# Structural Disorder in the Geometric Isomers of L-Tris{(−)propylenediamine}cobalt(III) Salts

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Single-crystal and *X*-ray powder data are used to show that salts of the complex ions *cis*- and *trans*-L-tris[(−)-propylenediamine]cobalt(III) fall into two classes with regard to disorder of the complex ions. In the first class typified by the dithionate and tris(malonato)-chromate(III) salts, the geometric isomers are indistinguishable since the cations are disordered giving rise to an average $D_3$ symmetry. In the second class typified by the bromide salt, the *cis*-isomer has an ordered ($C_3$ symmetry) structure. In this case the lattice does not have space to accommodate the disordered cation or the *trans*-isomer. The *trans*-isomer does not crystallise but forms an amorphous glass.

A survey of nine salts revealed none in which the *trans*-isomer had an ordered arrangement and it was, therefore, impossible directly to prove its existence by *X*-ray structure analysis.

DWYER and his co-workers[1] have demonstrated conformational isomerism in {(—)-pn}cobalt(III) complexes [(—)-pn = (—)-propylenediamine]. They were unable to prove the existence of the geometric *cis*- and *trans*-isomers shown in the Figure.

A crystal-structure analysis by Iwasaki and Saito[2] of the compound L-[Co{(—)-pn}$_3$]Br$_3$ prepared by a different method demonstrated the existence of the *cis*-isomer only. More recently MacDermott[3] has claimed to have separated both isomers as their bromides. Two solid phases appear when solutions of chromatographically pure L-[Co{(—)-pn}$_3$]Cl$_3$ are treated with an excess of concentrated hydrobromic acid; a crystalline phase of composition [Co{(—)-pn}$_3$]Br$_3$ asserted to be the same as Iwasaki and Saito's salt and an amorphous phase of composition [Co{(—)-pn}$_3$]Br$_3$,2H$_2$O. These phases were obtained with yields in the ratio 1 : 3 in accordance with the expected statistical distribution of the *cis*- and *trans*-isomers. MacDermott converted

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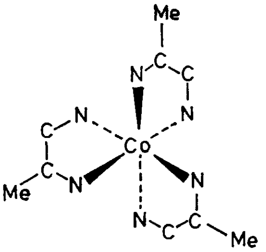
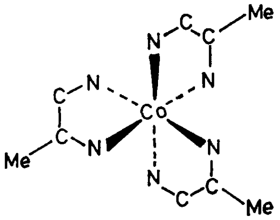
[1] F. P. Dwyer, F. L. Garvin, and A. Shulman, *J. Amer. Chem. Soc.*, 1959, **81**, 290; F. P. Dwyer, T. E. MacDermott, and A. M. Sargeson, *ibid.*, 1963, **85**, 2913; F. P. Dwyer, A. M. Sargeson, and L. B. James, *ibid.*, 1964, **86**, 590.

[2] H. Iwasaki and Y. Saito, *Bull. Chem. Soc. Japan*, 1966, **39**, 92.

[3] T. E. MacDermott, *Inorg. Chem. Acta*, 1968, **2**, 81.

both phases to the dithionate salts, $[Co\{(-)\text{-}pn\}_3]_2(S_2O_6)_3,3H_2O$ which he claimed could be distinguished by their *X*-ray powder patterns and i.r. spectra.


*cis*


*trans*

It seemed important to confirm this separation unambiguously and to this end we planned a single-crystal *X*-ray structure analysis of the *trans*-dithionate salt. Dr. MacDermott kindly made his samples available to us. The *X*-ray powder patterns of these dithionate salts obtained by MacDermott[3] contain the same major lines, but differed slightly in their relative intensities. We found their single-crystal photographs to be identical (*hk*0, 0*kl*, 1*kl* reciprocal levels; unit-cell data in Table 1). The large unit-cell sizes prohibited ready structure analysis and the photographs showed heavy streaking between reflections in the [001] direction. A survey was undertaken for more suitable salts. The following salts also gave very similar powder patterns for the *cis*- and *trans*-isomers: tris(oxalato)metallates (metal = Al, Cr, Co), tris(malonato)chromate, cobaltinitrite, tetraphenylborate, and thiosulphate. Other salts, namely the sulphates and phosphates, behaved in a similar manner to the bromide salts. The *cis*-salts in the latter cases gave *X*-ray powder patterns with many distinct lines, while the *trans*-salts gave no lines at all.

