

The Tris[(±)-1,2-propanediamine]cobalt(III) System*

S. E. HARNUNG, S. KALLESØE, A. M. SARGESON, and C. E. SCHÄFFER

Chemistry Department I (Inorganic Chemistry), University of Copenhagen, The H. C. Ørsted Institute, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark

The twenty-four isomers, $[\text{Co}(\pm)\text{pn}_3]\text{Cl}_3$ (pn = 1,2-propanediamine), constitute two catoptric (enantiomeric) series with the configurations Δ and Λ , respectively. In each of the series there are two methyl group isomers with the chelate-ring conformations le_1e_3 , four with $\text{le}_1\text{e}_2\text{ob}$, four with ob_2le_1 , and two isomers with the conformations ob_3 .

Equilibrium between the isomers can be established at 100°C (charcoal as catalyst, excess of diamine, pH = 7). By ion exchange chromatography (SP-Sephadex; eluent 0.1 M Na_3PO_4) of such an equilibrium mixture of racemic $[\text{Co}(\pm)\text{pn}_3]\text{Cl}_3$ one obtains four racemic fractions which are eluted in the sequence le_1e_3 , $\text{le}_1\text{e}_2\text{ob}$, ob_2le_1 , and ob_3 , the relative amounts being 35.0:41.1:18.0:4.0. Each fraction can be separated (SP-Sephadex; eluent 0.15 M (+)-tartrate) into equal amounts of catoptric forms, and the Δ forms are first eluted. Absorption- and circular dichroism spectra are recorded.

Using the figures mentioned, one can calculate the composition of the equilibrium mixture for an arbitrary ratio of $[(+)\text{pn}]/[(-)\text{pn}]$. Agreement between calculated and measured values is found.

The free energies at 100°C for the inter-conversion between the conformational isomers have been analysed. This leads to a ring-pair relationship model, which in terms of the mutual interaction between the chelate rings accounts for the equilibrium data in a two-parameter model.

By combination of paper and column chromatography some of the methyl group isomers have been partly separated. Such fractions show different ^1H NMR spectra whereas their circular dichroism spectra are virtually identical in the visible-ultraviolet spectral region.

1. INTRODUCTION

$[\text{Co}(\pm)\text{pn}_3]^{3+}$ (pn = 1,2-propanediamine) represents 24 isomers whose properties and relative

stabilities have attracted interest¹⁻³ in connection with optical activity problems⁴ and conformational analyses.⁵⁻⁸ The system has been studied previously¹⁻³ and some of the isomers, or mixtures of isomers, have been separated. In the present paper further separations are described, equilibrium data analysed and circular dichroism data presented.

In order for the reader to appreciate the discussion of the many isomers a nomenclature symbolism is introduced. This symbolism applies to the unsolvated complex ions and allows at the same time the estimation of their relative probabilities which govern an important part of the entropy terms of the isomer equilibria.

Firstly, we note that a coordinated propanediamine molecule has two conformers, the methyl group being either equatorial or axial. Corey and Bailar⁵ asserted that in tris(propanediamine) complexes the former conformer is the more stable one by at least 8 kJ per chelate ring. This means that at most 3% of the methyl groups will be axial at equilibrium. These numbers have not been confirmed experimentally in a quantitative sense but the pronounced stereospecificity which optically active propanediamine shows, particularly in tris(propanediamine) complexes, is a qualitative indication of the correctness of the above assertion. Unless the opposite is explicitly stated we shall ignore the existence of axial methyl groups in the following and base the discussion upon conformations fixed in the stable form with equatorial methyl groups. This will not in any way change the arguments, and will make the text easier to read.

Secondly, all $[\text{Co}(\pm)\text{pn}_3]^{3+}$ isomers have a pseudo three-fold axis which only in the case

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of four of the isomers [*fac* lel_3 (Δ, Δ) and *fac* ob_3 (Δ, Δ), see below] becomes a true three-fold axis.

2. A NOMENCLATURE SYMBOLISM AND AN ENUMERATION OF THE ISOMERS

The cause of the isomerism may be briefly characterized as an interplay of configurational and conformational isomerism,^{8,10} upon which a geometrical isomerism due to the methyl groups is superimposed.

The designation of configuration is, in accordance with IUPAC,^{11,12} based upon the edges of the octahedron spanned by the chelate rings. Two such edges form a pair of skew lines describing a screw which may be right-handed (designated delta) or left-handed (designated lambda). Because of the three-fold axis of the octahedron each of the three possible pairs of edges forms screws of the same handedness and this is used to characterize the configurational chirality Δ or Λ . It may be noted that when one of the edges spanned by a chelate ring is taken together with the three-fold axis, defined by the three edges spanned by the three chelate rings, these also form a pair of skew lines of the same chirality (Fig. 1). This was essentially the basis for Piper's original proposal¹³ of the symbols Δ and Λ for configuration. So, for tris(bidentate) complexes there is agreement between Piper's nomenclature and that of IUPAC.

The designation of conformation is, also in accordance with IUPAC, based upon the principle of a pair of skew lines. For propane-

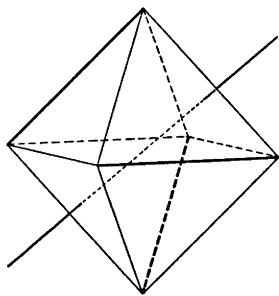


Fig. 1. The configuration Δ . Each pair of chelate rings defines by the edges they span a right-handed pair of skew lines and the same is true if the edge of a chelate ring is taken together with the three-fold axis.

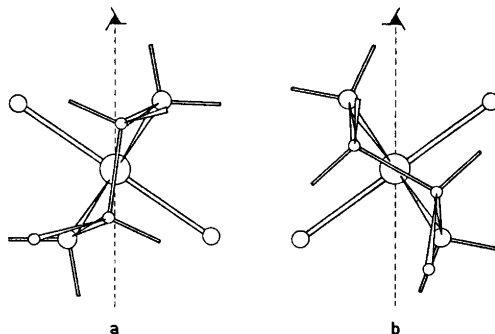


Fig. 2. The conformation λ of the chelate ligand *R*-(-)-1,2-propanediamine. (a) shows a part of a tris complex with the configuration Δ . The diamine connects the corner of the front edge of the octahedron shown in Fig. 1. The C-C bond is nearly parallel to the (pseudo) three-fold axis, which is indicated by the dotted line. (b) shows a part of a tris complex with the configuration Λ . Here the C-C bond of the diamine is oblique relative to the (pseudo) three-fold axis.

diamine one of these lines is defined by the two chelating nitrogen atoms and the other by the two carbon atoms in the chelate ring, and their chirality is designated by the symbols δ or λ (Fig. 2), IUPAC being in agreement with Liehr's original proposal.¹⁴ The absolute chirality of propanediamine is, also according to IUPAC,¹⁵ given by the *R*, *S*, nomenclature proposed by Cahn and Ingold.¹⁶ So (-)-propanediamine is *R*, and when chelated in the stable conformer with the methyl group equatorial, it is λ .

