

601. Configurations of Trisdiamine Complexes.

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The absolute configuration of (+)-*trans*-cyclopentane-1,2-diamine is corrected by utilising the optical rotatory dispersion curves of its complex compounds with cobalt(III). Using the principle that the configuration of the most stable isomer of $[M(\text{diamine})_3]^{n+}$ is determined by the absolute configuration of the diamine, the configurations of a number of complexes are determined. By comparison of Cotton effects for related transitions, the configurations of tris-complexes of optically inactive diamines are determined. The results of this method are related to those obtained by other methods.

CONFORMATIONAL analysis of saturated five-membered chelate rings showed¹ that tris-complexes of an optically active diamine have a most stable form (named "1el"). For example, the most stable isomer² of tris-(+)-propylenediaminecobalt(III) cation is (+)- $[\text{Co}(+\text{pn})_3]^{3+}$, which has the D-configuration, the same as that of (+)- $[\text{Co en}_3]^{3+}$,* determined by the anomalous diffraction of X-rays.³ In agreement with this, the Cotton effects shown by corresponding *d-d* transitions have the same sign, as shown in Table I.

The optically active diamines which have been used for stereospecific studies are propylenediamine (pn), butane-2,3-diamine (bn), *trans*-cyclohexane-1,2-diamine (chxn), and *trans*-cyclopentane-1,2-diamine (cptn).

The absolute configuration of (+)-pn is known⁴ from its relation to L-alanine. The absolute configuration of (+)-butane-2,3-diamine being known,⁵ it was predicted¹ that the

* The D-configuration of (+)- $[\text{Co en}_3]^{3+}$ is more rigorously described as $S(\text{C}_3)R(\text{C}_2)$.

¹ Corey and Bailar, *J. Amer. Chem. Soc.*, 1959, **81**, 2620.

² Dwyer, Garvan, and Shulman, *J. Amer. Chem. Soc.*, 1959, **81**, 290.

³ Saito, Nakatsu, Shiro, and Kuroya, *Acta Cryst.*, 1955, **8**, 729.

⁴ Reihlen, Weinbrenner, and Hessling, *Annalen*, 1932, **494**, 143.

⁵ Dickey, Fickett, and Lucas, *J. Amer. Chem. Soc.*, 1952, **74**, 944.

TABLE I.
Circular dichroism of trisdiaminecobalt(III) cations.

| Cation | Band I | | | | Band II | |
|---|--------------------------------|-----------------------------|--------------------------------|-----------------------------|------------------------------|-----------------------------|
| | $({}^1E_g \leftarrow {}^1A_1)$ | | $({}^1A_2 \leftarrow {}^1A_1)$ | | ${}^1E_g \leftarrow {}^1A_1$ | |
| | $\lambda_{\max.}$ | $(\epsilon_1 - \epsilon_d)$ | $\lambda_{\max.}$ | $(\epsilon_1 - \epsilon_d)$ | $\lambda_{\max.}$ | $(\epsilon_1 - \epsilon_d)$ |
| (+)-[Co en ₃] ³⁺ | 493 † | +1.89 | 428 § | -0.17 | 355 § | +0.25 |
| (+)-[Co(+pn) ₃] ³⁺ | 496 † | +1.9 | 441 | -0.53 | 346 | +0.27 |

† Agrees with value from Mathieu (see legend to Fig. 1). § Agrees with value from Mason, *Quart. Rev.*, 1963, **17**, 20.

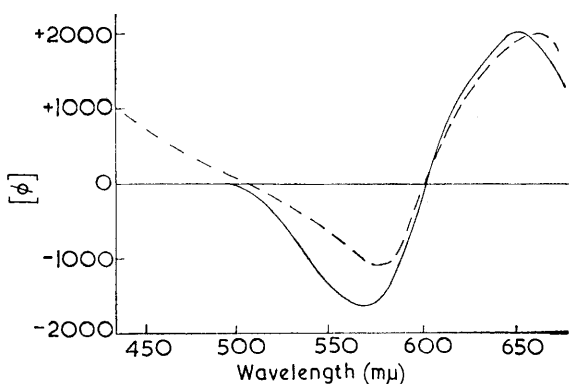
most stable isomer of [Co(+bn)₃]³⁺ should be dextrorotatory at the Na_p line. More fundamentally, it can be predicted from the configuration of (+)-bn that [Co(+bn)₃]³⁺ will have the D-configuration, and so {by analogy with D-(+)-[Co en₃]³⁺} will show a positive Cotton effect for the longest-wavelength transition. This was in fact found⁶ for D-(+)-[Co(+bn)₃]³⁺, which confirms the absolute configuration given for (+)-bn.

