CHEMISTRY

Promethium Oxide Structure

FROM the results of radiochemical distribution experiments, M. Bruno and U. Croatto[1] concluded that over a large range of temperatures promethium sesquioxide has a fluorite-type structure. We have examined a sample of promethium sesquioxide powder by means of X-ray diffraction and have found reflexions which are consistent with a fluorite-type structure. The promethium-147 oxide was about 99 per cent pure with the remaining impurity being the daughter, samarium-147. This oxide was prepared by heating promethium oxalate in air for 3 h at 750° C. About 15 mg of the oxide were placed in a lead sample holder, one end of which was closed by a film of 'Cellophane' tape through which the X-ray diffraction pattern was obtained by the use of a General Electric XRD-5 diffractometer.

Because of the poor crystalline nature of the oxide only four reflexions were observed and these are listed in Table 1.

Table 1. OBSERVED REFLEXIONS

Line No.	d (Å)	Relative intensity
1	3·16	10
2	2·73	4
3	1·94	6
4	1·66	6

The observed reflexions correspond to the (1,1,0), (2,0,0), (2,2,0) and (3,1,1) reflexions of a fluorite lattice with an average cell constant of 5·48 Å with an average deviation of 0·02 Å. The cubic form of the rare earth sesquioxides is a defect fluorite structure with two of the eight oxygens systematically removed[2] so that the unit cell is twice that of the fluorite cell or, in the case of promethium oxide, 10·96 Å. The lattice constants for the cubic form of the sesquioxides of samarium and neodymium are respectively 10·85 Å and 11·05 Å. Thus the lattice constant for the oxide of promethium, as expected, falls between samarium and neodymium.

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[1] Bruno, M., and Croatto, U., Nature, 183, 601 (1959).
[2] Strukturberichte, 2, 38 (1939).

Splitting of Energy-levels in Non-cubic Cobalt (III) Complexes

THE two absorption bands of octahedral cobalt (III) complexes, with O_h symmetry, are assigned as $^1T_{1g} \leftarrow {}^1A_{1g}$ for the lower frequency band (which may be called band I, following a recent paper[1]) and $^1T_{2g} \leftarrow {}^1A_{1g}$ for the higher frequency band (band II). Evidence for the splitting of these bands when the symmetry is lowered to D_3 has been given by Mason[2].

In considering the bis-chelate systems, such as the dihalogenobisethylenediaminecobalt (III) cations, the trans-isomer approximates to D_{4h} symmetry and the cis-isomer has C_{2v} symmetry. Bands I and II are both expected[3] to split, in either isomer. In band I, both components are magnetic-dipole-allowed[4] in the trans case (D_{4h}), and in the cis case (C_{2v}). The circular dichroism associated with these transitions may thus provide evidence on the splitting of the energy-levels which is often inaccessible from other sources. This is illustrated for two classes of compound in Tables 1 and 2.

Table 1. SPLITTINGS OF BAND I FOR DICHLOROTETRAMMINECOBALT (III) IONS

Compound		Band Ia	Band Ib	Method*
[CotrienCl₂]⁺	trans	16,100†	22,500	S^a
	cis	16,400	18,700	S^a
[Coen₂Cl₂]⁺	trans	16,120	22,490	S^b
	cis	16,230	18,700	CD^c
(+)[Co(+pn)₂Cl₂]⁺	trans	16,400	22,200	S^d
	cis	16,400	18,700	CD^c

* S, Spectrophotometry in solution; CD, circular dichroism in solution.

† Frequencies in cm⁻¹. ^{a} Gillard and Wilkinson, J. Chem. Soc. (in the press); ^{b} Linhard and Weigel, Z. anorg. Chem., 271, 101 (1953); ^{c} Mathieu, C.R. Acad. Sci., Paris, 199, 279 (1934); ^{d} Basolo, J. Amer. Chem. Soc., 72, 4393 (1950); ^{e} Mathieu, Ann. Phys., 19, 335 (1944).

Table 2. SPLITTINGS OF BAND I FOR bisAQUOTETRAMMINECOBALT (III) IONS

Compound		Band Ia	Band Ib	Method
(+)[Co(+pn)₂(H₂O)₂]³⁺	trans	18,200	22,800	S^a
	cis	18,300	20,700	CD^b

^{a} This work; ^{b} Mathieu, Bull. Soc. Chim., 4, 687 (1936).

A further class of compound where measurements of circular dichroism give more detailed insight than spectrophotometry into the splitting of bands I and II comprises the complexes of diaminotetracarboxylate anions with cobalt (III), which have approximately C_{2v} symmetry. The electronic spectrum in solution of the ethylenediamine tetra-acetatocobaltate (III) anion, [Co(EDTA)]⁻, shows[5] a very broad band I (ν_{max} 18·65, ε_{max} 90) and a narrower band II (ν_{max} 26·3, ε_{max} 62). The spectrum of propylenediamine tetra-acetatocobaltate (III) anion, [Co(PDTA)]⁻, is virtually identical. The electronic spectra of both [Co(+PDTA)]⁻ and [Co(±PDTA)]⁻, which are identical, obey the Beer–Lambert law, so that only monomeric species are present in both cases.

The circular dichroisms of (−)₅₄₆·₁[Co(EDTA)]⁻ and (−)₅₄₆·₁[Co(+PDTA)]⁻, given in Table 3, show the splitting of both bands I and II into two. A previous attempt[6] to locate the components was made by analysing the rotatory dispersion curve of [Co(EDTA)]⁻; the results obtained agree well with ours for band I, but only one Cotton effect was found in the region of band II. These compounds are seen to have the same configuration; that of (−)₅₄₆·₁[Co(+PDTA)]⁻ is known[7] from geometrical considerations to be of opposite helicity to that of (+)₅₈₉·₃ trisethylenediaminecobalt (III) cation, determined[8] by X-rays.

PDTA, (+)PDTA, and their complexes with cobalt (III) were prepared by the methods described by Dwyer and Garvan[9]; analyses, melting points and specific rotations agreed well. (−)₅₄₆·₁K[Co(EDTA)] was prepared by the method of Dwyer, Gyarfas and Mellor[10]; its optical rotatory dispersion curve was identical with that previously described.

Table 3. CIRCULAR DICHROISMS OF DIAMINOTETRACARBOXYLATOCOBALTATES (III)

Compound	Band I				Band II			
	ν_{max}	Sign	ν_{max}	Sign	ν_{max}	Sign	ν_{max}	Sign
(−)₅₄₆·₁[Co(EDTA)]⁻	17,010	+ ve	19,420	− ve	23,810	+ ve	27,470	+ ve
(−)₅₄₆·₁[Co(+PDTA)]⁻	17,040	+ ve	19,420	− ve	23,870	+ ve	27,550	+ ve