The concepts symbolized by Δ , Λ and δ , λ are invariant under proper rotations but are interchanged under improper rotations. The interplay of these concepts, however, gives rise to a characterization of the chelate ring which is invariant to both proper and improper rotations.¹⁰ This characterization, which is the relevant one when discussing stabilities, will be designated *lel* and *ob* using an extension^{4,9,10} of a nomenclature originally proposed by Corey and Bailar⁵ for characterizing a tris(diamine) complex as whole. Letting, for example, $\lambda(\Delta)$ mean a conformation λ associated with a configuration Δ the diastereoisomeric concepts

$$\begin{aligned} lel & [\equiv \lambda(\Delta) \text{ or } \delta(\Lambda)] \\ ob & [\equiv \delta(\Delta) \text{ or } \lambda(\Lambda)] \end{aligned} \quad (1)$$

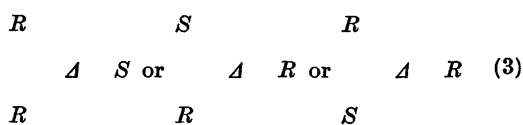
may be taken as the definition of *lel* and *ob*. A tris(diamine) complex $\Delta\lambda_2\delta$ may then alternatively be characterized by Δlel_2ob and the catoptric (enantiometric) complex $\Delta\delta_2\lambda$ by Δlel_2ob , so that together they constitute a *lel_2ob* pair. Corey and Bailar,⁵ who pointed out that the C—C bond in the stable conformer of the (–)-propanediamine chelate rings of $[Co(-)pn_3]^{3+}$ could be either parallel (*lel*) or oblique (*ob*) to the three-fold axis, used the symbols *lel* and *ob* for the isomer pairs which we now call *lel_3* and *ob_3*. These authors also asserted that the *lel_3* system was the energetically favoured one.

It should be emphasized that for a single chelate ring, as for example in $[Co\ pn(NH_3)_4]^{3+}$, the concepts *lel* and *ob* are not defined. Two or three chelate rings are necessary in order to define a kind of (pseudo) three-fold axis. For two chelate rings one has the conformational isomers *lel_2*, *lel ob*, or *ob_2*, and the relative energies of these systems are associated with the ring pair relationships *lel-lel*, *lel-ob*, and *ob-ob*, respectively.

It is useful to consider the configurational plus conformational isomerism by a building-up process. There are two configurations Δ and Λ and two conformations δ and λ for each of the three chelate rings giving altogether $2 \times 2^3 = 16$ possibilities of building-up a complex. Among these possibilities some isomers are represented more than once, the number of times being the statistical weight or relative probability which govern the inner-sphere entropy term for the isomerization reactions. A projection formula¹⁰ for an isomer of the type



may, for example, be written as



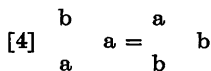
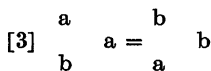
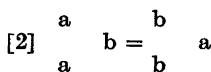
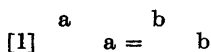
The situation is equivalent for the Δlel_2ob and for both Δob_2lel and Δob_2lel all of which obtain a statistical weight of 3, thus accounting for 12 of the 16 possibilities stated above. Adding the two *lel_3* isomers and the two *ob_3* isomers of weight 1 we have 8 isomers of *lel_3ob_3* type ($i+j=3$).

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The projections shown in eqn. (3) have been performed along the (pseudo) three-fold axis of the molecule, onto the plane perpendicular to this axis and containing the central ion. Provided that the symbols (Δ, Λ), (δ, λ), and (*R, S*) are manipulated properly, the projection formulas have the symmetries of the molecules themselves.¹⁰ A proper manipulation means that the symbols should be left invariant by proper rotations and be permuted within each associated enantiomeric pair of symbols by improper rotations.

We reiterate that as far as the configurational-conformational isomerism is concerned the complexes may be classified as *lel_3*, *lel_2ob*, *ob_2lel*, and *ob_3*, each class comprising a Δ and a Λ isomer. This classification applies to all tris(bidentate) complexes for which two conformations are possible for each chelate ring. For systems containing three propanediamine or three *trans*-1,2-cyclohexanediamine chelate rings bound to chromium(III),¹⁷ cobalt(III),¹⁸ rhodium(III),¹⁹ and iridium(III),²⁰ the isomers can be separated, and can be had individually in solution. For tris(ethylenediamine) systems all the isomers of a given configuration are in equilibrium in solution and the individual isomers can only be isolated in certain cases where they become trapped in solids.²¹

Within each of the four classes just mentioned the tris(propanediamine) systems have an additional methyl group isomerism which may now be discussed by the same kind of building-up procedure. Each methyl groups may be either above (a) or below (b) the projection plane containing the central ion giving $2^3=8$ possibilities which at once reduce to 4 because the configurational-conformational isomers do not distinguish between up and down



(4)

ob_2lel isomers could hardly be detected chromatographically even when the heterogeneous system had been allowed to react during a week. Apparently the charcoal lost activity in time. Even though we tried the charcoals which were commercially available to us and used different propanediamine buffers between pH 7 and 10 we were not able to find conditions under which equilibrium could be established at 25°C. We tested the different charcoals for their ability to racemize the optically active tris(ethylenediamine)cobalt(III) ions and found that the time required for 90 % racemization under equivalent conditions varied by several orders of magnitude. A particular charcoal delivered from Struer's in Copenhagen called "Medicinsk A" was chosen as the best one available to us. This charcoal was used also in an attempt to equilibrate a lel_2ob fraction and it transpired that the partial equilibrium with ob_2lel was almost established before lel_2 was present in significant amounts. It can be concluded that an equilibrium with respect to the propanediamine molecules already bound to a cobalt(III) ion is much faster than one which requires exchange with propanediamine molecules from the outer solution.

