The Absolute Configuration of *NNN'N'*-Tetrakis-(2'-aminoethyl)-1,2-diaminoethanecobalt(III) and Related Complexes

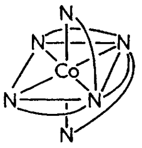
By J. R. GOLLOGLY and C. J. HAWKINS
(*Department of Chemistry, University of Queensland, Brisbane, Australia*)

NNN'N'-TETRAKIS-(2'-AMINOETHYL)-1,2-DIAMINOETHANE (penten) and the related 1,2-diaminopropane compound (mepenten) can co-ordinate as sexidentate ligands with metal ions, such as cobalt(III). The preparation of the former and some of its complexes has been described by Schwarzenbach and his co-workers[1] whereas the latter compound has only recently been prepared as the *lævo*-rotatory isomer *via* *R*-propylenediamine.[2]

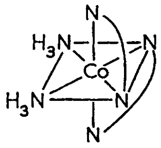
$[Co(penten)]^{3+}$ has C_2 symmetry and its absorption and circular dichroism spectra have been compared with those of $[Co\,en_2(NH_3)_2]^{3+}$, which has the same symmetry.[3] Mason and Norman concluded from these spectra that the two observed circular dichroism bands corresponding to the first cubic absorption band could be attributed to transitions with predominant E and A_2 trigonal parentage.[3] As the E transition for $(-)$-$[Co(penten)]^{3+}$ has a negative Cotton effect whereas those for $(+)$-$[Co\,en_2(NH_3)_2]^{3+}$ and $(+)$-$[Co\,en_3]^{3+}$ have positive Cotton effects, it was proposed that the absolute configuration of the penten complex is "enantiomeric" with that of the other two complexes.[3]

Recently a system of nomenclature for optical isomers of metal complexes based on an "octant sign" of the complexes was put forward by Hawkins and Larsen.[4] This system is applicable to complexes which derive their dissymmetry from the distribution and conformations of chelate rings. Based upon this, a tentative octant rule for cobalt(III) complexes was suggested.[5] This empirical correlation relied upon the assumption that the position of each chelate ring relative to all other chelate rings was most important in determining the sign of the Cotton effect of the various *d–d* transitions.

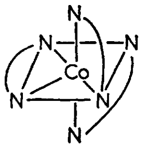
$[Co(penten)]^{3+}$ was thought to provide a good test of the postulated octant rule because the isomer with the absolute configuration (I) has a negative octant sign* and, according to the octant rule, would be expected to have in the region of the first cubic absorption band a transition with *E* symmetry with a negative Cotton effect. This conclusion is opposite to that which would be reached by those who consider that only the two apical chelate rings need be considered. According to this argument the complex (I) should be compared with (+)-$[\mathrm{Co\,en_2(NH_3)_2}]^{3+}$ (II)[6] and (+)-$[\mathrm{Co\,en_3}]^{3+}$ (III)[7] and would have an *E* transition with a positive Cotton effect.



(I)



(II)



(III)

Conformational analysis shows that (−)-mepenten, whose absolute configuration is *R* as it is made from *R*-propylenediamine, is relatively stereospecific. The complex with the same absolute configuration as (I) is the most stable as it has the methyl group in an equatorial position thereby minimising its interactions with the various atoms in the other chelate rings. As the complex was prepared in the presence of activated charcoal and as the difference in energy between the two isomers of the complex is greater than 8 kcal., it can be concluded that the complex isolated has the absolute configuration, (I).[2]

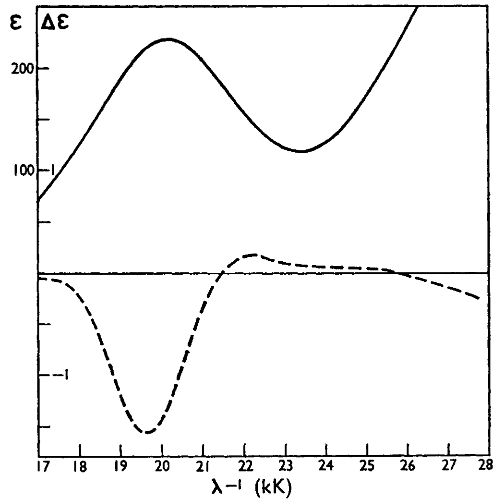


FIGURE. *Absorption* (—) *and circular dichroism* (- -) *spectra of an aqueous solution of* (−)-[Co(*R*-mepenten)]I_3.

The absorption and circular dichroism spectra of (−)-$[\mathrm{Co}(R\text{-mepenten})]^{3+}$ (Figure I) and (−)-$[\mathrm{Co(penten)}]^{3+}$ are very similar.[3] Both complexes show a negative Cotton effect for the transition with predominant *E* trigonal parentage. Therefore it can be concluded that both have the same absolute configuration, (I). This strongly supports the tentative octant rule and the octant sign system of nomenclature and shows that the absolute configuration of (−)-$[\mathrm{Co(penten)}]^{3+}$ is enantiomeric to that proposed by Mason and Norman.[3]

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* Can be assigned symbol *M* or *L*.

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[6] A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc.*, 1965, 5094.
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