

Chemical Communications

NUMBER 5/1965

10 MARCH

Spectroscopic and Configurational Assignments from Ion-pairing Effects

By S. F. MASON and (Miss) B. J. NORMAN

(School of Chemical Sciences, University of East Anglia, Norwich)

THE correlation of absolute configuration with optical activity in the series of dissymmetric transition-metal complexes requires general methods for identifying the symmetries of the electronic transitions which give rise to the observed Cotton effects.^{1,2} The methods used hitherto depend upon the plane-polarized^{3,4} or the circularly-polarized^{1,2} crystal spectra, and these methods are limited by the availability of appropriate crystals with known structures.

A solution-method is now suggested, based on the observation^{5,6} that phosphate and other polarizable anions change differentially the areas of the circular dichroism bands of cobalt(III) trisdiamine complexes by forming an ordered ion-pair in which the ligand field is modified. Subsequent studies of some forty polarizable anions and a variety of diamine-metal complexes show that the changes in band area described^{5,6} are qualitatively of the same form for the ion-pairs produced by the anions containing two or more oxygen atoms and the dissymmetric d^3 and d^6 hexamine metal complexes whether of trigonal or digonal symmetry (Figures 1—3).

Of the various oxyanions investigated, selenite

is found to be particularly convenient, producing large changes in band area, without precipitation of the complex ion, when added in low to moderate (0.2M) concentration to a 0.01M-aqueous solution of the complex. The effects of such an addition are a decrease and an increase in the respective areas of the longer and the shorter wavelength circular dichroism band in the region of the low-frequency unpolarized absorption (Figures 1 and 3) or, in the case of (+)-Cr(en)₃³⁺, the development of the shorter wavelength band from the envelope of the combined circular dichroism bands (Figure 2). In the trisethylenediamine and tris-active-propylenediamine complexes of chromium(III), cobalt(III), and rhodium(III) the longer and the shorter wavelength circular dichroism bands have been assigned on other grounds^{1,2,4} to electronic transitions polarized respectively perpendicular (E_a) and parallel (A_2) to the three-fold axis of the complex, so that a general relation between the direction of the change in the area of the two circular dichroism bands due to ion-pairing and the origin of those bands in the E_a or the A_2 transition may be assumed with some confidence for the trisdiamine complexes.

¹ R. E. Ballard, A. J. McCaffery, and S. F. Mason, *Proc. Chem. Soc.*, 1962, 331; *J.*, 1965, forthcoming.

² A. J. McCaffery and S. F. Mason, *Proc. Chem. Soc.*, 1962, 388; *Mol. Phys.*, 1963, 6, 359; *Trans. Faraday Soc.*, 1963, 59, 1.

³ T. S. Piper and R. L. Carlin, *J. Chem. Phys.*, 1960, 33, 608; 1961, 35, 1809; 1962, 36, 3330; *Inorg. Chem.*, 1963, 2, 260.

⁴ T. S. Piper and A. Karapides, *Mol. Phys.*, 1962, 5, 475; *J. Chem. Phys.*, 1964, 40, 674.

⁵ S. F. Mason and B. J. Norman, *Proc. Chem. Soc.*, 1964, 339.

⁶ H. L. Smith and B. E. Douglas, *J. Amer. Chem. Soc.*, 1964, 86, 3885.

The C_2 complexes *cis*-(+)-Co(en)₂(NH₃)₂³⁺ and (-)-Co(penten)³⁺ (penten = pentaethylenehexamine) are of lower symmetry than trigonal, but

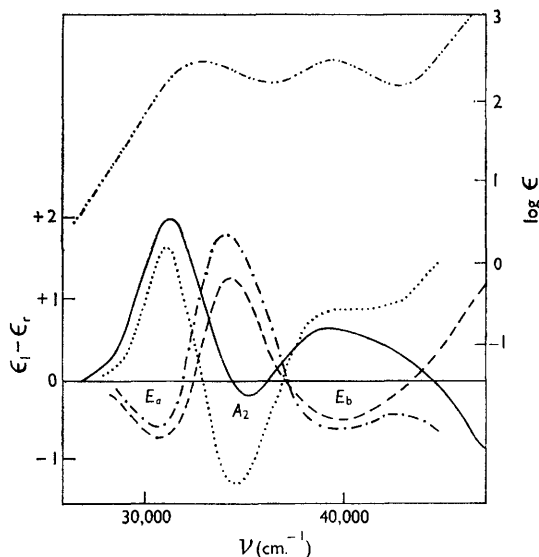


FIGURE 1. The circular dichroism spectrum of 0.01M (-)-Rh(en)₃(ClO₄)₃ — in water and in 0.2M aqueous sodium selenite. The circular dichroism spectrum of 0.01M (+)-Rh(-pn)₃(ClO₄)₃ - - - in water and - · - · in 0.2M aqueous sodium selenite. The absorption spectrum of Rh(en)₃(ClO₄)₃ - · - · in water.