The absolute configuration of (+)-*trans*-cyclohexane-1,2-diamine is known from two routes. (a) The most stable isomer of [Co(+chxn)₃]³⁺ is (-)-[Co(+chxn)₃]³⁺ which has

FIG. 1. Rotatory dispersion curves for (-)-*trans*-[Co(-AA)₂Cl₂]Cl.

Full line (-)-*trans*-[Co(-cptn)₂Cl₂]Cl;
Broken line (-)-*trans*-[Co(-pn)₂Cl₂]Cl.

[The results obtained by Mathieu (*J. Chim. phys.*, 1936, **33**, 78) for the rotatory dispersion of (+)-[Co(+pn)₂Cl₂]Cl are in good agreement with the mirror image of the broken curve.]



the D-configuration like D-(+)-[Co(+pn)₃]³⁺, as shown by their extremely similar rotatory dispersion curves.⁷ This shows⁸ that the absolute configuration of (+)-chxn is the same as that of (+)-pn. (b) The stable complex of (-)-*trans*-cyclohexane-1,2-diaminetetraacetic acid (CHXTA) with cobalt(III) is [Co(-CHXTA)]⁻ with a rotatory dispersion curve parallel to that of [Co(-PDTA)]⁻, where PDTA is propylenediaminetetraacetate. It was thus shown⁹ that (-)-chxn ≡ (-)-pn, in agreement with (a).

The absolute configuration of *trans*-cyclopentane-1,2-diamine (cptn) was obtained by an argument¹ resting on the sign of rotation of the cobalt complex. {It was argued that (+)-[Co(-cptn)₃]³⁺ and (+)-[Co en₃]³⁺ had the same configuration.} This is not true; the rotatory dispersion curves¹⁰ of these two cations are enantiomorphous. The true analogue of (+)-[Co en₃]³⁺ or (+)-[Co(+pn)₃]³⁺ is (-)-[Co(+cptn)₃]³⁺; these have exactly similar rotatory dispersion curves, indicating (+)-pn ≡ (+)-cptn. This has been checked by comparing the rotatory dispersion curve of (-)-*trans*-[Co(-pn)₂Cl₂]⁺ with that¹⁰ of (-)-*trans*-[Co(-cptn)₂Cl₂]⁺, as shown in Fig. 1. The asymmetric potentials engendered at the cobalt atoms are of the same sign and so give rise to Cotton effects of the same sign for (-)-pn and (-)-cptn, which therefore have the same configuration. The use of Cotton effects in complexes of cobalt(III) for deductions concerning configurations of ligands is

⁶ Woldbye, Tech. Report, European Research Office, U.S. Army, DA-91-508-EUC-246, 1959.

⁷ Jaeger and Bijkerk, *Proc. Acad. Sci. Amsterdam*, 1937, **40**, 116.

⁸ Gillard and Wilkinson, *J.*, 1964, 1368.

⁹ MacDermott and Sargeson, *Austral. J. Chem.*, 1963, **16**, 335.

¹⁰ Jaeger and Blumendal, *Z. anorg. Chem.*, 1928, **175**, 161.

essentially similar to the early work¹¹ on complexes of amino-acids with copper. Complexes of cobalt(III) are rather better for this purpose, since the stereochemistry and spectroscopic transitions concerned are more certain. It is increasingly apparent that signs of rotation at one wavelength are useless for comparisons of configurations, even of extremely similar compounds.

The diamines are now related as (+)-pn \equiv (+)-bn \equiv (+)-cptn \equiv (+)-chxn. This relationship is supported by the rotatory dispersion curves of (+)-pn, (+)-cptn, and (+)-chxn in the visible region. All have plain positive curves;¹² that of (+)-bn has not been measured.

