

**The Absolute Configuration of the
(+)-*cis*-Dinitrobis-(−)-propylenediaminecobalt(III) Ion**

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THE absolute configurations of *cis*-[Coen₂L₂]²⁺ and related complexes have been assessed by a comparison of their circular dichroism (C.D.) and

rotatory dispersion (R.D.) curves with that of (+)-[Coen₃]³⁺† of known absolute configuration; considerable spectral, theoretical, and chemical

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† (+) refers to the sign of rotation measured in the Na_D line.

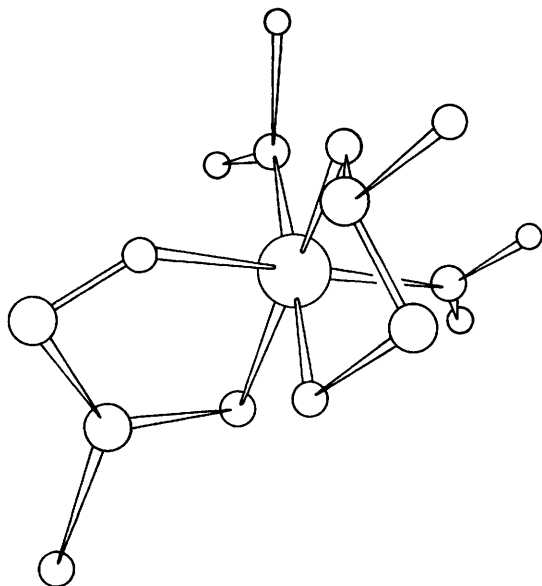


FIGURE 1

The structure of L-(+)-cis-dinitrobis(-)-propylenediaminecobalt(III) ion.

evidence has accumulated to test the validity of these comparisons.¹⁻⁵ However, despite the consistent agreement obtained by the diverse approaches to this correlation problem, the question always arises concerning whether the sign of the C.D. band associated with the first ligand-field band is carried over from the $[\text{Coen}_3]^{3+}$ ion to the $[\text{Coen}_2\text{L}_2]^{n+}$ ions with the same configuration.

The D_3 , (+)- $[\text{Coen}_3]^{3+}$ ion has two transitions in the first absorption band ($\sim 475 \text{ m}\mu$), one of E symmetry [(+)C.D.] and one of A symmetry [(-)C.D.] which transpose to transitions of A , B , and B symmetry respectively in the C_2 , $[\text{Coen}_2\text{L}_2]^{n+}$ complexes. The theoretical proposals^{2,6} suggest that the transitions of A and B symmetry in the C_2 complexes derived from the E (+) transition retain the positive C.D. sign, while the B transition derived from A (-) in the D_3 complex gives a negative C.D. curve. The difficulties in the interpretation of the C.D. spectra of solutions arise from the random orientation of the molecular ions and the small differences in energies between the transitions in both the D_3 and C_2 complexes and the consequent failure frequently to see the isolated C.D. peaks. The possibility of mixing between the two transitions of B symmetry in the C_2 complexes arises, and this factor might obscure the parentage of the dominant C.D. band observed.

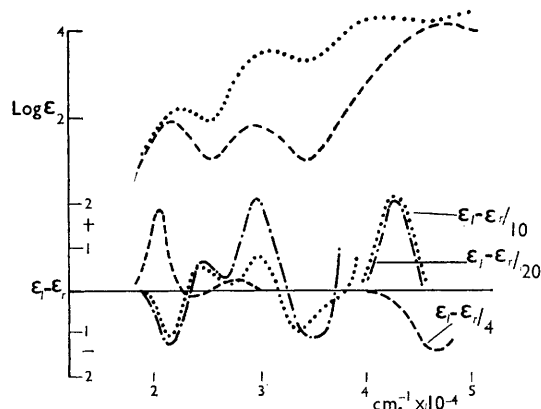


FIGURE 2

The circular dichroism ($\epsilon_1 - \epsilon_r$) and absorption spectra (ϵ) of (+)-tris(ethylenediamine)cobalt(III) perchlorate (---), (+)-cis-dinitrobis(-)-propylenediaminecobalt(III) iodide (····), and (-)-cis-dinitrobis(ethylenediamine)cobalt(III) perchlorate (····).