An *X*-ray structure analysis[4] of the compound $(-)\text{-}[Co\{(-)\text{-}pn\}_3](+)_{589}[Cr(malonate)_3],3H_2O$, prepared from *trans*$(-)\text{-}[Co\{(-)\text{-}pn\}_3]Br_3,2H_2O$ shows that the cobalt cation resided on a crystal site of 32 ($D_3$) symmetry. The *cis*-cation has symmetry 3 ($C_3$) while the *trans*-cation has only approximate three-fold symmetry and no overall symmetry. Both *cis*- and *trans*-cations become equivalent however when statistically disordered in the crystal on 32 symmetry sites. This result demonstrates how one class of the salts may give rise to very similar *X*-ray patterns from the two geometric isomers. In the case of the dithionates the space-group $P4_122$ (Table 1) does not require disorder of the above type by space-group symmetry considerations as is the case with the $[Cr(malonate)_3]^{3-}$ salt. Such disorder is still possible if the larger volume of the disordered cation is permitted by crystal packing.

Alternatively it appears that the *trans*-cation can interfere with the crystal packing and an amorphous glass results with a structure which only grossly resembles that of the *cis*-compound. We have re-examined the structure of *cis*$(-)\text{-}[Co\{(-)\text{-}pn\}_3]Br_3$ using the published *X*-ray single-crystal intensity data.[2] A Fourier map phased with the published atomic coordinates shows no evidence of disorder, no electron density was found at the predicted *trans*-methyl site. Least-squares refinement of the structure with half methyl carbon atoms at each of the six possible sites was undertaken. The occupancy factor at the original (*cis*) methyl site converged at 1·07, that at the potentially disordered (*trans*) site converged at 0·06. The overall *R* factor dropped from the originally reported value of 0·100 to 0·077 in this full matrix refinement. Furthermore the substituted disordered methyl group makes three close contacts to N and C atoms of other complex ions in the range 2·5 to 3·0 Å. Van der Waals' radii data[5] suggest that the lower limit for these values is 3·2 to 3·4 Å making them physically impossible. The *trans*-complex ion or the disordered *cis*- or *trans*-complex ions are thus unable to crystallise in the lattice of the *cis*-complex. This provides the physical basis for MacDermott's separation of the isomers. The *X*-ray powder pattern of MacDermott's *cis*-L-$[Co\{(-)\text{-}pn\}]Br_3$ sample (Table 2) is in good agreement with the pattern

TABLE 1

Single-crystal *X*-ray data for L-$[Co\{(-)\text{-}pn\}_3]$ salts

| Anion | Br[a] | $(+)_{589}$ Cr-(malonate)$_3$[b] | $S_2O_6^{2-}$ | $S_2O_3^{2-}$ |
|---|---|---|---|---|
| Space-group | $R6_3$ | $R32$ | $P4_122$ | $P4_122$ |
| Crystal class | Hexagonal | | Tetragonal | |
| *a* | 11·08 | 16·12 | 9·69 | 9·39 Å |
| *c* | 8·59 | 10·07 | 48·18 | 43·65 Å |
| *U* | 913 | 2265 | 4523 | 3849 Å$^3$ |
| $D_m$ | 1·91 | 1·52 | 1·63 | 1·59 |
| *Z* | 2 | 3 | 4 | 4 |
| $D_c$ | 1·90 | 1·53 | 1·64 | 1·60 |
| *M* | 520·6 | 693·6 | 1115·1 | 917·7 |

[a] From ref. 2. [b] From ref. 4. Formulae of the salts are L-$[Co\{(-)\text{-}pn\}_3]Br_3$, L-$[Co\{(-)\text{-}pn\}_3][Cr(mal)_3],3H_2O$, L-$[Co\{(-)\text{-}pn\}_3][S_2O_6]_3,4H_2O$, and L-$[Co\{(-)\text{-}pn\}_3][S_2O_3]_3,H_2O$. The number of water molecules in the last two salts has been deduced by best fit of $D_m$ and $D_c$.

TABLE 2

*X*-Ray *d*-spacings of L-$[Co\{(-)\text{-}pn\}]$

| Salt | Spacings (Å) |
|---|---|
| *cis*-L-$[Co\{(-)\text{-}pn\}_3]Br_3$ | 9·66s, 4·73w, 4·37m, 4·29w, 3·98w, 3·69s, 3·37s, 2·98s, 2·65w, 2·56w, 2·48w, 2·40w, 2·27m, 2·10m, 2·00w, 1·89m, 1·85w, 1·56m |
| *trans*-L-$[Co\{(-)\text{-}pn\}_3]Br_3,2H_2O$ | 9·61b, 3·85b, 3·44b |
| *cis*-L-$[Co\{(-)\text{-}pn\}_3]$ sulphate[a] | 5·45m, 4·88s, 4·06s, 3·66m, 3·19 m-w, 2·71m, 2·63w |
| *cis*- and *trans*-L-$[Co\{(-)\text{-}pn\}_3][Co(NO_2)_6]$[a] | 5·39m, 5·02s, 4·71s, 3·22m, 2·80m, 2·45m, 1·85s, 1·77s |
| *cis*- and *trans*-L-$[Co\{(-)\text{-}pn\}_3][BPh_4]$[a] | 4·30s, 3·52m, 3·07m, 1·84s, 1·76s |
| *cis*- and *trans*-L-$[Co\{(-)\text{-}pn\}_3]$ $[Al(oxalate)_3]$ | 5·18s, 4·74s, 4·31w, 4·11m, 3·89m, 3·64w, 3·37s, 3·14w, 2·75m, 2·62w, 2·52w, 2·38s, 2·31m, 2·12w, 2·06w |