The complexes of rhodium(III) with both cptn and chxn are known, the most stable isomers being (-)-[Rh(+cptn)₃]³⁺ and (-)-[Rh(+chxn)₃]³⁺. While these must have the D-configuration, the rotatory dispersion curves available⁷ unfortunately do not extend into regions of absorption. We have therefore examined the tris-complex of (-)-propylenediamine with rhodium(III); the most stable isomer, L(+)-[Rh(-pn)₃]³⁺, has a negative circular dichroism band at 315 m μ . (-)-[Rh en₃]³⁺ shows a positive circular dichroism band at 310 m μ ,¹³ and so is of the opposite configuration to L(+)-[Rh(-pn)₃]³⁺, i.e., it is D(-)-[Rh en₃]³⁺.

The stable isomer of tris-(+)-cyclohexanediaminechromium(III) cation is D(-)-[Cr(+chxn)₃]³⁺. This has a rotatory dispersion curve exactly similar⁷ to that of (+)-[Cr en₃]³⁺, which is therefore of the D-configuration. The rotatory dispersion curve⁶ of (-)-[Cr(tn)₃]³⁺ (where tn is propane-1,3-diamine) is parallel to that of D(+)-[Cr en₃]³⁺, so it may be assigned as D(-)-[Cr(tn)₃]³⁺.

In Table 2, the tris-compounds of inactive diamines are listed; the signs of rotation of the cation giving the less soluble diastereoisomers with the listed anions are given, with circular dichroisms. The conclusions reached from the solubility criterion are in full agreement with the configurations deduced from the conformational analysis of chelate rings, and comparison of optical rotatory powers. The conclusion from the method of partial racemates {that the configurations of (+)-[Co en₃]³⁺ and (-)-[Rh en₃]³⁺ are the same} is also verified.

For *d*⁶ complexes, the (¹T_{1g} \leftarrow ¹A_{1g}) transition of O_h (band I) splits¹⁴ into two components in complex ions of D₃ symmetry; in the case of chromium(III), (⁴T_{2g} \rightarrow ⁴A_{2g})

TABLE 2.
Configurations of trisdiamine complexes.

| Cation | D-config. ^a | (+) Tartrate | (+) Nitro-camphor | Active racemates | Circular dichroism | |
|---|------------------------|------------------|-------------------|------------------|----------------------|---------------------------|
| | | | | | λ (m μ) | $\epsilon_1 - \epsilon_d$ |
| [Co en ₃] ³⁺ | (+) | (+) ^b | Unknown | (+) ^g | 493 | +1.9 |
| [Rh en ₃] ³⁺ | (-) | (-) ^c | (-) ^d | (-) ^g | 310 | +1.4 |
| [Ir en ₃] ³⁺ | (-) | Unknown | (-) ^e | Unknown | 315 | +0.4 |
| [Cr en ₃] ³⁺ | (+) | Unknown | (+) ^f | Unknown | 460 | +1.7 |

^a This work. ^b Werner, *Ber.*, 1912, **45**, 121. ^c Jaeger, "Optical Activity and High Temperature Measurements," McGraw-Hill, New York, 1930, p. 92. ^d Werner, *Ber.*, 1912, **45**, 1229. ^e Werner and Smirnoff, *Helv. Chim. Acta*, 1920, **3**, 472. ^f Werner, *Ber.*, 1912, **45**, 3061. ^g Délépine and Charonnat, *Bull. Soc. Min. franc.*, 1930, **53**, 73.

of O_h splits into ⁴E_g and ⁴A_{1g} components. Complexes of the D-configuration should give rise to a positive A and a negative E component. It is particularly interesting that the longest-wavelength components of all the complexes in Table 2, and (+)-[Pt en₃]⁴⁺, are positive and therefore correspond to the E component. The only trisdiamine complex, other than those of cobalt, for which both components of band I have been observed is

¹¹ Pfeiffer, *Ber.*, 1944, **A**, **75**, 57.

¹² O'Brien and Toole, *J. Amer. Chem. Soc.*, 1954, **76**, 6009.

¹³ Mathieu, *J. Chim. phys.*, 1936, **33**, 78.