To check the correlations described above, the absolute configuration of the (+)- $[\text{Co}(-)\text{pn}_2(\text{NO}_2)_2]^+$ ion has been obtained using the known absolute configuration of $(-)\text{-pn}^7$ coupled with an X-ray crystal-structure analysis of (+)- $[\text{Co}(-)\text{pn}_2(\text{NO}_2)_2]\text{Cl}$.

Crystal data: (+)-cis-Dinitrobis(-)-propylenediaminecobalt(III) chloride, $\text{C}_6\text{H}_{20}\text{ClCoN}_6\text{O}_4$, $M = 334.7$. Orthorhombic, $a = 6.46$, $b = 9.62$, $c = 22.36 \text{ \AA}$, $U = 1390 \text{ \AA}^3$, $D_m = 1.60 \text{ g. cm.}^{-3}$, $D_x = 1.60 \text{ g. cm.}^{-3}$, $Z = 4$. Space group $P2_12_12_1$ from systematic absences.

The crystal is built up from chloride ions and complex cations which have the structure shown in Figure 1. The cobalt atom is surrounded by a slightly distorted octahedron of nitrogen atoms (Co-N distances 1.87—2.01 \AA). The nitro-groups are in *cis*-positions. Each of the nitro-groups is approximately coplanar with the cobalt atom; the two planes are approximately perpendicular to one another.

The methyl groups of the propylenediamine ligands are in *trans*-positions to one another, while they occupy *cis*-positions in the L(-)-tris(-)-propylenediaminecobalt(III) ion.⁸ However, the conformation of the chelate rings, as well as their absolute configuration about the cobalt atom is similar to that found in L(-)-tris(-)-propylenediaminecobalt(III) ion,⁸ in that firstly, the chelate rings have the k' conformation with equatorial methyl groups,⁹ and secondly, the absolute configuration of the complex ion (shown in Figure 1) may be described as "L", since it is related¹⁰ to

D-(+)-[Coen₃]³⁺ (*MC*₃, *PC*₂) as the mirror-image arrangement (*MC*₂) of the bidentate ligands when the ions are viewed along the C₂ axis. The symbols *M* and *P* are used to describe respectively the left-handed and right-handed arrangement of the chelate rings about the metal ion when viewed along a specified axis.²

The structure analysis is borne out by the relation of the C.D. curves in Figure 2. The C.D. band associated with the first ligand-field band derived from the ¹T_{1g} transition in Co(NH₃)₆³⁺, is positive for (+)-[Coen₃]³⁺ and negative for (+)-[Co(-)-pn₂(NO₂)₂]⁺. The entirely analogous (-)-[Coen₂(NO₂)₂]⁺ ion has a markedly similar C.D. curve to the propylenediamine complex and this, therefore, has the *MC*₂ configuration also. It

follows that (-)-[Co(-)-pn₂CO₃]⁺ and (-)-[Coen₂Cl₂]⁺, (-)-[Coen₂ClOH₂]²⁺, (-)-[Coen₂CO₃]⁺, (-)-[Coen₂(OH₂)₂]³⁺, and (-)-[Coen₂(NH₃)₂]³⁺ all have the *MC*₂ configuration since they have been related through reactions which occur with full retention of configuration.⁴ Similarly, the closely related α- and β-[CotrienX₂]ⁿ⁺ systems should conform to the same pattern.¹¹

The (+)-[Co(-)-pn₂(H₂O)₂]³⁺ and (+)-[Co(-)-pn₂(NO₂)₂]⁺ ions were prepared from the (-)-[Co(-)-pn₂CO₃]⁺ ion by adding acid and then nitrite ion; both reactions take place with full retention of configuration.^{12,13} These ions, therefore, must all have the same configuration.

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