Geometrical Isomerism arising from Different Orientations of Chelated (–)-Propylenediamine

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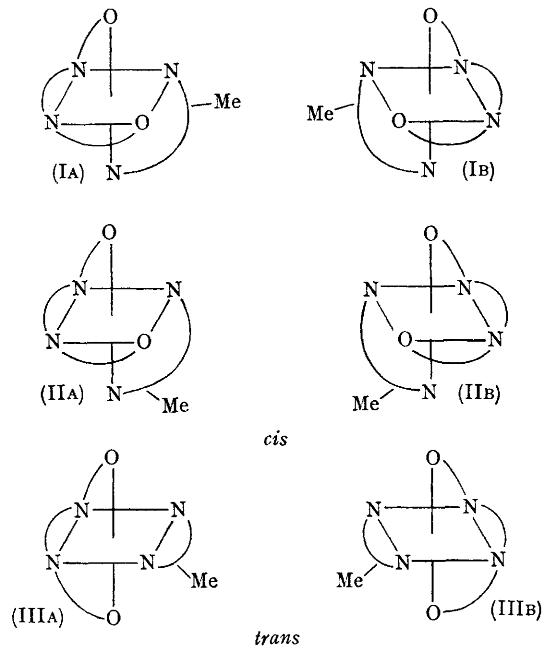
CONFORMATIONAL isomerism in (–)-pn [(–)-pn = (–)-propylenediamine] and mixed (–)-pn–en (en = ethylenediamine) cobalt(III) complexes has been demonstrated by Dwyer and his co-workers.[1] However, it is only recently that evidence for isomers differing only in the relative orientation of chelated (–)-pn has been obtained. Chromatography on cellulose of *trans*-$\{CoCl_2[(-)\text{-pn}]_2\}^+$ showed two green bands, one very much lighter than the other suggesting the presence of the *cis*- (with respect to the methyl groups) as well as the *trans*-isomer.[2] Chromatographic evidence is also available which supports geometric isomerism in $\{Co[(-)\text{-pn}]_3\}^{3+}$ and mixed (–)- and (+)-pn complexes.[3] Although single-crystal structure studies of these two complexes have revealed only one isomer (the isomer of highest symmetry) for each,[4] it should be kept in mind that the single crystals chosen for each study are not necessarily representative of the whole sample.

The separation of geometric isomers which differ only in the relative positioning of a chelated (–)-pn has been achieved through ion-exchange chromatography for the complex $\{Co(edda)\ (-)\text{-pn}]\}^+$ (edda = ethylenediamine-*NN'*-diacetate). Six isomers are expected, as shown. Pairs (I), (II), and (III) are not true optical isomers since both members of a pair possess (−)-pn. Isomer pairs (IA–IIA) and (IB–IIB) differ only in the relative positioning of (−)-pn.

{Co(edda)[(−)-pn]}$^+$ was prepared as previously reported,[5] and the solution of isomers was chromatographed on a strong acid ion-exchange column using 0·1M-NaClO$_4$ as the eluant at a rate of 0·2 ml./min. The descending band separated initially into two components. A component eluting first separated into two bands representing the two *trans*-isomers (IIIA and B) which have been isolated directly from the reaction solution and identified.[5] After six months the remaining small band separated into four closely-spaced but distinct bands, all of about equal intensity.

A more rapid elution was performed in which the *cis*-band was removed in 25 fractions. The middle fractions for each of the four components exhibited relatively constant circular dichroism (c.d.). The c.d. and visible spectra obtained for the four *cis*-isomers were compared with that obtained for *cis*-[Co(edda)(en)]$^+$, previously characterized,[6] which was resolved with (−)-α-bromocamphor-π-sulphonate. The spectra are very similar both in appearance and in position and relative intensity of the bands. The intensity ratios, signs, and relative positions of the bands of the four isomers of *cis*-{Co(edda)[(−)-pn]}$^+$ suggest that the isomers were eluted as pairs (II) and (III). Determination of the order of elution will depend on differentiating between the two possible orientations of the (−)-pn molecule. It is expected that upon isolation of the four isomers that ^{1}H n.m.r. spectroscopy and quantitative evaluation of c.d. data will lead to identification of the individual isomers as was done for the *trans*-isomers.[5]



Isomers expected for {Co(edda)[(−)-pn]}$^+$.

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