¹⁴ Piper and Carlin, *J. Chem. Phys.*, 1961, **35**, 1809.

L(+)-tris(-)-propylenediaminerhodium(III) iodide; results are shown in Fig. 2, with the partial curve¹³ for D(-)-trisethylenediaminerhodium(III) iodide for comparison.

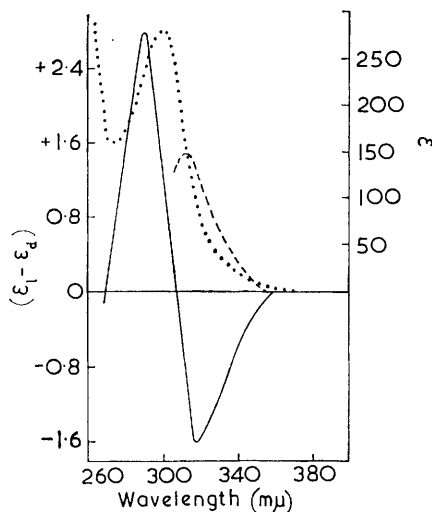


FIG. 2. Circular dichroisms of
 $[\text{Rh}(\text{AA})_3]\text{I}_3 \cdot \text{H}_2\text{O}$.
 Full line L(+)- $[\text{Rh}(-\text{pn})_3]\text{I}_3 \cdot \text{H}_2\text{O}$;
 Broken line¹³ D(-)- $[\text{Rh}(\text{en})_3]\text{I}_3 \cdot \text{H}_2\text{O}$.
 (Dotted line: absorption spectrum of
 $[\text{Rh}(\text{pn})_3]\text{I}_3$.)

EXPERIMENTAL

Microanalyses were by the Microanalytical Laboratory, Imperial College. Infrared spectra were obtained on a Grubb-Parsons Spectromaster grating instrument, electronic spectra on a Perkin-Elmer model 350 spectrophotometer, and rotatory dispersion curves with the attachment to this instrument. Specific rotations, $[\alpha]_D$, were taken on a Schmidt and Haensch polarimeter, with a 4-dm. tube.

Propylenediamine.—Resolution followed the method of Dwyer, Garvan, and Shulman.² After 14 recrystallisations of (-)-propylenediamine (+)-tartrate, the recovered (-)-propylenediamine (98 g.) had $[\alpha]_D^{20} -34.4^\circ$ (0.8% in benzene). It was redistilled before use, the fraction boiling at 114–116° being collected. (+)-Propylenediamine, recovered from (+)- $[\text{Co}(+\text{pn})_3]\text{Cl}$ tartrate trihydrate, had $[\alpha]_D^{20} +34.1^\circ$ (0.7% in benzene).

trans-Dichlorobis(-)-propylenediaminecobalt(III) bisaquohydrogen chloride, $\text{trans}-[\text{Co}(-\text{pn})_2\text{Cl}_2](\text{H}_5\text{O}_2)\text{Cl}_2$, was prepared by the method used by Werner and Fröhlich¹⁵ for the analogous compound of (+)-propylenediamine (Found: weight loss at 110°, 28.1. Required: 28.0%). The visible spectrum (in dilute hydrochloric acid) agreed with that recorded by Basolo.¹⁶ The circular dichroism is recorded elsewhere.¹⁷

Tris(-propylenediamine)rhodium(III) iodide hydrate, $[\text{Rh}(-\text{pn})_3]\text{I}_3 \cdot \text{H}_2\text{O}$, was prepared by the method used by Schmidtke¹⁸ for the analogous compound of (±)-propylenediamine (Found: I, 52.9. Calc. for $\text{C}_9\text{H}_{32}\text{I}_3\text{N}_6\text{ORh}$: I, 52.7%), λ_{max} . (in water) 300, 261, 225, $\text{m}\mu$ (ϵ 280, 7500, 35,000).

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¹⁵ Werner and Fröhlich, *Ber.*, 1907, **40**, 2225.

¹⁶ Basolo, *J. Amer. Chem. Soc.*, 1950, **72**, 4393.

¹⁷ Dunlop and Gillard, *Mol. Phys.*, 1964, **7**, 493.

¹⁸ Schmidtke, Cyanamid European Research Institute, Report P43, 1963.