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Geometric Isomers of Laevo-tris((-)propylenediamine)cobalt(III) Ion

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The cis *and* trans *isomers of* $L[Co(-)pn_3]^{3+}$ *(pn = propylenediamine) have been separated as the chloride and bromide salts. The halide salts of* trans-L-$[Co(-)pn_3]^{3+}$ *are isolated only as amorphous glasses while the* cis *isomer forms nicely crystalline salts. The two isomers form very similar crystalline dithionates which can be distinguished by X-ray powder studies and infra-red spectra. The n.m.r., u.v.-visible and circular dichroism spectra for these two isomers are indistinguishable.*

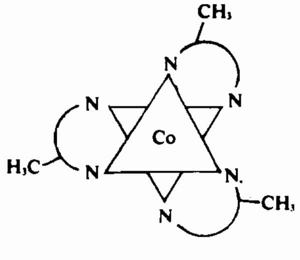
Introduction

It is well known that the introduction of a set of asymmetric bidentate ligands into an octahedral metal complex greatly increases the number of possible isomers. In the most general case the ligands may be different chemical species, they may contain an asymmetric centre, they may be capable of forming two distinct ring conformations upon chelation and finally the two donor sites in each may be distinguishable. Such a system gives rise to optical isomerism, position isomerism, geometric isomerism, and conformational isomerism and there are 2^{10} possible isomers.[1]

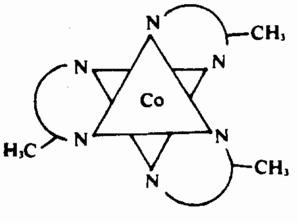
In the case of octahedral complexes containing propylenediamine the conformational isomerism is completely controlled by the optical isomerism of the ligand. The methyl group will always be equatorial with respect to the metal-ligand ring to which it is attached.[2] The optical isomerism of the ligand can also be completely controlled since it can be easily resolved[3] and the stable optical isomers may be studied independently. The optical isomerism of the metal can be studied in detail since the internal diastereoisomers can be separated either by chromatography[4] or fractional crystallisation.[3] Studies of the type outlined above have revealed that the optical asymmetry of the ligand not only completely specifies the conformational isomerism of the metal-ligand ring but also partially specifies the optical isomerism of the metal. This is in agreement with predictions of the only energy model which has so far been set up[2] to account for such effects in these systems.

Now this model effectively discounts the possibility of the attached methyl groups controlling, in any significant way, the Free Energy of the system provided they remain always in equatorial configurations. Within this same limitation, then, we can say that the occurrence of position isomers and geometric isomers in propylenediamine complexes will not be specified by the optical isomerism of either the metal or the ligand. The relative abundance of such isomers will be governed by statistical considerations (Entropy) alone.

The simplest possible octahedral complex of propylenediamine is that containing three identical isomers of the base. The ion $[Co(-)pn_3]^{3+}$ has been separated into D and L isomers by fractional crystallization[3] and by paper chromatography.[4] The most abundant isomer, $L[Co(-)pn_3]^{3+}$, is easily isolated and presents the simplest system for the study of the theoretically possible geometric isomerism. There are two such isomers possible and we will call them *cis* and *trans* ((I) and (II) respectively).



(I)



(II)

It is obvious that, while there is only one way to arrange three propylenediamine molecules to get the *cis* isomer, there are three ways of getting the *trans*. Under equilibrium conditions therefore, the ratio of *cis* to *trans* should be 1:3, *i.e.* 75% of the isolated L-$[Co(-)pn_3]^{3+}$ should be the *trans* isomer.

Iwasaki and Saito have carried out an X-ray structure determination[5] on a single crystal of a compound which they describe simply as $[Co(-)pn_3]Br_3$. The crystals they studied contain only *cis*-L$[Co(-)pn_3]Br_3$–I. While the structural study, which includes the determination of the absolute configuration of this isomer, is quite excellent and very important, the conclusion of these authors that "the isomer of highest symmetry is preferred" has no basis in the model discussed above and is not really proven by their work: in the first place the synthetic procedure used by these workers involved the

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(1) This number was estimated by an enlightened form of Herumprobieren which will be discussed elsewhere.

