

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713455674>

THE CIRCULAR DICHROISM OF THE TRIS[DI- μ -HYDROXO-BIS-(PROPYLENEDIAMINE)COBALT(III)COBALT(III) ION

Isao Masuda^a; Bodie E. Douglas^{ab}

^a Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania, U.S.A. ^b Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka, Japan

To cite this Article Masuda, Isao and Douglas, Bodie E.(1972) 'THE CIRCULAR DICHROISM OF THE TRIS[DI- μ -HYDROXO-BIS-(PROPYLENEDIAMINE)COBALT(III)COBALT(III) ION', *Journal of Coordination Chemistry*, 1: 3, 189 – 193

To link to this Article: DOI: 10.1080/00958977208070762

URL: <http://dx.doi.org/10.1080/00958977208070762>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

THE CIRCULAR DICHROISM OF THE TRIS[DI- μ -HYDROXO-BIS-(PROPYLENEDIAMINE)COBALT(III)]COBALT(III) ION¹

ISAO MASUDA and BODIE E. DOUGLAS†

*Contribution from the Department of Chemistry,
University of Pittsburgh, Pittsburgh, Pennsylvania U.S.A.
and the Department of Applied Chemistry, Faculty of Engineering,
Osaka University, Suita, Osaka, Japan*

(Received March 15, 1971)

Circular dichroism spectra are reported for two isomers of $[\text{Co}(+) - \text{pn}_2(\text{OH})_2]_3\text{Co}(\text{ClO}_4)_6$. It is suggested that earlier assignments of the CD peaks in the region of absorption of the CoO_6 chromophore be reversed. Assignments based upon intensities are without support where intensities are extraordinarily great, but the usual order of energy levels is expected. Absolute configurations are assigned based upon this interpretation of CD spectra.

INTRODUCTION

The resolution of the tris [di- μ -hydroxo-tetraaminocobalt(III)]cobalt(III) ion(I) was important in establishing Werner's views of the stereochemistry of metal complexes.^{2,3} Interest has continued in this and the corresponding compound containing ethylenediamine(II).^{4,5,6,7} These compounds are of particular interest with respect to their absorption and circular dichroism (CD) spectra^{5,7} because of possible metal-metal interaction. The CD spectra of (I) and (II) are surprisingly similar in view of the presence of only three chelate rings in (I). The corresponding complex containing optically active propylenediamine(III) is of interest with respect to the CD spectra and absolute configurations. Other polynuclear cobalt complexes containing propylenediamine have been investigated recently.⁸

EXPERIMENTAL SECTION

Resolution of Propylenediamine

The optical isomers were obtained by resolving commercial propylenediamine by Dwyer's method.⁹ The active pn, recovered from the chlorotartrate salt, $[\text{Co}(+) - \text{pn}_3]\text{Cl}(+) - \text{C}_4\text{H}_4\text{O}_6 \cdot 3\text{H}_2\text{O}$, after 4 recrystallizations, gave $\alpha_D = +0.62^\circ$ (1.828% solution in benzene), $[\alpha]_D = +33.9^\circ$, $+34.0^\circ$ reported. The (+)-pn recovered from the (+)-tartrate salt of pn after 10 recrystallizations gave

$\alpha_D = -0.69^\circ$ (1.980% solution in benzene), $[\alpha]_D = -34.8^\circ$, -34.2° reported.

$[\text{Co pn}_2(\text{OH})_2]_3\text{Co}(\text{ClO}_4)_6$. Complex ion(III) was prepared as the nitrate salt by a modification of Werner's method⁴ for the synthesis of the corresponding en complex(II). To 45.8 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 47 ml of water was added 95 ml of an aqueous solution containing 12 g of (+)-pn [or (-)-pn]. The mixture was allowed to stand for 30 min with stirring at room temperature and then filtered. The filtrate was concentrated to 70 ml by bubbling compressed air through the solution at room temperature. The solution was cooled in an ice bath and 105 ml of 95% ethanol was added dropwise. A gummy precipitate resulted if ethanol was added too rapidly. The precipitate was filtered and washed 2 or 3 times with a small amount of 95% ethanol and then air dried. Yield: 28 g. The nitrate salt can be recrystallized by dissolution in 100 ml. of 60% ethanol at 70-80° followed by cooling in an ice bath.

The perchlorate salt was obtained by dissolving 28 g of the nitrate salt in 35 ml of water followed by the addition of 22.2 g of $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ in 20 ml of water. The resulting solution was cooled in an ice bath, the precipitate was filtered, washed with cold 70% ethanol, then 95% ethanol, and air dried. Yield: 22.3 g. The complex as the perchlorate salt can be recrystallized by dissolution in the minimum amount of water at 65°, followed by cooling in an ice bath. The air dried perchlorate salt contained about 7 molecules of water of hydration which were lost upon drying for analysis at 70° over

P₂O₅. Anal. Calcd. for [Co₄(pn)₆(OH)₆](ClO₄)₆: Co, 17.10; pn, 32.25; C, 15.70; H, 4.83. Found: Co, 16.92; pn, 32.0; C, 15.71; H, 5.55.

