Absolute Configuration and Stereospecificity of the $(-)_{589}$-Sarcosinatobis(ethylenediamine)cobalt(III) Ion

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THE co-ordination of sarcosine, $CH_3{\cdot}NH{\cdot}CH_2{\cdot}CO_2H$, in the $[Co\,en_2\,sarcosinato]^{2+}$ ion leads to two asymmetric centres, one about the Co^{III} centre and one about the co-ordinated sarcosine nitrogen atom. Meisenheimer *et al.*[1] have claimed to have resolved both centres with the (+)-π-bromocamphorsulphonate ion, and to have observed the mutarotation of the nitrogen centre. More recently this work has been repeated.[2] It has been established that the nitrogen centre does not mutarotate and considerable evidence has been collected to show that the co-ordination of sarcosine is stereospecific.

For any one configuration about the Co^{III} atom, there are two possible configurations about the nitrogen centre. One of these should be sterically preferred to the other, because it involves smaller nonbonded interactions between the hydrogen atoms on the methyl groups and those on the adjacent ethylenediamine chelate rings. The

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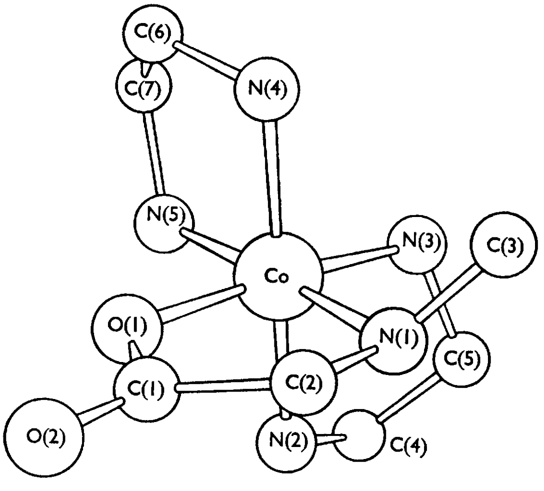
crystal structure analysis of the $(-)_{589}$-[Co en$_2$-sarcosinato]I_2,$2H_2O$ has now been accomplished (see Figure). It confirms the stereospecificity incorporated in the system.



FIGURE

The crystals of sarcosinatobis(ethylenediamine)-cobalt(III) di-iodide dihydrate are monoclinic, space-group $A2$, with $a = 7{\cdot}821$, $b = 8{\cdot}296$, $c = 28{\cdot}053$ Å, $\beta = 108{\cdot}03°$, $D_m = 2{\cdot}14 \pm 0{\cdot}02$ g.cm.$^{-3}$, $Z = 4$, $D_c = 2{\cdot}14$ g.cm.$^{-3}$. Intensities of 3269 reflexions (710 unobservably weak) were measured with a Supper equi-inclination diffractometer, Cu-K_α radiation. The structure analysis was carried out by standard Patterson and Fourier methods, refinement by full-matrix least-squares with allowance for anomalous dispersion and anisotropic thermal parameters for Co and I^-, and individual isotropic thermal parameters for the lighter atoms. The absolute configuratioh was established by taking into account the relative intensities of pairs of *hkl* and *hkl* reflexions.[3] The final reliability index is $R = 0{\cdot}077$ (including unobserved reflexions) but, since the Co and I^- atoms alone account for 90% of the X-ray scattering, the standard deviations of the bond-lengths are *ca.* 0·01 Å for the six bonds involving Co, and 0·02 Å for the remaining bonds.

The structure and absolute configuration of the lævo-ion $(-)_{589}$ are shown in the Figure. The bond-lengths and angles are normal [Co–O(1), 1·91 Å; mean Co–N(amino), 1·97 Å; mean N–C, 1·48 Å; mean C–C, 1·52 Å; mean Co–N–CH_2, 109°; mean H_2N–C–CH_2, 107°). The Co-sarcosinate ring is slightly puckered, the displacements of the Co and N(1) atoms from the carboxyl plane C(1)C(2)O(1)O(2) being 0·14 and 0·26 Å (in the same sense), respectively. The Co(en) chelate rings have mirror-image conformations. The combination of ring conformations presumably minimises the H(methyl)· · ·H(amino) interactions.

The absolute configuration is related to that of the $(-)_{589}$-[Co en$_3$]$^{3+}$ ion through the arrangement of the bis(en) chelate rings. Assuming that the sarcosinato-residue can be neglected, the complex has effectively C_2 symmetry. It is then related to other bis(ethylenediamine)cobalt(III) complexes as well as to the $(-)$-[Co en$_3$]$^{3+}$ ion through a common C_2 axis [bisecting the angle N(5)–Co–N(3) in the Figure]. Its c.d. curve[2] is indeed consistent with the sign predicted on this assumption for the circular dichroism band associated with the first ligand-field band. Meason *et al.*[4] have established that the transition of E symmetry dominates the sign of the c.d. for the first ligand-field band in the Co en$_3$$^{3+}$ ion and they suggest that this sign is carried over to the A_2 and B transitions in the C_2 complexes which derive from the transition of E symmetry in the D_3 complex. These suggestions are supported by the recent structural analysis of the (+)-[Co(−)pn$_2$(NO_2)$_2$]$^+$ ion[5] and appear to hold also for the $(-)_{589}$-[Co en$_2$ sarcosinato]$^{2+}$ ion.

It is also likely that Co^{III} has the same environment in those [Co en$_2$ α-amino-acid]$^{2+}$ complexes[6] whose first ligand-field bands give rise to dominant negative c.d. bands, namely $(-)_{546}$-[Co en$_2$-L-alaninato]$^{2+}$, $(-)_{546}$-[Co en$_2$-D-alaninato]$^{2+}$, $(-)_{546}$-[Co en$_2$-glycinato]$^{2+}$, $(-)_{546}$-[Co en^2-D-leucinato]$^{2+}$, $(-)_{546}$-[Co en$_2$-L-leucinato]$^{2+}$, $(-)_{546}$-[Co en$_2$-D-phenylalaninato]$^{2+}$, and $(-)_{546}$-[Co en$_2$-L-phenylalaninato]$^{2+}$.

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