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

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

(4) (a) F. P. Dwyer, T. E. Mac Dermott, and A. M. Sargeson, *J. Am. Chem. Soc.*, *85*, 2613 (1963); (b) F. P. Dwyer, A. M. Sargeson, and L. M. James, *J. Am. Chem. Soc.*, *86*, 590 (1964).

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

reaction between chloropentaamminecobalt(III) ion and (−)propylenediamine. It is not obvious that such a reaction occurs under equilibrium conditions. Secondly the isolation of D$[Co(-)pn_3]^{3+}$ from an equilibrium mixture in seven percent yield[3,4] has been achieved. It so happens that Iwasaki and Saito's procedure involving the preparation as the chloride, precipitation as the bromide and slow recrystallisation of the bromide from aqueous solution will remove any D isomer formed in the original reaction. However it is unreasonable to expect that the theoretically predominating *trans*-L$[Co(-)pn_3]^{3+}$ would also disappear during this process. Thirdly as Legg[6] has pointed out, the single crystals chosen for this study are not necessarily representative of the whole sample. On the other hand single-crystal work involves repeated sampling which would scarcely overlook the presence of two distinct crystal types. Furthermore, since Iwasaki and Saito show that molecules of the *cis* isomer are required to have a three-fold symmetry by the space group to which the bromide belongs, it follows that the bromide of the *trans* isomer must belong to a different space group with a predictably different crystalline habitat.

From these considerations we were led into a closer study of L$[Co(-)pn_3]Br_3$. We were careful to use a true equilibrium mixture of D and L$[Co(-)pn_3]^{3+}$ and to separate the D isomer by known methods.[3,4a] We then carried out the following study of the L isomer.

Results and Discussion

Tris((−)propylenediamine)cobalt(III) chloride was synthesized by the method described by Dwyer and Garvan[3] and D$[Co(-)pn_3]Cl_3$ was separated either by paper chromatography[4] or fractional crystallisation.[3] When an aqueous solution of chromatographically pure L$[Co(-)pn_3]Cl_3$ and LiCl is allowed to evaporate slowly it deposits some needles but much of the compound remains in an aqueous syrup (addition of HBr to this syrup causes the slow deposition of a non-crystalline glass, apparently the *trans* bromide described below).

When chromatographically pure L$[Co(-)pn_3]Cl_3$ is treated in concentrated aqueous solution with excess concentrated hydrobromic acid the bromide precipitates almost quantitatively. When this product is allowed to crystallize slowly from aqueous solution during several weeks large needles grow for some time and then an amorphous glass forms (X-ray evidence). The needles can be separated by hand and recrystallized in the same way to give very pure large single crystals which are shown by analyses to be anhydrous $[Co(-)pn_3]Br_3$ (Table I). Slow evaporation of an aqueous solution of the amorphous material gives amorphous hemi-spheres which grow slowly from the floor of the crystallizing vessel. No crystals are obtained. This "recrystallized" glass appears from analyses to have two moles of water present (Table I). Treatment of a hot aqueous solution of this bromide salt with excess potassium iodide gives a granular shining product which, on close inspection under a polarising microscope is seen to consist of non-crystalline half-spheres.

The only crystals formed are the needles described above. They appear to be homogeneous and are undoubtedly the *cis*-$[Co(-)pn_3]Br_3$ whose X-ray structure has been elucidated.[5] The yield of needles from a 1.05-g sample is 0.30 g leaving 0.75 g of the glass. This is a crude measure since the first crop of needles is contaminated with some of the glass and recrystallization gives pure needles but not in quantitative yield. The predicted abundance of 25% for the *cis* isomer is consistent with this observed value if we conclude that the glass contains only the *trans* isomer.

