pm \sqrt{2} \Re_{\sigma}$$

KARIPIDES and PIPER⁽³⁾ have shown that, in our notation $(\alpha + \sqrt{2}\beta) + \gamma = 0$ if in the evaluation of these molecular integrals one uses undeviated nitrogen orbitals. Our result shows clearly that this is not permissible. Indeed, it is the "misdirection" of the nitrogen orbitals⁽²⁰⁾ that leads to a breakdown of KARIPIDES and PIPER's result.

Regardless of the *sign* of the \Re 's we would expect the $\Re(^1A_1 \rightarrow ^1A_2)$ to be about 1.4 as strong as the axial $\Re(^1A_1 \rightarrow ^1E)$. The *absolute* signs of the two rotatory strengths is seen to be solely determined by the molecular integrals α , β and γ . McCAFFERY and MASON⁽²⁾ measured the C.D. of D [Co(en)₃³⁺] both in solution and axially in a single crystal. In both cases they found a positive C.D. curve centred about 20,000 cm⁻¹, however, the intensity of the solution spectrum is only 5 % of the intensity observed in the crystal. In addition a new, negative C.D. absorption appears at 23,000 cm⁻¹ but *only* in solution. McCAFFERY and MASON interpret the latter band as being due to the $^1A_1 \rightarrow ^1A_2$ transition.

We have demonstrated that the trigonal splitting of 1E and 1A_2 in the crystal of Co(en)₃³⁺ does not exceed 10 cm⁻¹. This leads then to the interesting question: What is the negative C.D. at 23,000 cm⁻¹ ascribed by McCAFFERY and MASON⁽²⁾ as the 1A_2 band due to? Even if it is true that the difference between two observed C.D. maxima by no means corresponds to the "true" electronic splitting⁽²⁴⁾ ⁽²⁵⁾ we have been unable to generate on an electronic computer the observed C.D. results, assuming a splitting of *less than* ≈ 400 cm⁻¹.

We believe, however, to be able to solve this puzzle in the following way. We assume with WOLDBYE⁽²⁶⁾ that the complex can exist in two conformers *in solution but not in the crystal*. Now, with a negligible splitting of the electronic state we should get for the $^1T_{1g}$ band

$$\frac{\Re_{\text{sol}}}{\Re_{\text{axial}}} = \frac{\frac{1}{3}(\Re_{\pi} + 2\Re_{\sigma})}{\Re_{\sigma}}$$

with $\Re_{\pi} = \pm \sqrt{2}\Re_{\sigma}$ this ratio is equal to 0.2 if the \Re 's have opposite sign but 1.1 if the \Re 's have the same sign. If a fraction of the compound should be found in a different conformation, these ratios should be multiplied with a number less than one. Anyhow, comparing these numbers with the experimental findings it is seen that it is much more likely for the two rotatory strengths to have the opposite signs.

Some authors⁽²⁷⁾ ⁽²⁸⁾ have taken it for granted that \mathfrak{R}_σ and \mathfrak{R}_π should have opposite signs. It is true that *calculations based on a specific model* namely *d-p* mixing⁽²⁹⁾, shows that \mathfrak{R}_σ and \mathfrak{R}_π here have different signs, but since this mixing is not the primary cause of optical activity in these systems⁽³⁰⁾, the appropriateness of the calculation to the sign question is rather doubtful.

That the "other" form of $\text{Co}(\text{en})_3^{+++}$ should possess an energy difference $\Delta E(^1A_1 - ^1T_1)$ which is a few hundred wavenumbers larger than the "crystal form" is not unreasonable. This difference will indeed presumably mostly be found when the excited states of the two conformers are compared. These states are antibonding in nature and therefore more susceptible to changes in the molecular geometry than is the ground state. It is therefore not expected a priori that variations in the respective C.D. intensities due to small changes in temperature will occur, since the Boltzmann Distribution in the ground states may not be altered significantly, at least so long as we can still speak of solutions.

Our conclusion is therefore that the "negative" C.D. found at $23,000 \text{ cm}^{-1}$ is due to the presence of a different conformation of $\text{Co}(\text{en})_3^{+++}$ than that found in the crystal, and that \mathfrak{R}_π and \mathfrak{R}_σ have different signs.

The rotatory strength of the "second" band ($^1T_{2g}$) also presents us with a small problem. The level is not connected with the ground state by the magnetic dipole operator. Under the trigonal crystal field the two E components of T_{1g} and T_{2g} can of course mix, and we get

$$(^1E(T_1) | \mathcal{O}_T^0 | ^1E(T_2)) = \Delta.$$

However, by a curious coincidence, we have also that the trigonal splitting of both 1T_1 and 1T_2 is equal to Δ . Experimentally Δ is found to be around 10 cm^{-1} . Thus in fact $^1E(T_2)$ does not "borrow" significantly amounts of angular momentum from $^1E(T_1)$ via the trigonal field. What angular momentum it carries must have been stolen from a higher excited state. Hence the two low-lying 1E states are not coupled together.

Conclusions

The experiments show quite conclusively that the intensity in the $\text{Co}(\text{en})_3^{3+}$ ion in crystals is predominantly vibronic in origin. Furthermore these vibronic terms have been individually observed and correlated with possible IR frequencies. Deuteration of the $\text{N}-\text{H}_2$ groups in the ethylene diamine does not give rise to any large change in the spectra.

In estimation electronic splitting parameters such as the trigonal field parameter Δ , found here to be $\pm 10 \text{ cm}^{-1}$, values derived from ν_{max} positions are at the best, likely to be misleading, and are probably quite often incorrect in sign as well as magnitude.

Due to differing crystal influences the spectra of the d, l and the D crystals of $2[\text{Co}(\text{en})_3\text{Cl}_3] \cdot \text{NaCl} \cdot 6\text{H}_2\text{O}$ are somewhat altered in finestructure. The C.D. results of McCaffery and Mason are explained assuming two conformers of $\text{Co}(\text{en})_3^{+++}$ to be present in solution as originally suggested by Woldbye.

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