4. RESULTS AND DISCUSSION

a. Separation of isomers

The racemic mixture of $[Co(\pm)pn_3]Cl_3$ was separated into four fractions using either paper

chromatography or a Sephadex column (0.2 M sodium phosphate eluent). For both methods the ratio of the first moving fraction (lel_2) to the second one (lel_2ob) was the same, whereas the ratios of the last two fractions differed. This difference arose from the fact that portion of the ob_2lel fraction was resolved into Δ and Λ forms on the paper and that one (or some) of the Δ isomers coincided with the ob_2 fraction. However, for the separation on Sephadex all four fractions were optically inactive. These four fractions are $\Delta, \Delta lel_2$; $\Delta, \Delta lel_2ob$; $\Delta, \Delta ob_2lel$; and $\Delta, \Delta ob_2$ (eluted in this sequence) and we shall show later that these assignments are correct. The slowest moving fraction from the separation on paper was then eluted on the Sephadex column with phosphate and an optically active Δob_2lel fraction and the inactive ob_2 fraction were separated.

The four fractions obtained from the Sephadex separation of the racemic mixture were then resolved into Δ (first eluted) and Λ configurations using Sephadex with (+)-tartrate as eluent. The circular dichroism (CD) of the resolved forms of the fastest and the slowest moving racemic fraction coincided with those obtained from the lel_2 and ob_2 forms of $[Co(-)pn_3]Cl_3$ and $[Co(+)pn_3]Cl_3$. Moreover,

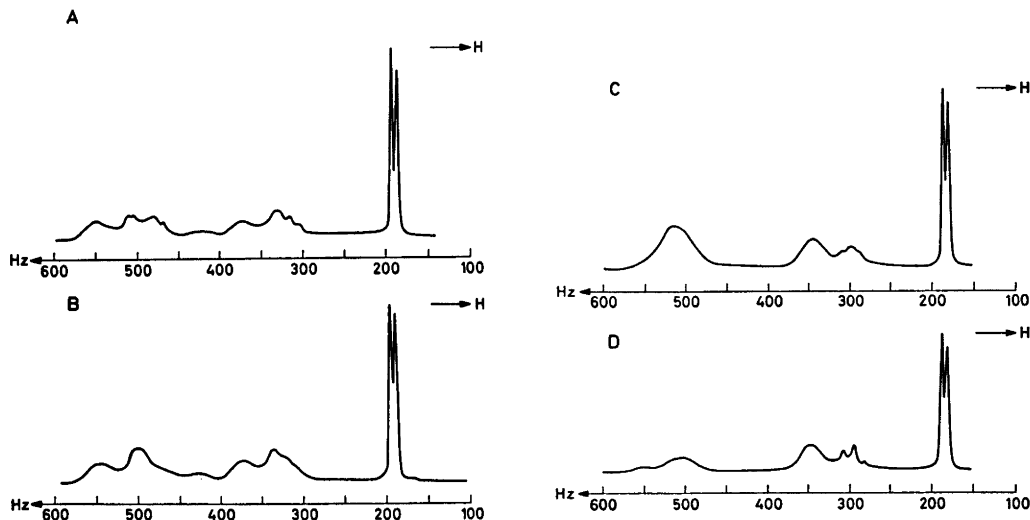


Fig. 3. A, B: 100 MHz 1H NMR spectra of Δob_2lel isomers in $D_2O + D_2SO_4$ with TMS as external standard. A. The fraction last eluted (paper). B. The fraction first eluted (paper). C, D: 100 MHz 1H NMR spectra of racemic lel_2 isomers in $D_2O + D_2SO_4$ with TMS as external standard. C. The fraction last eluted (column). D. The fraction first eluted (column).

the Δob_2lel fraction from the column experiments was separated completely on paper into two Δ fractions (first eluted: last eluted $\sim 2:1$) with virtually identical CD curves in the visible and ultraviolet region but different 1H NMR spectra. These fractions are therefore either a mixture of three methyl isomers and one methyl isomer or two pairs of methyl isomers. The 1H NMR spectra, Fig. 3a, b, indicate that the first possibility is the more likely one.

All the Δ forms of ob_2lel run together with the fastest moving Δ fraction on paper and the methyl isomers for the Δ fraction could not be separated by these eluents. Similarly the methyl isomers of the lel_2ob fraction were not resolved.

Racemic lel_3 was eluted on Sephadex columns (~ 7 m) with 0.1 M sodium phosphate until a minimum was observed in the sorbed fraction. The first half and the last third of the fraction on either side of the minimum were collected and recovered. The 1H NMR spectra for these fractions are given in Fig. 3c,d. They show marked differences in the region of the NH (~ 5 ppm) absorption although there is little difference in the CH_2CH_2 (~ 3.5 ppm) and CH_3 (~ 2 ppm) absorptions. This result might be anticipated because the chemical shift differences for protons attached to saturated N atoms are usually much larger than those for saturated C atoms. In addition the two fractions showed a large difference in behaviour toward concentrated hydrobromic acid. The faster (less abundant) moving fraction was almost insoluble in concentrated hydrobromic acid but the slower moving fraction did not crystallize at all. On the basis of this evidence and the second experiment (see below) on an active lel_3 fraction we assert that the first fraction which crystallizes is the *fac* isomer and the second, more abundant, fraction is the *mer* isomer.

Δlel_3 was also eluted on Sephadex columns (~ 11 m) with 0.1 M sodium phosphate and two fractions were collected on either side of the observed minimum the less abundant fraction ($\sim 1/4$ of total) gave a crystallized bromide also here and its properties coincide with those of the isomer described previously²⁴ as Δfac - $[Co(-)pn_3]^3+$. The more abundant form is the *mer* isomer and is difficult if not impossible

to crystallize as the bromide in keeping with previous observations.^{25,26}

The *fac* and *mer* ob_3 isomer have been separated ion exchange chromatographically by Yamasaki *et al.*²⁷

b. Energy differences between lel_2ob_j isomers

$[Co(-)pn_3]^{3+}$ consists of the configurational-conformational isomers Δlel_3 and Δob_3 . The equilibrium constant $K(ob_3 \rightarrow lel_3)$ for the reaction



was determined by separating the isomers from the equilibrium mixture within the $[Co(-)pn_3]^{3+}$ system and simply measuring the relative amounts of Δob_3 and Δlel_3 . The same constant was also determined from the equilibrium mixture within $[Co(\pm)pn_3]^{3+}$ but in this case three independent constants were measured at 100°C (Table 1)

$$K(ob_3 \rightarrow lel_3) = \frac{[lel_3]}{[ob_3]} = 8.75$$

$$K(ob_2lel \rightarrow lel_2ob) = \frac{[lel_2ob]}{[ob_2lel]} = \frac{41.1}{18.0} = 2.28 \quad (7)$$

$$K(lel_2ob \rightarrow lel_3) = \frac{[lel_3]}{[lel_2ob]} = \frac{35.0}{41.1} = 0.852$$