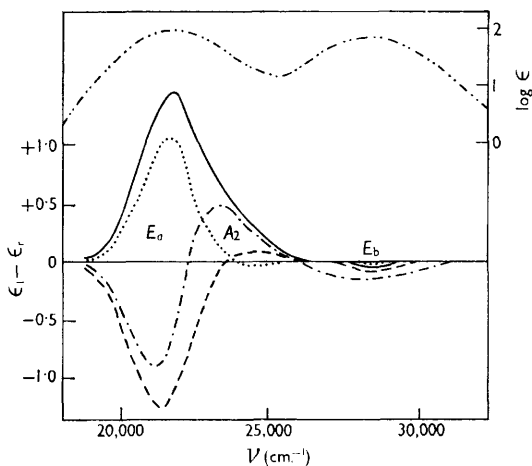


FIGURE 2. The circular dichroism spectrum of 0.01M (+)-Cr(en)₃(ClO₄)₃ — in water and in 0.2M sodium selenite. The circular dichroism spectrum of 0.01M (-)-Cr(-pn)₃(ClO₄)₃ - - - in water and - · - · in 0.2M sodium selenite. The absorption spectrum of Cr(en)₃(ClO₄)₃ - · - · in water.

the circular dichroism band area changes due to outer-sphere co-ordination are of the same form for these complexes as^{5,6} for (+)-Co(en)₃³⁺ (Figure 3). As yet, independent experimental assignments are not available for the electronic transitions of the metal complexes with C_2 symmetry, but the ion-pairing effect suggests that, for the C_2 hexamine complexes, the first three circular dichroism bands from longer to shorter wavelengths are due to transitions with predominant E_a , A_2 , and E_b trigonal parentage, respectively.

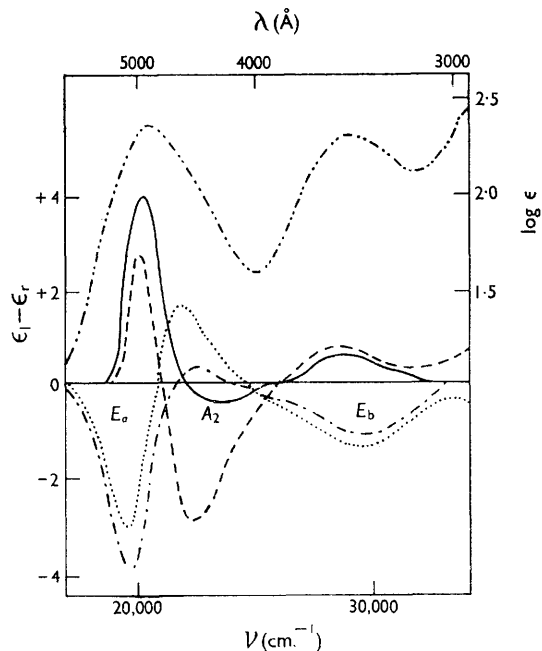


FIGURE 3. The circular dichroism spectrum of 0.01M *cis*-(+)-Co(en)₂(NH₃)₂(ClO₄)₃ — in water and in 0.2M sodium selenite. The circular dichroism spectrum of 0.01M (-)-Co(penten)(ClO₄)₃ - · - · in water and in 0.2M sodium selenite. The absorption spectrum of Co(penten)(ClO₄)₃ - · - · in water. The left-hand ordinate scale refers directly to the circular dichroism of (-)-Co(penten)³⁺ and to the circular dichroism of (+)-Co(en)₂(NH₃)₂³⁺ multiplied by a factor of ten.

The parentage is rigorous, as the forbidden A_1 trigonal transition does not give rise to circular dichroism absorption in the C_2 hexamine complexes where this transition has A symmetry and becomes formally allowed. The sign of the circular dichroism band mainly of E_a trigonal

parentage indicates⁷ that *cis*-(+)-Co(en)₂(NH₃)₂³⁺ and (-)-Co(penten)³⁺ have an absolute configuration which is respectively the same as, and enantiomeric with, that of (+)-Co(en)₃³⁺.

The trigonal parentage of each of the two circular dichroism band given in the region of the long-wavelength absorption by other complexes *cis*-Co(en)₂L₂³⁺, where the ligand L is monodentate (L = H₂O, Cl⁻, N₃⁻, NO₂⁻, CN⁻), is probably more mixed since the observed band area changes due to ion-pairing are smaller in magnitude. The ion-pairing effect is small for the complexes Co(en)₂L₂³⁺, where the ligand LL is conjugated and bidentate (LL = oxalate, carbonate, acetylacetonate), which give a single circular dichroism

band in the long-wavelength absorption region. This band is of equal *E_g* and *A₂* trigonal parentage, and the ion-pairing effects upon the rotational strengths of the parent transitions are opposed and mutually cancel.

In general the spectroscopic and configurational assignments based upon the observed changes in the circular dichroism band areas due to outer-sphere co-ordination are reliable mainly for the dissymmetric hexamine complexes, although those changes afford an indication of the dominant trigonal parentage of a circular dichroism band given by the complexes *cis*-Co(en)₂L₂³⁺ with the ligand L monodentate.

(Received, February 2nd, 1965.)

⁷ S. F. Mason, *Quart. Rev.*, 1963, **17**, 20.