[a] Strongest lines only; b = broad, s = strong, m = medium, and w = weak intensity.

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[4] K. R. Butler and M. R. Snow, *Chem. Comm.*, 1971, 550.

[5] A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.

predicted from the single-crystal data of Iwasaki and Saito.[2] Only two very broad lines appear in the pattern of the *trans*-sample and these are close to positions of strong lines in the *cis*-sample. The glassy *trans*-structure may therefore have some overall resemblance to the crystalline *cis*-structure.

In conclusion it appears unlikely that an ordered *trans*-isomer structure will be found, the combination of a high pseudo-symmetry $C_3$ with no symmetry overall gives rise to the possibility of entropy gain by disorder of the cation alone or by irregular packing of the whole structure (glass). In this context it is impossible to directly prove the existence of the *trans*-isomer by *X*-ray structure analysis since the disordered cations of the *cis*- and *trans*-isomers are indistinguishable.

## EXPERIMENTAL

The following salts were prepared using analytically pure *cis*-L-$[Co\{(-)\text{-pn}\}_3]Br$ and *trans*-L-$[Co\{(-)\text{-pn}\}_3]Br_3,2H_2O$. The scale of the preparations was too small for analysis. The *cis*-salts were prepared in similar manner to the *trans*-salts.

*Sulphate Salts.*—The bromides were passed down an anion-exchange resin (Deacidite FF) in the sulphate form and eluted with distilled water. The eluant was tested for bromide ion and the complex sulphate was crystallised by evaporation over calcium chloride; *cis*-salt: large hexagonal plates and some needle crystals; *trans*-salt: glassy material. The powder pattern shows no Bragg lines.

*Phosphate Salts.*—The bromides were converted into the phosphates with silver phosphate following the method of Chang *et al.*:[6] *cis*-salt: large needles; *trans*-salt: glassy material. The powder pattern shows no Bragg lines. Silver phosphate was prepared by the method of Baxter and Jones.[7]

*Salts of the Complex Anions* $[M(\text{oxalate})_3]^{3-}$, M = Al, Cr, Co.—A solution of the bromide salt (0·5 mg/0·5 ml) was layered on a solution of $K_3[Al(\text{oxalate})_3]$ of equal concentration. Crystals grew at the solution interface (interfacial growth). Both *cis*- and *trans*-isomers of all anions gave insoluble microcrystals.

*Tris(malonato)chromate*(III) *Salts.*—The same method as employed for the oxalato-anions was used. Both *cis*- and *trans*-isomers gave long needle crystals; $K_3[Cr(\text{malonate})_3]$,-$3H_2O$ was prepared by the method of Chang.[8]

*Cobaltinitrite, Tetraphenylborate, and Thiosulphate Salts.*—These salts were prepared by interfacial growth using the reagents $Na_3[Co(NO_2)_6]$, $NaBPh_4$, and $Na_2S_2O_3$ respectively. The *cis*- and *trans*-isomers of the first two salts gave microcrystals. The *cis*-thiosulphate salt formed small needles, the *trans* formed large tabular crystals. The *X*-ray powder patterns were identical for each set of salts.

*X*-Ray powder patterns were recorded using a Nonius general-purpose camera (radius = 28·65 mm) with Co-$K_\alpha$ radiation filtered through iron foil. The films were uncalibrated. Weissenberg and Precession cameras were used to obtain the single-crystal data. (Mo-$K_\alpha$, Zr filter, $\lambda$ Mo-$K_\alpha$ = 0·7107 Å or Cu-$K_\alpha$, Ni filter, $\lambda$ Cu-$K_\alpha$ = 1·542 Å).

Computer programs of the CRYST system described previously[9] were run on the CDC 6400 computer at the University of Adelaide.

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[8] J. C. Chang, *J. Inorg. Nuclear Chem.*, 1968, **30**, 945.

[9] In K. R. Butler and M. R. Snow, *J. Chem. Soc.* (*A*), 1971, 565, reference 22.