This conclusion immediately explains why the X-ray study never revealed any crstals containing the *trans* isomer. It also explains why Iwasaki and Saito find their crystalline material anhydrous[5] while Smirnoff[7] reports two moles of water in his product.

We have attempted to initiate crystallization of this *trans*-L$[Co(-)pn_3]Br_3 . 2H_2O$ by taking a saturated aqueous solution, diluting it with water (1:1) and dropping in liquid bromine. This causes a yellow-orange product to grow in thin needles from the bromine drops which settle to the bottom of the beaker. When all the bromine has disappeared the mixture is stirred, filtered quickly and washed with ethanol and acetone. This crystalline product gives a completely different X-ray powder pattern from the needles of the *cis* isomer. However analyses reveal that the bromine content is much higher. The yellow crystals appear to contain

Table I. Microanalyses [a]

		C	H	N	Br	S
cis-L$[Co(-)pn_3]Br_3$	Calcd	20.73	5.76	16.12	46.06	
	Found	20.77	5.67	16.08	46.20	
cis-L$[Co(-)pn_3]_2(S_2O_6)_3 . 3H_2O$	Calcd	19.71	6.02	15.33		17.52
	Found	19.64	5.92	15.34		17.62
trans-L$[Co(-)pn_3]Br_3 . 2H_2O$	Calcd	19.39	6.10	15.08	43.09	
	Found	20.06	6.07	15.04	43.20	
trans-L$[Co(-)pn_3]Br_3 . 2HBr$	Calcd	15.81	4.68	12.30	58.56	
	Found	15.57	4.33	12.35	58.66	
trans-L$[Co(-)pn_3]Br_3 . 0.28HBr$	Calcd	19.96	5.54	15.54	48.06	
	Found	19.40	5.47	15.03	46.79	
trans-L$[Co(-)pn_3]_2(S_2O_6)_3 . 3H_2O$	Calcd	19.71	6.02	15.33		17.52
	Found	19.43	5.97	15.10		17.58

[a] Carried out by Preben Hansen, Chemistry Department II, University of Copenhagen.

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(6) J. I. Legg, *Chem. Comm.*, 675 (1967).

(7) A. P. Smirnoff, *Helv. Chim. Acta*, 3, 177 (1920).

$[Co(-)pn_3]Br_3 \cdot 2HBr$ (Table I). By drying overnight at 100°C under reduced pressure most (90%) of the HBr can be removed (Table I). The infrared spectrum of this hydrobromide salt is identical with that of the original glass while these differ in various details from the spectrum of the *cis* isomer (Figure 1 (a) and (b)).

The *cis* and *trans* isomers described above have identical ultraviolet-visible, circular dichroism and nuclear magnetic resonance spectra. They also have identical R_f values in all chromatographic studies carried out so far (*e.g.* when eluted on a paper chromatogram with water-saturated n-butanol containing 2.5% concentrated hydrobromic acid). The only chromatographic distinction is that the *trans* isomer moves as a compact spot while the *cis* isomer spreads to almost double the size.

Spectral differences do occur in the infrared which are shown in Figure 1. For the *cis* isomer shoulders appear on each of the strong NH stretching modes (3055, 3170 cm^{-1}) while for the *trans* these peaks are unsplit. The NH_2 deformation for the *cis* is a sharp singlet at 1580 cm^{-1} with small low-energy shoulders; for the *trans* is a partially resolved triplet at 1550, 1570 and 1590 cm^{-1}. The absorption at 1230 cm^{-1} for the *cis* has an indication of a shoulder at 1232 cm^{-1}. For the *trans* this pair is split, though not well resolved, into a doublet at 1230 and 1245 cm^{-1}.