Resolution of the Complex

Mellor's method⁶ for the resolution of the en complex(II), using the antimonyl tartrate salt of the complex ion, gave an intractable gummy precipitate which was not easily handled when used for III. The nitrate salt was very soluble and was not well suited for fractional separation of optical isomers. The perchlorate salt was fractionally recrystallized to yield the desired optical isomers without a resolving agent. The perchlorate salt of the complex was dissolved in water at 27–30° (5 ml for each g of complex) and the solution was filtered to remove any residue. The solution was allowed to stand for 1 hour at 0° and the precipitate (fraction 1) was centrifuged, keeping the temperature below 5°. The precipitate was washed with 95% ethanol using one half of the volume of water used to dissolve the complex. To the filtrate was added 95% ethanol (one fifth of the volume used to dissolve the complex), and the resulting mixture was cooled in an ice bath for one hour to yield fraction 2. To the filtrate from fraction 2 was added 95% ethanol (one half of the volume of water used to dissolve the complex) to give fraction 3. Fractions 2 and 3 were centrifuged, washed, and air dried as for fraction 1. Four grams of the complex used in the resolution gave 1.90, 0.82, and 0.14 g of the respective fractions.

Fraction 1 was purified by a similar recrystallization procedure. The rotation was constant after 4 or 5 recrystallizations. Upon purification, the apparent solubility in water decreases since larger volumes of water are required for each successive recrystallization, in the approximate ratios 6:7:8. The pure complex separates as a gellatinous precipitate which was dried in a vacuum desiccator over CaCl₂ at room temperature. About 1 g of pure (+)-isomer was obtained from 11 g of the complex perchlorate salt, $[M]_D = +37,500^\circ$.

Fraction 3 was recrystallized in the same way as fraction 1, using 6 ml of water for each gram of complex. About 20 mg of the (–)-isomer was obtained from 4 g of the complex perchlorate salt, $[M]_D = -29,600^\circ$. It was more difficult to isolate pure products from fraction 2. This was the only observation which might suggest that additional isomers were present in the initial product.

Analyses were performed at Osaka University, Faculty of Engineering.

Measurements

The CD spectra were obtained in aqueous solution using a Roussel-Jouan Dichrograph. Optical rotations were measured in aqueous solution in a 1 dm tube at room temperature. Absorption spectra were recorded on a Cary Model 14 spectrophotometer.

RESULTS AND DISCUSSION

Only one pair of isomers was isolated for the complex [Co(+)-pn₂(OH)₂]₃Co(ClO₄)₆ and only the more easily purified (–)-isomer was isolated for the corresponding complex containing (–)-pn. The possible isomers (for one active isomer of pn) include $\Delta(\Delta\Delta\Delta)$, $\Delta(\Delta\Delta\Lambda)$, $\Delta(\Delta\Lambda\Lambda)$, $\Delta(\Lambda\Lambda\Lambda)$ and those of opposite chirality, in addition to the geometrical isomers resulting from different positions for the methyl groups. Recent work with binuclear complexes⁸ indicates that the stereoselectivity of active pn should limit the isomers formed and make it possible to assign absolute configurations.

Kern and Wentworth⁷ reported that 4 of the 8 possible isomers of [en₂Co(OH)₂]₃Co⁶⁺ were formed, and only 2 of these were resolved under their conditions. The absorption bands at 16,000 and 20,000 cm⁻¹ (Table I, Figure 1) correspond to those of the en complex which have been assigned to the ${}^1A_1 \rightarrow {}^1T_1(O_h)$ transitions for the CoO₆ and CoN₄O₂ groups, respectively^{5, 7}. The CD peaks at ca. 16,300 and 20,100 cm⁻¹ correspond closely to those of the en complex^{5, 7} assigned as the E_a components for the CoO₆ and CoN₄O₂ groups, respectively. The weaker CD peak at ca. 14,500 cm⁻¹ corresponds to that assigned as the A_2 component for CoO₆ for the en complex^{5, 7}(II). This assignment (A_2 at lower energy than E_a for CoO₆) was based upon the expected greater intensity of E_a . The E_a component is usually at lower energy than A_2 for complexes with trigonal compression, while the reverse order was reported¹⁰ for Co(tn)₃³⁺, where the angle subtended by the chelating at the central metal ion is greater than 90°. Strong trigonal compression resulting from the 4-membered chelate rings is expected for CoO₆, suggesting that E_a should be at lower energy than A_2 , or the reverse of the earlier assignment^{5, 7}. For Co(C₂O₄)₃³⁻, polarized crystal spectra¹¹ indicate that E_a (16,350 cm⁻¹)

