Inorganica Chimica Acta, 23 (1977) 95–96

The Tris-(R)-(–)-Propylenediamine Complexes of Rhodium(III)

J. A. HEARSON, S. F. MASON, and J. W. WOOD
Chemistry Department, King's College, Strand, London WC2R 2LS, U.K.

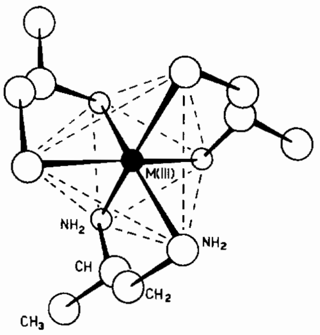
Received October 4, 1976

The reaction between (R)-(–)-propylenediamine and aqueous rhodium trichloride gives 62% of the lel-*isomer and 38% of the* ob-*form of* $[Rh(R\text{-}pn)_3]^{3+}$, *measured by circular dichroism spectroscopy.*

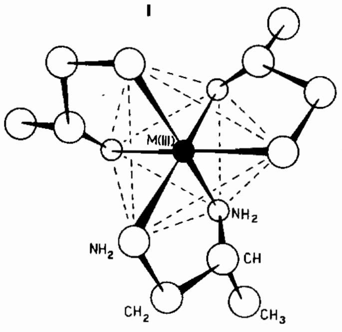
Introduction

Early descriptions [1, 2] of the circular dichroism (CD) spectrum of the tris-(R)-(–)-propylenediamine complex of rhodium(III) are poorly concordant and both are at variance with a subsequent report [3] of that CD spectrum. In our previous work [1] on this complex it was assumed that the coordination of the chiral diamine to rhodium(III) is substantially stereospecific and, from the known absolute configuration [4] of (R)-(–)-propylenediamine, that the thermodynamically more stable *lel*-isomer [5], $\Delta(\lambda\lambda\lambda)$-$[Rh(R\text{-}pn)_3]^{3+}$, is the principal product. On account of the quasi-equatorial preference of the methyl group, (R)-(–)-propylenediamine chelate rings are restricted to the λ-conformation, in which the N····N direction and the C–C bond form a segment of a left-handed helix. If the chelate rings of a $[M(R\text{-}pn)_3]^{n+}$ complex form a right-handed three-bladed propellor, viewed along the direction of the C_3 three-fold rotational symmetry axis of the complex, the C–C bond of each chelate ring is parallel, or nearly so, to the C_3 axis, giving the *lel*-isomer [5], specified as $\Delta(\lambda\lambda\lambda)$ (I). On the other hand, if the three chelate rings present the appearance of a left-handed propellor, the C–C bond of each ring is obliquely inclined with respect to the C_3 axis, giving the thermodynamically less-stable *ob*-isomer [5], characterised as $\Lambda(\lambda\lambda\lambda)$ (II).

The discrepencies between the CD spectra reported [1–3] suggest that significant amounts of the *ob*-isomer are formed in addition to the principal *lel*-isomer in preparations of $[Rh(R\text{-}pn)_3]^{3+}$, and that the two isomers were fractionated to differing degrees in the several preparations. Accordingly the previous work [1–3] has been repeated and extended to an estimation of the relative abundance of the two isomers formed in the reaction of (R)-(–)-propylenediamine with rhodium(III).



I



II

Experimental

Isomers of $[Rh(R\text{-}pn)_3]Cl_3$. The mixture of isomers was prepared as previously described [1–3]. (R)-(–)-Propylenediamine [6] (3 ml) was added to a solution of rhodium trichloride (2 g) in water (4 ml) and the mixture was heated on the steam bath until colourless (2 hr). The mixture of $[Rh(R\text{-}pn)_3]Cl_3$ isomers formed was precipitated by the addition of ethanol and the absorption and CD spectrum of the isomer mixture was recorded (Figure). The mixture was divided into two parts, one being converted into the iodide salt and fractionally crystallised [3], while the other was transformed into the chloride (+)-tartrate salt and similarly fractionally crystallised. The progress of each resolution was followed by CD spectroscopy, the limiting CD spectra being those recorded (Figure).

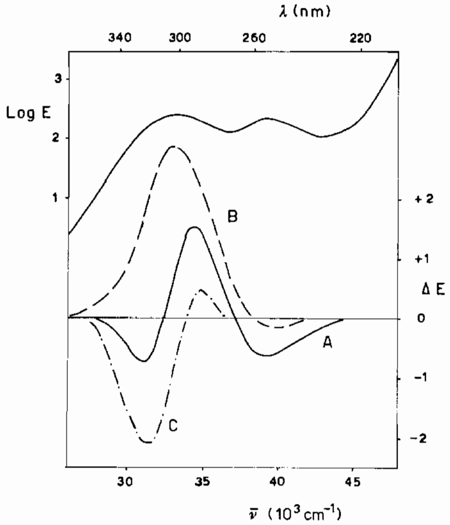


Figure 1. The absorption spectrum (upper curve) and circular dichroism spectra (lower curves) of (A) the mixture of isomers resulting from the reaction of (R)-(−)-propylenediamine with rhodium trichloride, (B) the *ob*-form, Λ(λλλ)-(−)-[Rh(R-pn)$_3$]$^{3+}$, forming the less-soluble chloro (+)-tartrate salt, and (C) the *lel*-form, Δ(λλλ)-(+)-[Rh(R-pn)$_3$]$^{3+}$, forming the less-soluble iodide salt.