It is apparent from the above discussion that, if geometric isomers of $L[Co(-)pn_3]^{3+}$ have been separated, their physical properties are extremely similar. However, while this may be very reasonable considering the close similarity of the isomers, it makes such measurements poor means of establishing the fact of the isomer separation. Indeed the most convincing internal proof that a separation has been achieved lies in the very different handling properties of the bromides juxtaposed to the very close resemblance of the dithionates which are readily formed from the bromides.

The *cis* bromide crystallizes easily and is anhydrous. The *trans* bromide is about twice as soluble and does not crystallize but separates as a glass. When a hot concentrated aqueous solution of either of these bromides is mixed with a hot aqueous solution containing excess sodium dithionate and the mixture is allowed to cool, crystals form in both cases and both products conform to the empirical formula $[Co(-)pn_3]_2(S_2O_6)_3 \cdot 3H_2O$ (Table I). X-ray powder patterns are sufficiently similar that one might conclude that the crystals are isomorphous; however, the many real differences are easily seen and prove that these analytically pure crystals are not identical (Figure 2).

In the dithionates as with the bromides infrared spectra (Figure 1 (b) and (c)) show subtle but consistent differences. The *trans* isomer shows slightly higher complexity around 2900, 1250, 1110, 800, 520 and 460 cm^{-1}; and the peaks of the doublets at 990 and 850 cm^{-1} change in relative intensities on going from *cis* to *trans*.

Experimental Section

Infrared spectra were run using KBr vacuum-pressed pellets in a Perkin-Elmer 337 Grating spectrophotometer. Some spectra are shown in Figure 1.

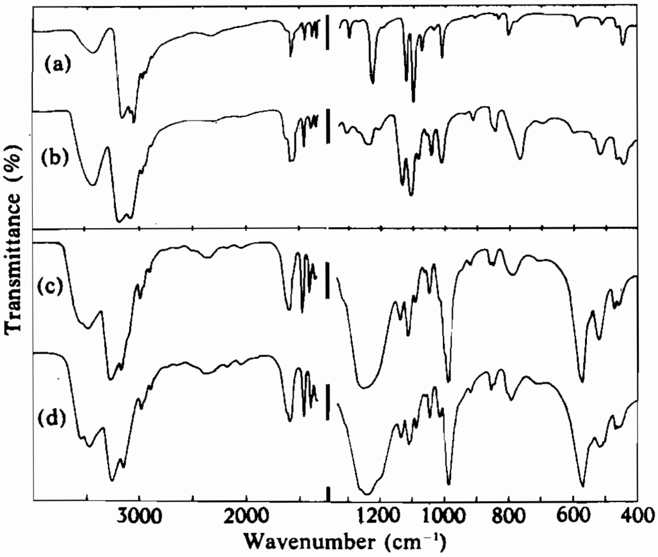

Figure 1. Infra-red spectra of (a) *cis*-$L[Co(-)pn_3]Br_3$. (b) *trans*-$L[Co(-)pn_3]Br_3 \cdot 2H_2O$. (c) *cis*-$L[Co(-)pn_3]_2(S_2O_6)_3 \cdot 3H_2O$. (d) *trans*-$L[Co(-)pn_3]_2(S_2O_6)_3 \cdot 3H_2O$.

N.M.R. spectra were measured in an A60 Varian n.m.r. spectrophotometer. The *cis* and *trans* bromides were measured separately in saturated D_2O solution (the *trans* isomer was about twice as soluble in this solvent as the *cis*). The region of the methyl absorption was closely observed for each isomer and then the solutions were mixed and this region carefully scanned again. No splitting of the methyl doublets could be observed in any spectrum. We conclude that n.m.r. does not distinguish these isomers and that, as far as the methyl groups are concerned, the three metal ligand rings are independent.

