The Absolute Configuration of the $(+)_{436}$-Sarcosinatotetra-amminecobalt(III) Ion

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THE resolution of co-ordinated secondary amine moieties in cobalt(III) complexes has led to questions concerning the interpretation of their circular dichroism. The spectral properties and the c.d. change substantially with the types and symmetries of the complexes. Therefore the absolute configurations of several of these asymmetric nitrogen centres must be determined before the c.d. can be interpreted with any degree of certainty in these and related systems.

We report the absolute configuration, determined from single crystal *X*-ray diffraction data, of the $(+)_{436}$-sarcosinatotetra-amminecobalt(III) ion.[1]

The salt $(+)_{436}$-sarcosinatotetra-amminecobalt(III) nitrate crystallizes from $0{\cdot}01\text{M-HNO}_3$ as thin,

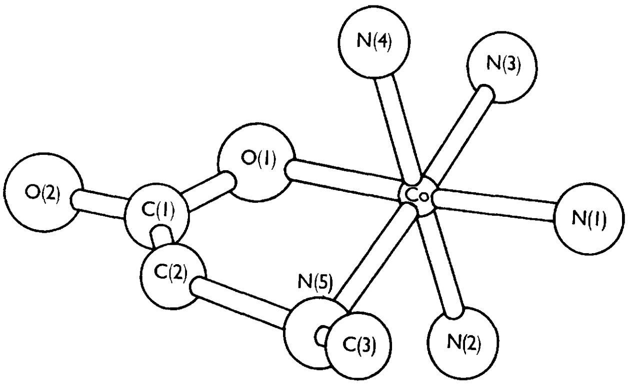

FIGURE 1. *The absolute configuration of the* $(+)_{436}$*-sarcosinatotetra-amminecobalt*(III) *ion.*

red–brown hexagonal plates. Under the polarizing microscope, with crossed Nicol prisms and with light perpendicular to the plate faces, the crystals show sharp extinction parallel to one pair of the plate edges. They exhibit little pleochroism (red-brown to brown).

The crystals are orthorhombic, space group $P2_12_12_1$, $a = 11{\cdot}865 \pm 0{\cdot}005$, $b = 14{\cdot}88 \pm 0{\cdot}01$, $c = 7{\cdot}279 \pm 0{\cdot}003$ Å. $D_m = 1{\cdot}76 \pm 0{\cdot}01$ g./cm.^{3}, $Z = 4$ and $D_c = 1{\cdot}75 \pm 0{\cdot}01$ g./cm.^{3}. The plate faces are $\{010\}$. The unit-cell dimensions were determined from Guinier photographs calibrated with silicon powder using Cu-K_α radiation.

1250 independent non-zero reflections were measured visually from multiple film equi-inclination Weissenberg photographs taken with Cu-K_α radiation incident upon crystals mounted about the crystallographic c- and a-axes. The data were corrected for the usual geometrical factors, placed on a common relative scale, and then used to solve the structure by standard Patterson and heavy-atom Fourier methods.

The absolute configuration of the complex cation was determined by comparing the relative intensities of pairs of reflections, hkl and $\bar{h}\bar{k}\bar{l}$, with the squares of the structure amplitudes, calculated taking into account the anomalous dispersion of Cu-K_α radiation by cobalt.[2] The absolute configuration is shown in Figure 1, in which the structure of the ion is projected down the crystallographic b-axis on to the ac-plane.

The postulated atomic co-ordinates were refined by the full matrix least-squares method. Anisotropic temperature factors for all atoms were included as variables. The present R factor is 0·161.

All the interatomic distances and angles for the ions in the structure have expected values. The cobalt–sarcosinate ring is slightly puckered, with C(1) on the opposite side and C(2) on the same side of the O(1)–Co–N(5) plane as the methyl group, C(3), as was observed for the $(+)_{436}$-, $(-)_{589}$-sarcosinatobis(ethylenediamine)cobalt(III) ion.[3]

The c.d., visible, and u.v. absorption spectra of the antimer $(-)_{436}$-sarcosinatotetra-amminecobalt(III) ion are given in Figure 2. It is apparent from the dichroism that at least two transitions are involved in the first ligand field band. If it is assumed that the chromophore is essentially CoN_5O (C_{4v}) then the ${}^1A_{1g}$ (O_h) $\rightarrow$ ${}^1T_{1g}$ (O_h) transition should split into the two transitions A_1 (C_{4v}) $\rightarrow$ A_2 (C_{4v}) and A_1 (C_{4v}) $\rightarrow$ E (C_{4v}). Several theoretical and spectral studies[4] for systems of this type have shown that the E (C_{4v}) level is lower in energy than the A_2 (C_{4v}) level. A

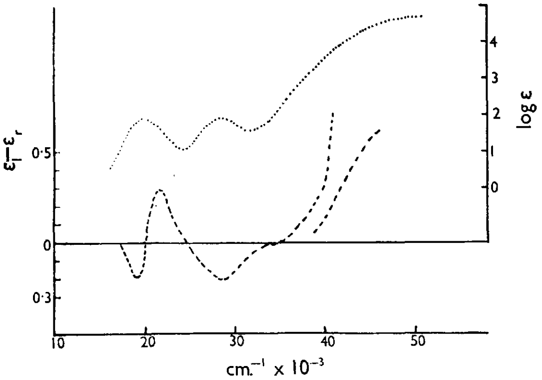

FIGURE 2. *The absorption spectrum* (· · ·) *and circular dichroism* (- - -) *of* $(-)_{436}$*-sarcosinatotetra-amminecobalt* (III) *nitrate in* 0·1M-$HClO_4$.

negative dichroism to the E-level and a positive dichroism to the A-level are therefore assigned for the $(-)_{436}$,sarcosinatotetra-amminecobalt(III) ion.

The absolute configuration of the optically active nitrogen centre in $(-)_{436}$-sarcosinatotetra-amminecobalt(III) ion is the same as that in the $(-)_{436}$,$(+)_{589}$-sarcosinatobis(ethylenediamine)-cobalt(III) ion.[3] It should be noted that the configuration correlates with that deduced from a study of the relation between the o.r.d. curves of L-$(-)_{589}$-sarcosinatobis(ethylenediamine)cobalt(III) ion, D-$(+)_{589}$-glycinatobis(ethylenediamine)-cobalt(III) ion, and the antimer of the present complex ion.[5] The correlation supports the assertion that contributions to rotatory power from the asymmetric cobalt and ligand centres are essentially additive.[5,6]

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