where in eqn. (7) each concentration symbol designates the sum of the concentrations of all the methyl group isomers embodied in the symbol. The corresponding standard free energies $\Delta G^\circ = -RT \ln K$ at 100°C are

$$\Delta G^\circ(ob_3 \rightarrow lel_3) = -6.73 \text{ kJ}$$

$$\Delta G^\circ(ob_2lel \rightarrow lel_2ob) = -2.56 \text{ kJ} \quad 373 \text{ K} \quad (8)$$

$$\Delta G^\circ(lel_2ob \rightarrow lel_3) = +0.50 \text{ kJ}$$

These ΔG° values may be corrected for the building-up-statistical inner-sphere entropy terms $T\Delta S'$ mentioned in section 2

$$T\Delta S'(ob_3 \rightarrow lel_3) = 0$$

$$T\Delta S'(ob_2lel \rightarrow lel_2ob) = 0 \quad 373 \text{ K} \quad (9)$$

$$T\Delta S'(lel_2ob \rightarrow lel_3) = RT \ln (1/3) = -3.41 \text{ kJ}$$

to obtain a kind of ΔH° term which we shall designate $\Delta H'^\circ = \Delta G^\circ + T\Delta S'^\circ$

$$\Delta H'^\circ(ob_3 \rightarrow lel_3) = -6.73 \text{ kJ}$$

$$\Delta H'^\circ(ob_2lel \rightarrow lel_2ob) = -2.56 \text{ kJ} \quad 373 \text{ K} \quad (10)$$

$$\Delta H'^\circ(lel_2ob \rightarrow lel_3) = -2.91 \text{ kJ}$$

Table 1. Equilibrium isomer distribution at 100°C.

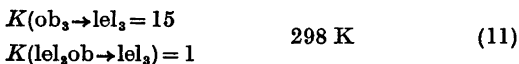
Isomer	Experimental composition %			Calculated composition % $F = 1.90^d$
	$F = 1.00^a$	$F = 1.90^b$	$F = 1.90^c$	
Δlel_3	35.0	37.9	37.9	38.0
Δlel_3		5.6	5.5	5.5
$\Delta\text{lel}_2\text{ob}$		23.6	22.4	23.5
$\Delta\text{lel}_2\text{ob}$	41.1	12.4	11.9	12.4
$\Delta\text{ob}_2\text{lel}$		5.1	5.1	5.4
$\Delta\text{ob}_2\text{lel}$	18.0	10.2	10.0	10.3
Δob_3		—	—	0.6
Δob_3	4.0	3.9	4.0	4.3
Total	98.1	98.7	96.8	100.0

^a The isomer distribution of an equilibrium mixture made by refluxing a mixture of $[\text{Co}(\pm)\text{pn}_3]^{3+}:(\pm)\text{pn} = 1.00:1.50$ at 100°C as described in section 2. Approximately 1 mmol cobalt was placed on the column. ^b By use of the ratios of the β_3 constants of eqn. (23) as determined in experiment (a) one can calculate the composition required for the initial mixture in order that F of eqn. (25) is equal to 1.90 when equilibrium is established. Such calculation makes use of the ratio $B = [(\pm)\text{pn}]_b / [(-)\text{pn}]_b$ of complex bound diamine. With $[(+)\text{pn}]_b = 3([\Delta(+)\text{pn}_3] + [\Delta(+)\text{pn}_3]) + 2([\Delta(+)\text{pn}_2(-)\text{pn}] + [\Delta(+)\text{pn}_2(-)\text{pn}]) + ([\Delta(-)\text{pn}_2(+)\text{pn}] + [\Delta(-)\text{pn}_2(+)\text{pn}])$ and an analogous expression for $[(-)\text{pn}]_b$, one obtains

$$B = \frac{3F^3 \left(\frac{\beta_3(\text{ob}_3)}{\beta_3(\text{lel}_3)} + 1 \right) + (2F^2 + F) \left(\frac{\beta_3(\text{lel}_2\text{ob})}{\beta_3(\text{lel}_3)} + \frac{\beta_3(\text{ob}_2\text{lel})}{\beta_3(\text{lel}_3)} \right)}{3 \left(\frac{\beta_3(\text{ob}_3)}{\beta_3(\text{lel}_3)} + 1 \right) + (2F + F^2) \left(\frac{\beta_3(\text{lel}_2\text{ob})}{\beta_3(\text{lel}_3)} + \frac{\beta_3(\text{ob}_2\text{lel})}{\beta_3(\text{lel}_3)} \right)}$$

The figures in column (b) show the isomer distribution of an equilibrium mixture with the initial composition (cf. section 2) $\Delta[\text{Co}(+)\text{pn}_3]\text{Cl}_3:(\pm)\text{pn}:(-)\text{pn} = 1.00:0.34:1.27$. At equilibrium the diamine ratios are $F = 1.90$ and $B = 2.42$. Approximately 2 mmol cobalt was placed on the column. ^c Equilibrium mixture as described in (b) and in section 2. Approximately 1 mmol cobalt was placed on the column. ^d The calculated composition of an equilibrium mixture with $F = 1.90$. Use has been made of eqns. (24), (26), (28), and (23) together with the results in column (a).

Equilibrium data have previously been determined at 25°C for the first and the third of the reactions of eqns. (7)–(10). These data, valid at 25°C, are ^a



and from them the corresponding ΔH° values can be derived

$$\begin{aligned} \Delta H^\circ(\text{ob}_3 \rightarrow \text{lel}_3) &= -6.77 \text{ kJ} \\ \Delta H^\circ(\text{lel}_2\text{ob} \rightarrow \text{lel}_3) &= -2.75 \text{ kJ} \end{aligned} \quad 298 \text{ K} \quad (12)$$

It is gratifying that the ΔH° values at the two different temperatures [eqns. (10) and (12)] are the same within the experimental uncertainty.