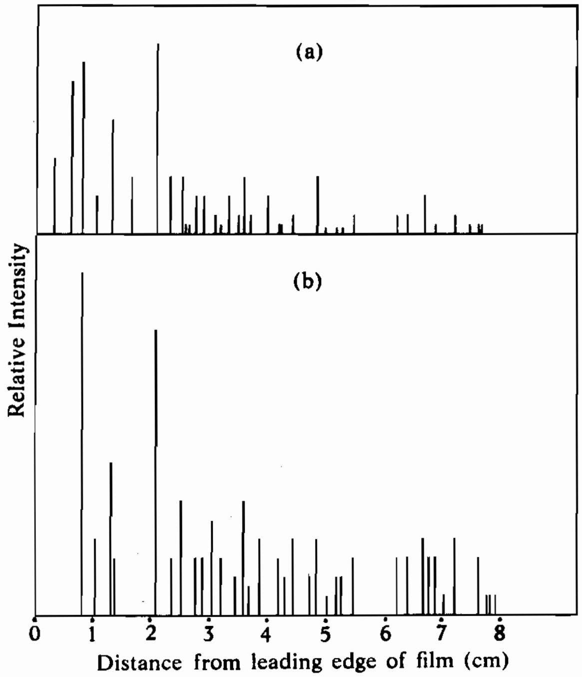

Figure 2. X-ray powder patterns of (a) *cis*-$L[Co(-)pn_3]_2(S_2O_6)_3 \cdot 3H_2O$. (b) *trans*-$L[Co(-)pn_3]_2(S_2O_6)_3 \cdot 3H_2O$.

U.V.-Visible spectra were measured on a Cary 14 spectrophotometer for 5×10^{-3} *M* solution in the visible and 2.5×10^{-5} *M* solution in the ultra-violet regions. The peaks for the two isomers at 467, 339 and 197 mμ are exactly superimposable.

Circular Dichroism spectra were measured on the Jouan Dichographe in 1-cm cells using 5×10^{-3} *M* solutions. Peaks at 345 and 493 mμ are completely superimposable while the peak at 440 mμ is sligthly more intense (~3%) for the *trans* isomer than for the *cis*.

X-ray Powder photographs were taken using a Bradley-type camera. Some of these patterns are represented in Figure 2. While the powder pattern for *cis*-L[Co(–)pn_3]Br_3 is very sharp and clear the pattern for the *trans*-L[Co(–)pn_3]$Br_3 . 2H_2O$ described in this work reveals only very diffuse indications of perhaps two lines. These correspond in position to the two most intense lines of the *cis* isomer and may be due to a slight contamination with this isomer.

In a comparison of the powder patterns of the *cis* and *trans* dithionates it is important to notice that, while most lines are present in both patterns, relative intensities often differ, but not always in the same direction.

Conclusion

We conclude that geometric isomerism in the cobalt-propylenediamine system is probably governed only by statistics. Such a view is supported by our separation of geometric isomers of D and L[Coen(–)pn_2]$^{3+}$ and also by the work of Legg[6] who has found two pairs of isomers of [CoEDDA(–)pn]$^+$ which differ only in the geometric disposition of the (–)propylenediamine. There is a faint chromatographic indication[8] that *trans*-[$CoCl_2$(–)pn_2]$^+$ also exhibits this isomerism, and we have now found and isolated in their predicted relative abundance the geometric isomers of L[Co(–)pn_3]$^{3+}$.

The physical properties generally are extremely similar for the two isomers. The symmetry of the metal atom is essentially the same in both, and theoretical considerations which have ignored this geometric isomerism need not be rejected for this reason.

The proof of the separation of these isomers depends chiefly on the ability of the *cis* bromide to form nice crystals on slow evaporation of an aqueous solution while the *trans* bromide is always deposited in a non crystalline form; while at the same time the dithionates metathetically derived from these bromides are very similar crystalline materials, analytically identical but distinguishable by their X-ray powder patterns and infrared spectra.

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(8) T. E. MacDermott, *Chem. Comm.*, 223 (1968).
(9) C. J. Hawkins and E. Larsen, *Acta Chem. Scand.*, *19*, 1915 (1965).