Optical Configurations of Tris-chelate Compounds

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THE relation between absolute stereochemistry and optical rotatory power of metal complexes has been debated intensively. One drawback to the use of the methods applicable in organic stereochemistry is that among complex compounds conversions in which configuration is certainly retained are uncommon, though a few examples are known.[1] Till now, no tris-chelate of the type [MA_3] has been chemically related to a spectroscopically distinct complex [MB_3], though[2] L-[Co en_2 gly]$^{2+}$ has been converted into L-$[Co\,en_2(ser)]^{2+}$. We now report the first example of chemical correlation between two distinct tris-chelate compounds.

The green complex anion of cobalt(III) with cysteinate has been formulated[3] as $[Co^{III}(H_2NCH(CO_2)CH_2S)_3]^{3-}$. We have prepared this compound using L-cysteine, and find that only one of the many possible isomers is formed. This probably has the L-configuration, judged by the negative Cotton effect for the *d–d* band at 590 mμ (Figure 1). The cysteine ligands are attached to cobalt through the -NH_2 and -S group (rather than N and O, or S and O) as suggested[3] by Neville and Gorin. The geometrical structure is not yet certain, though the remarkable stereoselectivity of formation probably arises from the potential terdentate nature of cysteine.[4]

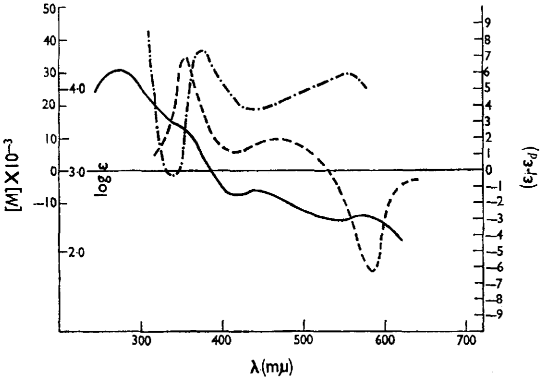

FIGURE 1. *Properties of* $K_3[Co^{III}(NH_2{\cdot}CH{\cdot}CO_2{\cdot}CH_2S)_3]$
(———) absorption spectrum;
(- - -) circular dichroism;
(—·—·—) optical rotatory dispersion.

When this complex is treated with hydrogen peroxide, a yellow compound is formed very rapidly. The formulation of this second compound as the tris-cysteine-sulphinate complex, $[Co^{III}(H_2N{\cdot}CH{\cdot}CO_2{\cdot}CH_2{\cdot}SO_2)_3]^{3-}$ is based on the work of Schubert.[5]

The green and the yellow complex have related optical configurations, since no bonds at the cobalt centre have been broken. As shown in Figure 2, the longest wavelength *d–d* band of the tris-sulphinate complex has a negative Cotton effect, as has the corresponding band for the original tris-cysteinate. The present case is a clear example of the validity of comparing configuration of trischelated compounds of cobalt(III) by use of the sign of the Cotton effect of the long wavelength ligand-field band.

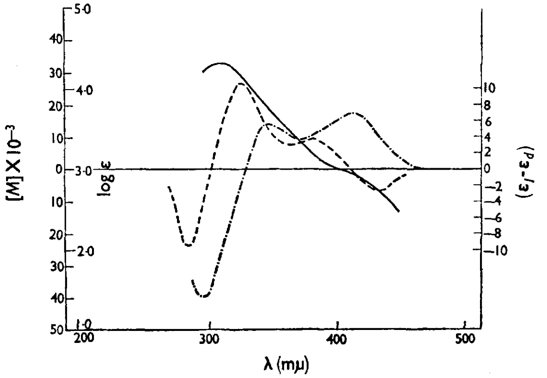

FIGURE 2. *Properties of* $K_3[Co^{III}(NH_2{\cdot}CH{\cdot}CO_2{\cdot}CH_2{\cdot}SO_2)_3]$
(———)absorption spectrum;
(- - -) circular dichroism;
(—·—·—) optical rotatory dispersion.

One further point of interest is that the salt $K_3[Co(sulphinate)_3]$ reacts with ethylene diamine to give the insoluble salt $[Co\,en_3][Co(sulphinate)_3]$ in which the cation has the L-configuration. This might be a very good method of resolving certain cations, and this was established by experiments using racemic tris-ethylenediaminecobalt(III) salts and $K_3[Co^{III}(sulphinate)_3]$. The insoluble fraction contains optically pure L-(—)-$[Co\,en_3]^{3-}$.

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