Under the assumption that the full ΔH° values, including all inner-sphere and outer-sphere entropy terms, are also temperature-independent, the relation

$$\Delta H^\circ = R \frac{T_1 T_2}{T_2 - T_1} \ln \frac{K(T_2)}{K(T_1)} \quad (13)$$

is valid and gives, using eqns. (7) and (11)

$$\begin{aligned} \Delta H^\circ(\text{ob}_3 \rightarrow \text{lel}_3) &= -6.6 \text{ kJ} \\ \Delta H^\circ(\text{lel}_2\text{ob} \rightarrow \text{lel}_3) &= -2.0 \text{ kJ} \end{aligned} \quad (14)$$

These ΔH° values are probably not very good, but still it is interesting that they compare so well with the corresponding ΔH° values of eqns. (10) and (12), because this comparison does provide some support to the proposition that the building-up-statistical inner-sphere entropy terms are the essential entropy terms for these reactions in solution.

c. ΔH° values and the ring pair relationship model

The ΔH° data may be used to establish a model based upon the ring pair relationships

lel-lel, lel-ob, and ob-ob, mentioned in section 2. In the ob_3 complexes there are three ob-ob relationships and in the lel_3 complexes three lel-lel relationships. One may now with reference to the practice in conformational analysis,^{5,6} try to interpret $\Delta H^\circ(ob_3 \rightarrow lel_3)$ as the energy required to transform 3 (ob-ob) relationships into 3 (lel-lel) relationships so that from the first equation of eqn. (10) one obtains

$$\Delta H^\circ(ob-ob \rightarrow lel-lel) = -2.24 \text{ kJ per ring pair} \quad (15)$$

A similar comparison of the ob_2lel and lel_2ob isomers can be made. These isomers have two lel-ob relationships in common and differ only in that ob_2lel has an additional ob-ob relationship and lel_2ob and additional lel-lel relationship. So the second equation of (10) may be rewritten

$$\Delta H^\circ(ob-ob \rightarrow lel-lel) = -2.56 \text{ kJ per ring pair} \quad (16)$$

Eqns. (15) and (16), which are completely independent experimentally as well as with respect to the pair relationship model, indicate an approximate additivity of the enthalpies of pair relationship changes. Using this additivity the last equation of eqn. (10) gives

$$\Delta H^\circ(lel-ob \rightarrow lel-lel) = -1.45 \text{ kJ} \quad (17)$$

and when this is combined with the average of eqns. (15) and (16):

$$\Delta H^\circ(ob-ob \rightarrow lel-lel) = -2.40 \text{ kJ} \quad (18)$$

one obtains

$$\Delta H^\circ(ob-ob \rightarrow lel-ob) = -0.95 \text{ kJ} \quad (19)$$

Comparison of eqns. (17) and (19) shows that it costs 50 % more to transform a lel-lel relationship into a lel-ob one, than to transform a lel-ob relationship into an ob-ob one.

It should be emphasized that this result, obtained from the tris(propanediamine)cobalt(III) complexes, may not apply to the corresponding *cis*-bis(propanediamine) complexes. For example, optically active propanediamine has only a small stereospecific effect²⁸ in the oxalatobis(propanediamine)cobalt(III) system.

d. Application of the pair relationship model to the tris(ethylenediamine)cobalt(III) system

The assumption of equatorial methyl groups being completely dominant in the tris(propanediamine)cobalt(III) system makes a comparison with the tris(ethylenediamine) system possible. This assumption, which is necessary, not in order to characterize all the $(Co \text{ } pn_3)^{3+}$ -isomers as lel_1ob_j but in order to give these symbols their literal meaning, implies that the enthalpy-like concepts ΔH° of the pair relationship model really refer to such pair relationship changes. Therefore this model can be applied to the tris(ethylenediamine) system as well, this system being governed by the same statistical factors as the tris(propanediamine) system as far as lel_1ob_j isomers are concerned (*cf.* section 2). Using the data from eqns. (15) and (17) one calculates the equilibrium ratios

$$lel_3:lel_2ob:ob_2lel:ob_3 = 34.9:41.1:20.0:4.0 \quad (20)$$

applicable at 100°C. A different way of evaluating the pair relationship model, which is a two parameter model, is to compare the results of eqn. (20) with the experimental results in column 1 of Table 1, which contain three independent experimental quantities.

The data of eqn. (11) can also be used with the pair relationship model, and give the equilibrium ratios

$$lel_3:lel_2ob:ob_2lel:ob_3 = 40.4:40.4:16.4:2.7 \quad (21)$$

applicable at 25°C.

If one assumes that both the steric interactions involving the equatorial methyl groups and the interactions with the solvent do not influence the relative stability of the lel_1ob_j isomers then the results expressed in eqns. (20) and (21) are applicable also to the tris(ethylenediamine)cobalt(III) system. In this case, however, the ratios will refer to the different lel_1ob_j isomers, which for a given configuration about the cobalt ion exist together in equilibrium. These possible consequences of the experimental equilibrium results for the $[Co(\pm)pn_3]^{3+}$ system on the conformational equilibria of $[Co \text{ } en_3]^{3+}$ have previously been discussed by Hawkins.²⁹

The data of eqns. (20) and (21), when used for the $[Co \text{ } en_3]^{3+}$ system, agrees well with

some recent NMR data.^{20,21} The NMR data allow the determination of the mol fraction of the diamine which exist as lel in the solution. This quantity may be calculated from eqns. (20) and (21) as 0.69, valid at 100°C, and 0.73, valid at 25°C, to be compared with the experimental quantities, 0.79 ± 0.03, valid at 93°C and 0.75 ± 0.07, valid at 17°C. For the [Rh en₃]³⁺ system the NMR values are 0.71 ± 0.02 at 93°C and 0.68 ± 0.05 at 17°C. Our calculated values for the mol fraction of the lel decreases with increasing temperature as a consequence of the fact that all reactions involving an increase in lel conformers have negative Δ*H*^o values [cf. eqns. (10), (12), and (14)].

5. THE IDENTIFICATION OF THE ISOMERS

Till now we have assumed that the isomers were already identified. They were in fact identified mainly on the basis of the equilibrium experiments as we shall now see.

The complexity of each of the isomers of [Co(±)pn₃]³⁺ can be described by the constant

$$\beta_3 = \frac{[\text{Co pn}_3]^{3+}}{[\text{Co}^{3+}][\text{pn}]^3} \quad (22)$$

which is of almost the same magnitude as β₃ for [Co en₃]³⁺, *i.e.*²² about 10³⁰ mol⁻³ l³. The constants of eqn. (22) may be classified according to lel₁ob₁

$$\begin{aligned} \beta_3(\text{lel}_3) &= \frac{[\Delta\text{lel}_3]}{[\text{Co}^{3+}][(-)\text{pn}]^3} = \frac{[\Delta\text{lel}_3]}{[\text{Co}^{3+}][(+)\text{pn}]^3} \\ \beta_3(\text{lel}_2\text{ob}) &= \frac{[\Delta\text{lel}_2\text{ob}]}{[\text{Co}^{3+}][(-)\text{pn}]^2[(+)\text{pn}]} = \\ &= \frac{[\Delta\text{lel}_2\text{ob}]}{[\text{Co}^{3+}][(+)\text{pn}]^2[(-)\text{pn}]} \\ \beta_3(\text{ob}_2\text{lel}) &= \frac{[\Delta\text{ob}_2\text{lel}]}{[\text{Co}^{3+}][(+)\text{pn}]^2[(-)\text{pn}]} = \\ &= \frac{[\Delta\text{ob}_2\text{lel}]}{[\text{Co}^{3+}][(-)\text{pn}]^2[(+)\text{pn}]} \\ \beta_3(\text{ob}_3) &= \frac{[\Delta\text{ob}_3]}{[\text{Co}^{3+}][(+)\text{pn}]^3} = \frac{[\Delta\text{ob}_3]}{[\text{Co}^{3+}][(-)\text{pn}]^3} \end{aligned} \quad (23)$$

where, as in eqn. (7), the [lel₁ob₁] symbols embrace all possible methyl group isomers.

