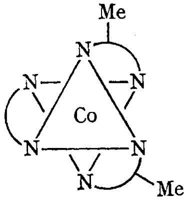
Partial Separation of the Geometric Isomers of D- and L-Ethylenediaminebis[(−)-propylenediamine]cobalt(III) Ions

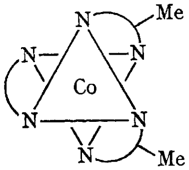
By THOMAS E. MACDERMOTT

(*Chemistry Department A, The Technical University of Denmark, Lyngby, Denmark*)

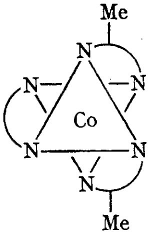
THE ion ethylenediaminebis[(−)-propylenediamine]cobalt(III) may exist in six isomeric forms (if we ignore conformational isomerism). In three of these forms the metal has the D and in three the L absolute configuration. We depict the three L-isomers in (I), (II), and (III), and call (I) *cis*- and (II) and (III) *trans*-isomers (with respect to the two octahedral faces shown in these projections).



(I)



(II)



(III)

Such projections enable the molecules to be systematically named by writing the ligands in a clockwise sequence and placing an asterisk against the ligand whose methyl group is remote from the viewer:†

(I) L-$[\mathrm{Co\,en}(-)\mathrm{pn}_2]^{3+}$

(II) L-$[\mathrm{Co\,en}(-)\mathrm{pn}^*(-)\mathrm{pn}]^{3+}$

(III) L-$[\mathrm{Co\,en}(-)\mathrm{pn}(-)\mathrm{pn}^*]^{3+}$

These formulae immediately distinguish (I) from (II) and (III). The latter two are sequential isomers differing only in the clockwise ordering of their ligands. Both have C_2 symmetry. (I) has C_1 symmetry and will show unique polarisation properties. Separative procedures which depend on such properties should more readily distinguish (I) from (II) and (III), than (II) and (III) from each other.

We have established, using descending chromatography on paper sheets eluted with water-saturated n-butanol containing 2·5% 10N-hydrochloric acid (eluent 1), that the slowest moving component of the mixed (+)- and (−)-propylenediamine-cobalt(III) system[1] (equation 1) corresponds to

$$\mathrm{CoCl_2} + \mathrm{HCl} + 3\ rac\text{-}\mathrm{pn} \xrightarrow[\mathrm{C}]{[\mathrm{O}]} \text{mixture of tris(diamine)cobalt(III) species} \quad (1)$$

(Product 1)

the second slowest band of the eluent 1 separation of the ethylenediamine-(−)-propylenediamine-cobalt(III) system (equation 2). It follows that

$$\mathrm{CoCl_2} + \mathrm{HCl} + \mathrm{en} + 2\ (-)\mathrm{pn} \xrightarrow[\mathrm{C}]{[\mathrm{O}]} \text{mixture of tris(diamine)cobalt(III) species} \quad (2)$$

(Product 2)

there is no tris(propylenediamine)cobalt(III) species in the slowest band of this latter separation. Therefore our previous identification[2] of the four components into which this band separates on elution with water-saturated n-butanol containing 10% of concentrated perchloric acid, must be partly in error.

The fastest moving component in this last separation was identified[2] as D-$[\mathrm{Co}(-)\text{-}\mathrm{pn}_3]^{3+}$ by its relative abundance (about 7% of the amount of L-$[\mathrm{Co}(-)\mathrm{pn}_3]^{3+}$ salts obtained) and by its specific rotation at two wavelengths. We now suggest that these data are also consistent with identification of this fastest component as *cis*-D-$[\mathrm{Co\ en}(-)\mathrm{pn}_2]^{3+}$ ion. Consequently we identify the second most rapidly eluted component in this mixture as a mixture of the two *trans*-D-$[\mathrm{Co\ en}(-)\mathrm{pn}_2]^{3+}$ ions.

