A New Type of Atropisomeric Cobalt(III) Complex[1]

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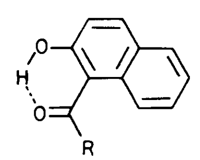
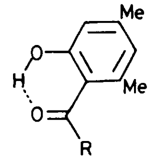
The synthesis and c.d. spectra of optically active cobalt(III)-tren [tren = tris(2-aminoethyl)amine] complexes of a β-diketone are described; the chirality of the complexes arises from restricted rotation of the aryl group.

Recently, we reported optically active cobalt(III)-tren complexes of γ-substituted acetyl acetone whose chirality arises from restricted rotation of an aryl ring.[1] The complexes are similar to the dis-symmetric biphenyls reported previously.[2]

In the present communication, a new type of axially-chiral cobalt(III)-tren [tren = tris(2-aminoethyl)amine] complex is reported. When a β-diketone-type ligand, (**1**) or (**2**), co-ordinates to a cobalt(III)-tren complex ion, the 2-methylnaphthalene ring should be forced to adopt an orientation almost perpendicular to the co-ordination plane and not be able to

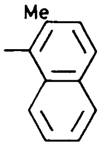


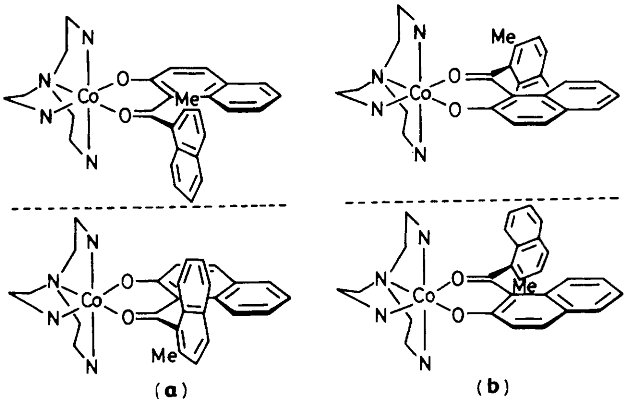
(1)



(2)

R =





(a) (b)

rotate around the pivotal bond (indicated by a thick line). The effective C_s symmetry of the cobalt(III)-tren part disappears upon co-ordination of (**1**) or (**2**) and thus a pair of enantiomers is expected for each of two geometrical isomers as shown in (**a**) and (**b**).

The 2-methylnaphthalene ring which determines chirality is located on one side of the six-membered chelate ring of the β-diketone ligand. The situation in these complexes differs from that in the dis-symmetric biaryls and other reported atropisomers in which restricted-rotation axes are along the central axis of molecule. Optically active cobalt(III)-tren complexes containing (**1**) or (**2**) have now been successfully prepared and their c.d. spectra are reported.

Ligands (**1**) and (**2**) were prepared from the reactions of 2-methylnaphthoyl chloride with naphth-2-ol or 3,5-dimethylphenol, respectively, under Friedel–Crafts conditions. Cobalt(III)-tren complexes of these ligands were prepared in a manner similar to [Co(β-diketone)tren]$^{2+}$ complexes.[3]

The geometrical isomers were isolated by ion exchange chromatography using an SP-Sephadex column and 0.5 M NaCl solution as eluant [the two geometrical isomers were labelled as (**3f**) and (**3s**) or (**4f**) and (**4s**), **f** and **s** denote fractions eluted fast and slow, respectively].

All of the four geometrical isomers were completely resolved by ion exchange chromatography using 0.15 M antimonyl potassium tartrate solution as eluant (the enantiomers eluted first and second were labelled as **a** and **b**, respectively).

Two c.d. spectra of these optically active complexes are shown in Figure 1. The spectra of (**a**) and (**b**) of this series are symmetrical and confirms that (**a**) and (**b**) are enantiomeric. The absorption spectra of these chelates are very complex owing to complicated strong absorptions of the many electronic transitions of the ligands (**1**) and (**2**) and charge transfer interactions, making it difficult to assign the electronic transitions. The c.d. spectra of these complexes show several important features. Thus the c.d. peaks of (**3f**)—(**4s**) are similar in position, but random in intensity and sign. The two c.d. peaks are observed in the first absorption region of all the complexes. This variation of c.d. intensities suggests electronic interactions between the d→d* and π→π* transitions [see intense c.d. peak at 23.0 × 10^3 cm^{-1} of (**4s**)].

The (**a**) isomers of (**3f**)—(**4s**) show (+) 18.6—19.3 × 10^3, and 38.9—40 × 10^3 cm^{-1}, and (−) 43.9—44.2 × 10^3 cm^{-1} c.d. components and the (**b**) isomers show almost the inverse peaks. This agreement of signs in the four isomers suggests important information in relation to their absolute configurations.

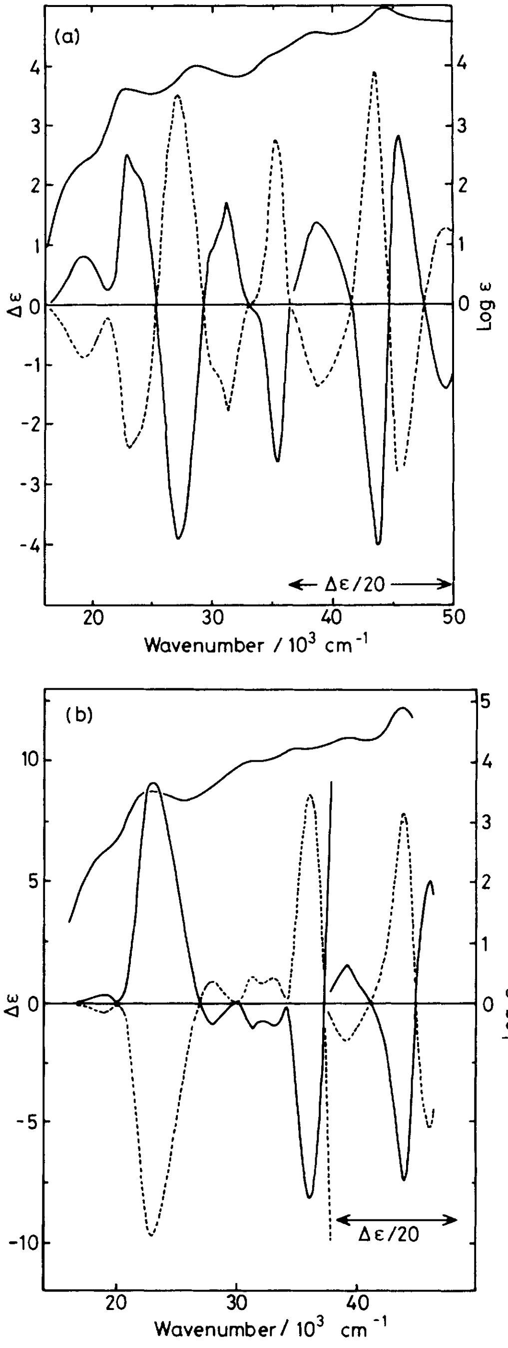


Figure 1. Absorption and c.d. spectra of (a) (**3sa**) (solid line) and (**3sb**) (broken line) and (b) (**4sa**) (solid line) and (**4sb**) (broken line).

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