From eqn. (23) [see also eqn. (7)] the following relationships can be derived

$$\frac{[\Delta\text{lel}_3]}{[\Delta\text{ob}_3]} = \frac{[\Delta\text{lel}_3]}{[\Delta\text{ob}_3]} = \frac{[\text{lel}_3]}{[\text{ob}_3]} = \frac{\beta_3(\text{lel}_3)}{\beta_3(\text{ob}_3)} = K(\text{ob}_3 \rightarrow \text{lel}_3) \quad (24)$$

$$\frac{[\Delta\text{lel}_2\text{ob}]}{[\Delta\text{ob}_2\text{lel}]} = \frac{[\Delta\text{lel}_2\text{ob}]}{[\Delta\text{ob}_2\text{lel}]} = \frac{[\text{lel}_2\text{ob}]}{[\text{ob}_2\text{lel}]} = \frac{\beta_3(\text{lel}_2\text{ob})}{\beta_3(\text{ob}_2\text{lel})} = K(\text{ob}_2\text{lel} \rightarrow \text{lel}_2\text{ob})$$

Those isomer ratios, not occurring in eqn. (24), depend on the ratio *F* between the (+) and the (-) propanediamine

$$F = \frac{[(+)\text{pn}]}{[(-)\text{pn}]} \quad (25)$$

For example,

$$\frac{[\Delta\text{lel}_3]}{[\Delta\text{lel}_2\text{ob}]} = \frac{\beta_3(\text{lel}_3)}{\beta_3(\text{lel}_2\text{ob})} \frac{[(-)\text{pn}]^2}{[(+)\text{pn}]^2} = K(\text{lel}_2\text{ob} \rightarrow \text{lel}_3) F^{-2} \quad (26)$$

$$\frac{[\Delta\text{lel}_3]}{[\Delta\text{lel}_2\text{ob}]} = \frac{\beta_3(\text{lel}_3)}{\beta_3(\text{lel}_2\text{ob})} \frac{[(+)\text{pn}]^2}{[(-)\text{pn}]^2} = K(\text{lel}_2\text{ob} \rightarrow \text{lel}_3) F^2$$

where for *F* = 1 the two equations of eqn. (26) may be combined to yield

$$\frac{[\Delta\text{lel}_3] + [\Delta\text{lel}_2\text{ob}]}{[\Delta\text{lel}_2\text{ob}] + [\Delta\text{lel}_3]} = \frac{[\text{lel}_3]}{[\text{lel}_2\text{ob}]} = K(\text{lel}_2\text{ob} \rightarrow \text{lel}_3) \quad (27)$$

which is the last equation of eqn. (7), valid only for experiments with racemic diamine, whereas eqn. (24), which corresponds to the two first equations of eqn. (7), is valid independently of *F*.

Further, equilibrium concentration ratios for catoptromers depend on *F* only

$$\frac{[\Delta\text{lel}_3]}{[\Delta\text{lel}_3]} = \frac{[\Delta\text{ob}_3]}{[\Delta\text{ob}_3]} = F^{-3} \quad (28)$$

$$\frac{[\Delta\text{lel}_2\text{ob}]}{[\Delta\text{lel}_2\text{ob}]} = \frac{[\Delta\text{ob}_2\text{lel}]}{[\Delta\text{ob}_2\text{lel}]} = F^{-1}$$

Finally, it is noted that the ratios between the eight lel₁ob₁ isomers depend only on the three constants of eqn. (7), which were determined using racemic diamine, and the ratio *F* which can be fixed experimentally (Table 1).

The relative concentrations of the methyl isomers do not possess any mass action dependence and will within each lel₁ob₁ be constants for a given temperature in a given medium. It is the fact that we do find a mass action dependence in agreement with eqn. (23) and

Table 2. Spectral data of $\Delta[\text{Co}(\text{pn})_3]\text{Cl}_2$. The measurements were carried out on $\Delta\epsilon_{1,3}$, $\Delta\epsilon_{1,2,1}$, $\Delta\epsilon_{2,1}$, $\Delta\epsilon_{2,3}$, and $\Delta\epsilon_{3,2}$ in concentrations as stated in the legend to Fig. 4. The molar decadic extinction coefficient, ϵ , is given for the maxima of the ABS-spectra and correspondingly $\Delta\epsilon = \epsilon_l - \epsilon_r$, is given for the extrema of the CD-spectra.

$\Delta\epsilon_{1,3}$			$\Delta\epsilon_{1,2,1}$			$\Delta\epsilon_{2,1}$			$\Delta\epsilon_{2,3}$			
ABS kK (ϵ)	CD kK ($\Delta\epsilon$)	ABS kK (ϵ)	CD kK ($\Delta\epsilon$)	ABS kK (ϵ)	CD kK ($\Delta\epsilon$)	ABS kK (ϵ)	CD kK ($\Delta\epsilon$)	ABS kK (ϵ)	CD kK ($\Delta\epsilon$)	ABS kK (ϵ)	CD kK ($\Delta\epsilon$)	
21.39(100.5)	20.3(-2.66) 22.8(+0.65) 29.0(-0.35)	21.35(94.6)	20.4(-2.25) 23.6(+0.05) 28.4(-0.25)	21.33(89.1)	20.7(-2.34) 25.5(-0.05) 27.8(-0.15)	21.37(90.2)	21.1(-2.49) 26.0(-0.06) 27.1(-0.07) 29.4(+0.04) 31.6(-0.04) 34.7(-0.01) 41.5(-1.7)	29.41(96.0)	46.7(+39)	47.4(26.3 $\times 10^3$)	47.2(+32)	47.0(21.4 $\times 10^3$)
47.5(24.7 $\times 10^3$)				47.2(27.3 $\times 10^3$)			36 (0) 38.4(-0.1) 47.2(+28)					47.4(+21)

the derived eqns. (24), (26), (27), and (28) [Table 1], which shows that the le_1ob_j classification is the correct one for characterizing the chromatographically separated fractions.

