Polarized Crystal Spectra of the Cobalt(III) Trisethylenediamine Ion

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THE cobalt(III) trisethylenediamine ion, Co en_3^{3+} has been the basis of many studies concerned with anomalous rotatory dispersion[1] and circular dichroism[2] in pseudo-octahedral, six-co-ordinated, transition-metal complexes. The identification of the electronic transitions involved in such studies by some independent method is of paramount importance.

Single-crystal spectral data, which can provide such an identification, have been reported by Yamada and Tsuchida[3] and by Karipides and Piper,[4] but there still exist a number of uncertainties concerning the optical absorption in these crystals.

We report, as part of a detailed study of trigonally distorted octahedral complexes at low temperatures, π, σ, and axial spectra for a number of Co-en_3^{3+}-containing crystals in the temperature range 5—300°K. The model crystal described here is *dl*(Co en_3 $Cl_3)_2$,NaCl,$6H_2O$ since the spectra of the other complexes are easily correlated.

The general features of the spectrum are,

(i) At 300°, 77°, and 5°K the σ and the axial spectra coincide, showing conclusively that the spectra are almost entirely electro-dipole in nature.

(ii) The appearance of considerable absorption intensity in the π spectrum in the region of the $^1T_{2g}(O_h)$ absorption and the temperature-dependence of the total intensity show that the static D_3 selection rules are *not* rigorously obeyed, that vibronic contributions to the intensity are of considerable importance and that the C_3 site symmetry must be included in discussing the optical properties of the crystals.

(iii) In all the crystals studied the λ_{max} values show that in the region of $^1T_{1g}(O_h)$ the ^1E state lies at higher energy than the $^1A_2$ state, in direct contradiction to the result obtained from circular dichroism studies.[2]

More specifically, if we focus attention on the low-energy side of the $^1T_{1g}(O_h)$ absorption, it is seen that considerable vibrational fine structure develops in the 5°K spectra. A detailed analysis of this structure yields the following information.

(iv) For each vibrational line (i) holds true and, from the correspondence of the vibrational lines in π, σ, and axial spectra, it is concluded that the splitting of the $^1T_{1g}(O_h)$ state by the trigonal field of the ligands is 0 ± 2 cm.$^{-1}$. (The spectra were taken at high resolution, dispersion ~3Å/mm. and the error is mainly a result of the vibrational band widths, $\Delta\nu_{\frac{1}{2}} \simeq 30$ cm.$^{-1}$ for (O, O). Now it is even more striking to note the contradiction between the trigonal field splittings derived from λ_{max} values, from the (O, O) values and from the circular dichroism studies.

(v) The vibrational structure provides sure evidence as to the presence and the extent of the vibronic contribution to the intensity and we find the important non-totally-symmetrical vibrations to be 185 ± 5 cm.$^{-1}$, 345 ± 5 cm.$^{-1}$, and $\simeq 400 \pm 20$ cm.$^{-1}$—very reasonable values for t_{1u} and t_{2u} vibrations of the CoN_6 octahedron. The only totally-symmetrical mode which can be found is 255 ± 5 cm.$^{-1}$ and it appears in several different progressions.

(vi) The static and vibronic contributions to the intensity have been estimated from the vibrational pattern (extrapolated over the whole system since the vibrational structure is lost after 5 or 6 quanta of the totally-symmetrical vibration) and it is concluded that $f_{static} \leqslant 10$—15% of the total intensity.

The above information applies directly to the *dl*-crystal but in the main part it applies as well to the crystal D-(Co en_3 $Cl_3)_2$,NaCl,$6H_2O$. The small differences between the two spectra can be rationalized in terms of the different crystal structures[5,6] and by a different site symmetry influence in the two crystals. The major difference in that f_{static} in the optically active crystal appears to be only about 10% of that in the racemic crystal.

These results raise some questions regarding the recent treatments of the optical activity of this compound. Firstly, the calculations of Piper and Karipides[4,7] are based on a trigonal field parameter K which is orders of magnitude greater than that found here and thus their derived values of q_0, q_1,

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[1] E. Drouard and J. P. Mathieu, *Compt. rend.*, 1953, **236**, 2395.
[2] A. J. McCaffery and S. F. Mason, *Mol. Phys.*, 1963, **6**, 359.
[3] S. Yamada and R. Tsuchida, *Bull. Chem. Soc. Japan*, 1960, **33**, 98.
[4] A. G. Karipides and T. S. Piper, *J. Chem. Phys.*, 1964, **40**, 674.
[5] K. Nakatsu, M. Shiro, Y. Saito, and H. Kuroya, *Bull. Chem. Soc. Japan*, 1957, **30**, 158.
[6] K. J. Watson, private communication.
[7] T. S. Piper and A. Karipides, *Mol. Phys.*, 1962, **5**, 475.

and q_2 may not be valid. Secondly, the ionic model [7,8] can no longer be used to explain the dichroism of the so called ^1E_b band, nor can it be used to describe the dichroism of the ^1E_a and $^1A_2$ bands since with $K = 0$ the model predicts zero optical activity in solution in these regions. Thirdly, the importance of the site symmetry in the analysis of the intensities probably means that in this case at least, dichroism results may not be transferred from crystal to solution.

Finally, the recent suggestion[9] that the N–H and C–H stretching modes are important in the production of static intensity does not seem to be valid since the 255 ± 5 cm.$^{-1}$ frequency accounts for most of the spectral properties.

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[8] S. Sugano, *J. Chem. Phys.*, 1960, **33**, 1883.

[9] S. F. Mason and B. J. Norman, *Chem. Comm.*, 1965, 48.