Discussion

The molecular structure and absolute configuration of the *lel*-isomer [7], Δ(λλλ)-(−)-[Co(R pn)$_3$]$^{3+}$ (I) and of the *ob*-isomer [8], Λ(λλλ)-(+)-[Co(R-pn)$_3$]$^{3+}$ (II) have been determined by X-ray diffraction, and the CD spectra of these two complexes [9] provide reference standards for the assignment of the stereochemical configuration and the chelate ring conformation of analogous tris-diamine coordination compounds. The isomer (+). [Rh(R-pn)$_3$]$^{3+}$ forming the less soluble iodide salt has a CD spectrum associated with the $^1A_{1g} \rightarrow {}^1T_{1g}$ octahedral transition near 300 nm consisting of a major negative and a minor positive CD band (Figure), similar to the two CD bands arising from the corresponding transition of Δ(λλλ)-(−)-[Co(R-pn)$_3$]$^{3+}$. Accordingly this isomer is a *lel*-form, Δ(λλλ)-(+)-[Rh(R-pn)$_3$]$^{3+}$. The isomer forming the less-soluble chloro (+)-tartrate salt gives a single major positive CD band in the region of the $^1A_{1g} \rightarrow {}^1T_{1g}$ absorption near 300 nm (Figure), resembling the CD band associated with the corresponding transition of Λ(λλλ)-(+)-[Co(R pn)$_3$]$^{3+}$. Thus the second isomer is the *ob*-form, Λ(λλλ)-(−)-[Rh(R-pn)$_3$]$^{3+}$.

The CD spectrum of the mixture of isomers formed in the reaction between (R)-(−)-propylenediamine and rhodium trichloride, when compared with the corresponding spectra of the individual *lel*- and *ob*-forms, indicates that the mixture consists of 62% of the *lel*- and 38% of the *ob*-isomer. If the reaction were under thermodynamic control the ratio of the *lel*- to the *ob*-form is expected to be larger, in the region of the value of 15 found [10] in equilibration studies of the corresponding isomers of [Co(R-pn)$_3$]$^{3+}$. The *lel*/*ob* ratio found in the present work is similar to that measured [11] for the corresponding isomers of [Pt(R-pn)$_3$]$^{4+}$ resulting from the reaction of (R)-(−)-propylenediamine with platinum (IV) in dimethylformamide solution at ambient temperature where 60% of the *lel*-form and 40% of the *ob*-form are produced. In the [Co(R-pn)$_3$]$^{3+}$ complexes equilibration between the *lel*- and *ob*-isomers is mediated by traces of cobalt(II), which is labile to substitution, whereas platinum(II) complexes are more robust and do not catalyse the interconversion of the *lel*- and *ob*-forms of [Pt(R-pn)$_3$]$^{4+}$. It has been pointed out [12] that the [Rh(R-pn)$_3$]$^{3+}$ and [Ir(R-pn)$_3$]$^{3+}$ complexes are expected to resemble their platinum(IV) analogues in giving *lel*/*ob* ratios governed by kinetic rather than thermodynamic factors, since rhodium(II) and iridium(II) are not readily accessible and are probably inert to substitution.

References

1 A. J. McCaffery, S. F. Mason and R. E. Ballard, *J. Chem. Soc.*, 2883 (1965).

2 J. H. Dunlop, R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 3160 (1964).

3 S. K. Hall and B. E. Douglas, *Inorg. Chem.*, *7*, 533 (1968).

4 H. Reihlen, E. Weinbrenner and G. V. Hessling, *Annalen*, *494*, 143 (1932).

5 E. J. Corey and J. C. Bailar, *J. Am. Chem. Soc.*, *81*, 2620 (1959).

6 F. P. Dwyer, F. L. Garvan and A. Shulman, *J. Am. Chem. Soc.*, *81*, 290 (1959).

7 H. Iwasaki and Y. Saito, *Bull. Chem. Soc. Japan*, *39*, 92 (1966).

8 R. Kuroda and Y. Saito, *Acta Cryst.*, *B30*, 2126 (1974).

9 A. J. McCaffery, S. F. Mason, B. J. Norman and A. M. Sargeson, *J. Chem. Soc. A*, 1304 (1968).

10 F. P. Dwyer, T. E. MacDermott and A. M. Sargeson, *J. Am. Chem. Soc.*, *85*, 2913 (1963).

11 F. P. Dwyer and A. M. Sargeson, *J. Am. Chem. Soc.*, *81*, 5272 (1959).

12 A. M. Sargeson in "Chelating Agents and Metal Chelates", eds. F. P. Dwyer and D. P. Mellor, Academic Press, New York and London, 1964, p. 202.