Regarding the experimental identification of the le_1ob_j isomers the following can be said. The set of isomers, le_3 and ob_3 , can be recognized by their CD spectra as the same isomers which arise as the only isomers when a pure catoptromer of the amine is used for the experiments [see also eqn. (23)]. Further, within this set the le_3 isomer is here known from the X-ray structure analysis^{33,34} on *fac-Δ(-)*₅₉₉[Co{(R)(-)*pn*}_3 $\lambda\lambda\lambda$]Br₃ and for that matter the ob_3 isomer is also known³⁵ from *fac-Δ(-)*₅₉₉[Co{(S)(+)*pn*}_3 $\delta\delta\delta$]Co(CN)₆·3H₂O but this is a superfluous piece of information from the present point of view. Thus these identifications mean that the le_3 isomers pass through the column with phosphate first, then comes the set of isomers le_2ob , ob_2le_1 in two separate fractions and finally the ob_3 isomers.

The assumption that the second fraction is le_2ob and the third one is ob_2le_1 leads to the whole discussion of section 4. It should, however, be noted that equilibrium experiments by themselves do not distinguish between isomers which contain the same ratio of the catoptric forms of diamine bound in them. For example, the mass action behaviour of Δle_2ob is the same as that of Δob_2le_1 . On the other hand the assumption that the second fraction is ob_2le_1 and the third accordingly le_2ob leads to a complete breakdown of the pair relationship model discussed in section 4c. This is most easily seen by studying the effect that the assumption has on the form of eqns. (15) and (16). Eqn. (15) is derived from the first equation of eqn. (10) and remains unchanged. Eqn. (16) is derived from the second equation of eqn. (10), which now reads

$$\Delta H^\circ(ob_2le_1 \rightarrow le_2ob) = +2.56 \text{ kJ} \quad (29)$$

leading to a changed version of eqn. (16)

$$\Delta H^\circ(ob \rightarrow le-le) = +2.56 \text{ kJ} \quad (30)$$

Even though a quantitatively working additivity model for pair interaction energies could not be expected, it is absurd to make an assumption which does not associate the

relative energies of the le_1ob_j isomers with pair relationships at all. We therefore conclude that our first assumption, that le_2ob precedes ob_2le_1 on the column is correct. It turns out that a series of other properties of the isomers also exhibit a regular behaviour only on this assumption.

It is natural to add here that the le_1ob_j isomers were correctly identified in the original work on their separation,³ the assignments being based upon some of the properties to be described below.

6. PROPERTIES OF THE ISOMERS

Absorption (ABS) and circular dichroism (CD) spectra were recorded in the visible (VIS) and ultraviolet (UV) region. Fig. 4 and Table 2. The four le_1ob_j types of isomers were measured under identical conditions in a medium containing lithium chloride. The only effect of the lithium chloride on the spectra is to enhance the extinctions slightly without shifting the absorption frequencies. It is seen that the net rotational strength under the first cubic spin-allowed absorption band ${}^1A_1(O) \rightarrow {}^1T_1(O)$ at 21–22 kK is negative for the Δ series. Also the residual wing of the transition $A_1(O)A_1-(D_3) \rightarrow T_1(O)A_2(D_3)$ identified on the basis of the assignments in the tris(ethylenediamine)-cobalt(III) ion and observed at 23 kK in the le_3 complex, gradually vanishes through the series $le_3 \rightarrow ob_3$. An apparently opposite effect is noted in the circular dichroism under the ultraviolet absorption band.

Solubility of catoptromers. The least soluble chloride(+)tartrate of [Coen₃]³⁺, [Coptn₃; le_3]³⁺, and [Coptn₃; ob_3]³⁺ are known from the X-ray results³⁴ to be the Δ forms. The catoptromer, which according to the previous investigation gives the least soluble chloride(+)tartrate in the le_2ob set, is also Δ . It must be noted, however, that the ob_2le_1 set has not been resolved in this way, but only on the column.

Outer sphere complexes. Recent investigations³⁵ show that the association constant K of the pair [Co *pn*₃; le_3]³⁺SO₄²⁻ is greater than that of [Co *pn*₃; ob_3]³⁺SO₄²⁻. Our experiments on the elution of these complexes from the Sephadex cation exchange column show that, even though the cation of course is the im-