The separation of D-$[\mathrm{Co\ en}(-)\mathrm{pn}_2]^{3+}$ into two parts has also been achieved by chromatographing the slowest component from the eluent 1 separation on a paper sheet using n-butanol, pyridine, water, acetic acid (40 : 30 : 20 : 10) as eluent (eluent 2). Once again this mixture separates (during 3 days) into four parts, the fastest and next fastest of

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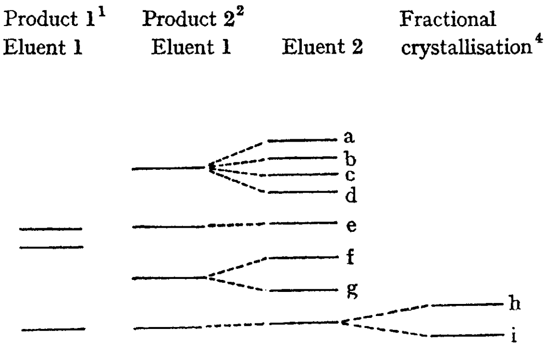
† This procedure is general and can be used to name and count all isomers in tris(bidentate) systems.

which are again proposed to be *cis*- and *trans*-D-[Co en(−)pn$_2$]$^{3+}$ respectively.

Further confirmation comes from the separation of the second fastest moving component of the eluent 1 separation, into two well-defined bands using eluent 2. In this case also, the faster band is about half as intense as the slower—fitting the suggested designation of *cis*- and *trans*-L-[Co-en(−)pn$_2$]$^{3+}$ [(I) and (II) + (III)] respectively. This identification is very convincing since the entire band was previously studied[2] by isolation, elemental analyses, fractional crystallisation, and determination of the en:(−)pn ratio. It is not unreasonable that the eluent which partly separates the L-isomer into geometric components should also succeed with the corresponding D-isomer.



(a) (±)-[Co en$_3$]$^{3+}$; (b) D-[Co en$_2$(−)pn]$^{3+}$; (c) *trans*-D-[Co en(−)pn$_2$]$^{3+}$; (d) *cis*-D-[Co en(−)pn$_2$]$^{3+}$; (e) D-[Co(−)-pn$_3$]$^{3+}$ + L-[Co en$_2$(−)pn]$^{3+}$; (f) *trans*-L-[Co en(−)pn$_2$]$^{3+}$; (g) *cis*-L-[Co en$_2$(−)pn]$^{3+}$; (h) *cis*-L-[Co(−)pn$_3$]$^{3+}$; (i) *trans*-L-[Co(−)pn$_3$]$^{3+}$.

Finally we conclude that the third fastest component from the initial eluent 1 separation is a mixture of D-[Co(−)pn$_3$]$^{3+}$ and L-[Co en$_2$-(−)pn]$^{3+}$. No separation is achieved by elution with eluent 2. However this does not create a real problem since D-[Co(−)pn$_3$]$^{3+}$ may be obtained easily[2] from the mixture of D- and L-[Co(−)pn$_3$]$^{3+}$. Also in the reaction wherein en:(−)pn = 2:1, the ratio of D-[Co(−)pn$_3$]$^{3+}$: L-[Co en$_2$(−)pn]$^{3+}$ is only 1:99.

Here again[3,4] is an indication that the relative abundance of geometric isomers (methyl position) in propylenediamine complexes is governed only by statistics and that free enthalpy does not vary much from one such isomer to another. Such a situation is implicit in the conformational model outlined by Bailar and Corey.[5]

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[1] F. P. Dwyer, A. M. Sargeson, and B. L. James, *J. Amer. Chem. Soc.*, 1964, **86**, 590.

[2] F. P. Dwyer, T. E. MacDermott, and A. M. Sargeson, *J. Amer. Chem. Soc.*, 1963, **85**, 2913.

[3] J. I. Legg, *Chem. Comm.*, 1967, 675.

[4] T. E. MacDermott, *Inorg. Chim. Acta*, to be published.

[5] J. C. Bailar and E. J. Corey, *J. Amer. Chem. Soc.*, 1959, **81**, 2620.