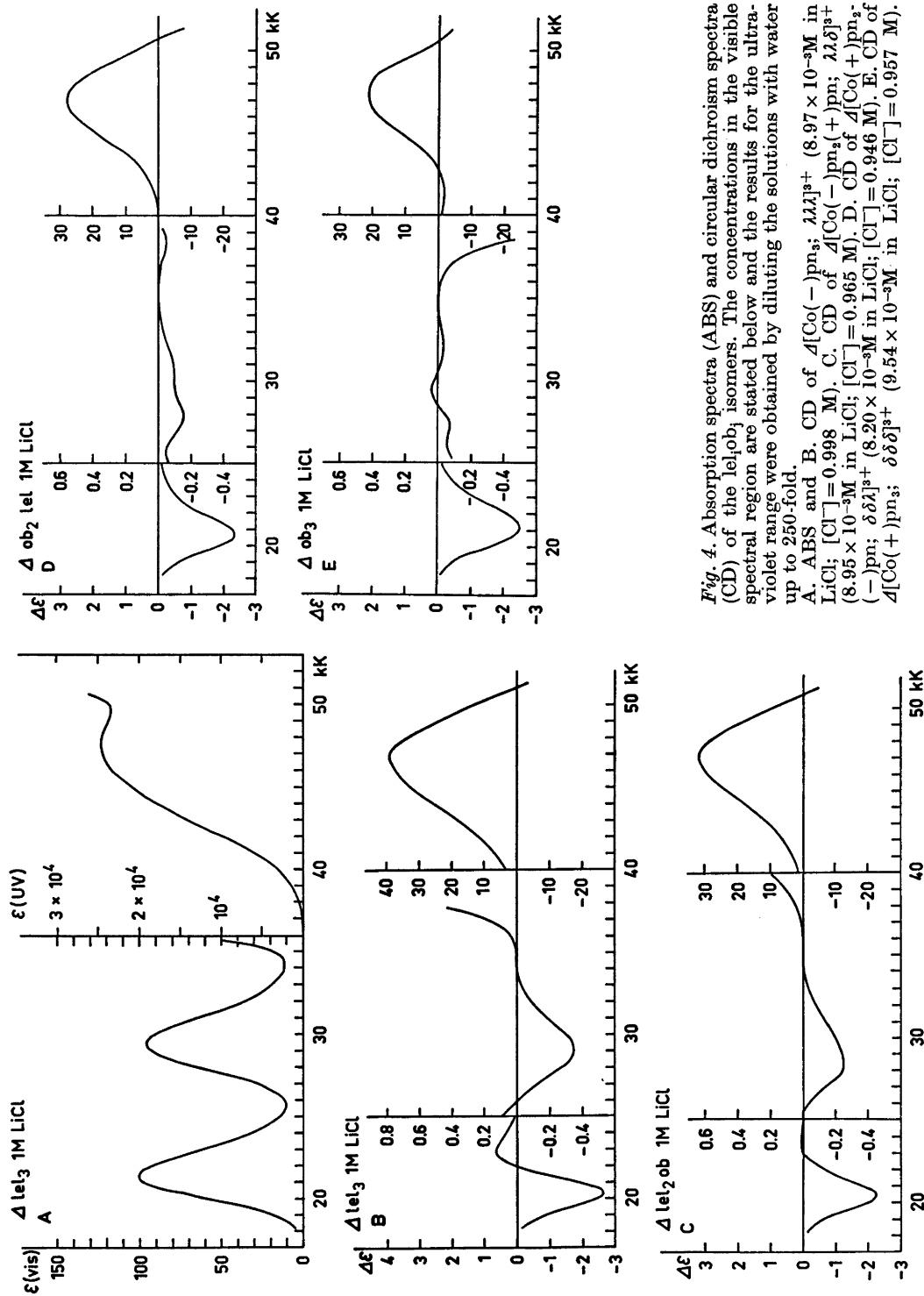


Fig. 4. Absorption spectra (ABS) and circular dichroism spectra (CD) of the leloj isomers. The concentrations in the visible spectral region are stated below and the results for the ultraviolet range were obtained by diluting the solutions with water up to 250-fold.

A. ABS and B. CD of $\Delta[\text{Co}(-)\text{pn}_3; \lambda\lambda]^{3+}$ ($8.97 \times 10^{-3}\text{M}$ in LiCl ; $[\text{Cl}^-] = 0.998\text{M}$). C. CD of $\Delta[\text{Co}(-)\text{pn}_3(+)\text{pn}$; $\lambda\lambda\delta]^{3+}$ ($8.95 \times 10^{-3}\text{M}$ in LiCl ; $[\text{Cl}^-] = 0.965\text{M}$). D. CD of $\Delta[\text{Co}(+)\text{pn}_3(-)\text{pn}$; $\delta\delta\lambda]^{3+}$ ($8.20 \times 10^{-3}\text{M}$ in LiCl ; $[\text{Cl}^-] = 0.946\text{M}$). E. CD of $\Delta[\text{Co}(+)\text{pn}_3; \delta\delta\delta]^{3+}$ ($9.54 \times 10^{-3}\text{M}$ in LiCl ; $[\text{Cl}^-] = 0.957\text{M}$).

portant one for driving the complexes through, the relative elution rates depend predominantly on the anion, and using phosphate the order of elution is $1e_1e_3$, $1e_1ob_3$, $ob_3e_1e_3$, ob_3 . It seems likely that $1e_1e_3$ conformations somehow have a greater affinity to phosphate than do ob_3 conformations in agreement with the facts mentioned for sulphate. This is also supported experimentally through the NMR results^{30,31} on the tris(ethylenediamine) systems of rhodium(III) and cobalt(III), which show that the equilibrium between the $1e_1ob_3$ isomers, which is mobile in the ethylenediamine as opposed to the propanediamine systems, shifts toward a higher mol fraction of $1e_1e_3$ on increasing the phosphate concentration. It has similarly been found³⁵ that $K(\Delta[\text{Co } pn_3; 1e_1e_3]^{3+}(+) \text{-tart}) > K(\Delta[\text{Co } pn_3; 1e_1e_3]^{3+}(+) \text{-tart}) > K(\Delta[\text{Co } pn_3; ob_3]^{3+}(+) \text{-tart}) > K(\Delta[\text{Co } pn_3; ob_3]^{3+}(+) \text{-tart})$. Our experiments on the elution of the catoptromers from the Sephadex cation exchange column using (+)-tartrate also agrees with these association constants since it is a general feature that the Δ configurations are eluted first.

7. CONCLUSIONS

The isomers in the $[\text{Co}(\pm)pn_3]^{3+}$ system have almost the same standard free energies in solution, the difference between the most and the least abundant ones being at 100°C only about 7 kJ/mol which is of the order of magnitude of small van der Waals energies. The same is true of their enthalpy differences. This is in itself understandable since all the truly chemical bonds are the same in all the isomers and no apparent steric hindrances exist when the methyl groups of the coordinated propanediamine molecules are equatorial. However, the relative free energies, as well as enthalpies, vary with the $1e_1ob_3$ -classified isomers in a remarkably regular manner in view of the fact that the solvation processes are involved here as well.

It should be noted that similar regularities also have been found with the mixed tris-diamine cobalt(III) system containing ethylenediamine and (-)-propanediamine² and also with the tris-[(±)-*trans*-1,2-cyclohexanediamine]cobalt(III) system¹⁸ and the tris(propanediamine)chromium(III) system.³⁶

The absolute configuration of the complexes determines the net rotational strength of the magnetically allowed cubic parentage⁴ transition ${}^1A_1(O) \rightarrow {}^1T_1(O)$, the strength being positive for all Δ isomers, in agreement with the results for the tris(ethylenediamine)-cobalt(III) system and the tris[(±)-*trans*-1,2-cyclohexanediamine]-cobalt(III) systems. In a perturbation model this net rotational strength corresponds to the effect of the term of $A_{1u}(O_h)$ symmetry⁴ in a potential expansion and the sign of the net rotational strength to the sign of this term.

The sign of the net rotational strength of the ultraviolet band around 47 kK also depends on the absolute configuration, being positive for the Δ isomers. The $\Delta\epsilon$ values at the main extremum points can in fact be given within the experimental uncertainty by adding a configurational contribution $(\Delta\epsilon)\Delta = +30$ and a conformational contribution $(\Delta\epsilon)\lambda = +3$ where the contributions from the catoptromeric situations, of course, have opposite signs. Such an additivity rule has been reported previously³⁷ but with different numerical values. The present investigation, however, has shown that the circular dichroism spectra of the optically active ob_3 -isomer are in fact different from the previously published data. It is noted that the additivity rule does not apply quite so well to the net rotational strengths.

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