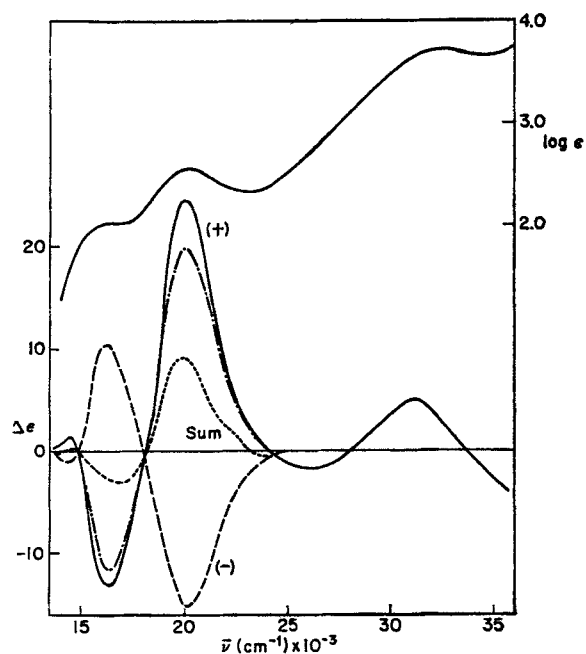


FIGURE 1. Absorption (upper curve) and circular dichroism spectra for (+)_D-[Co(+)-pn₂(OH)₂]₃Co(ClO₄)₆ (—) and (-)_D-[Co(+)-pn₂(OH)₂]₃Co(ClO₄)₆ (—) and (-)_D-[Co(+)-pn₂(OH)₂]₃Co(ClO₄)₆ (---). The sum of these two CD curves (····) and the difference curve (---) for one half of the sum curve subtracted from the CD curve for (+)_D-isomer are also plotted.

is at lower energy than A_2 (16,500 cm^{-1}). For the larger chelate ring in the case of Co(acetylacetonate)₃ the reverse order has been given.¹²

The CD peak intensities observed for compounds of the type [CoN₄(OH)₂]₃Co⁶⁺ are much larger than usual for the $d-d$ absorption region, suggesting possible metal-metal interaction, and that the usual intensity criteria for assignments might not apply. The spectra are remarkably similar for the

series of complexes containing NH₃, en, (-)-pn, or (+)-pn (Table I). This is particularly surprising for the CoN₄O₂ group where the replacement of NH₃ by diamines has only a slight effect. For the en complex,⁷ the configuration of the Co(OH)₆ group was considered to be opposite that of all, or at least 2 out of 3, of the CoN₄O₂ groups. It seems even more reasonable to exclude the possibilities where the CoN₄O₂ groups do not have the same configuration in the case of the complex containing active pn.⁸ The results presented here are consistent with this assumption, but an X-ray structure determination would be required for final proof.

The E_a component is usually more intense than A_2 for tris(bidentate) complexes, but the reverse is true¹³ for Co(NH₃)₄(-)-pn³⁺, where the optical activity arises from the presence of the optically active ligand. Let us assume as a working hypothesis, that the Co(+)-pn₂(OH)₂⁺ units have the preferred λ or Λ ¹⁴ configuration with the pn ring conformations δ (CH₃ groups equatorial).⁸ The two internal diastereomers are $\Delta(\Lambda\Lambda\Lambda)$ and $\Lambda(\Lambda\Lambda\Lambda)$ (Figure 2). As noted by Kern and Wentworth,⁷ these isomers have strikingly different stereochemical configurations. Models show that $\Delta(\Lambda\Lambda\Lambda)$ is the height of one octahedron, very wide and flat (3:1 ratio for width:height), with the pseudo C_3 axes parallel for all four octahedra. The pn rings project outward from the edges of the terminal octahedra, so that the amine hydrogens and the OH⁻ groups are unblocked, allowing easy access by solvent molecules. The model of the $\Lambda(\Lambda\Lambda\Lambda)$ diastereomer is much higher and not as wide (3:2 ratio). The pseudo C_3 axes of the Co(+)-pn₂(OH)₂⁺ octahedra define a left spiral about the C_3 axis of the CoO₆ octahedron. Three of the pn rings project above the plane of the four Co³⁺ ions and three of them project below this plane. The amine hydrogens and OH⁻ groups are blocked to a

TABLE I

Comparison of Circular Dichroism Data for [Co pn₂(OH)₂]₃Co(ClO₄)₆ and Related Complexes

Complex	cm ⁻¹	$\Delta\epsilon_{\text{max}}$	cm ⁻¹	$\Delta\epsilon_{\text{max}}$	cm ⁻¹	$\Delta\epsilon_{\text{max}}$	cm ⁻¹	$\Delta\epsilon_{\text{max}}$
(+) _D - [Co(+)-pn ₂ (OH) ₂] ₃ Co(ClO ₄) ₆	14,500	+ 1.3	16,300	- 13.3	20,100	+ 24.4	25,900	- 1.7
(-) _D - [Co(+)-pn ₂ (OH) ₂] ₃ Co(ClO ₄) ₆	14,300	- 1.1	16,200	+ 10.8	20,200	- 15.3	25,600	+ 0.4
(-) _D - [Co(-)-pn ₂ (OH) ₂] ₃ Co(ClO ₄) ₆	14,500	- 1.5	16,300	+ 13.2	20,100	- 24.2	25,900	+ 1.9
(+) _D - [Co en ₂ (OH) ₂] ₃ Co ⁶⁺ ⁷	14,600	+ 5.0	16,500	- 16.0	20,200	+ 20.4	25,600	- 1.0
(-) _D - [Co(NH ₃) ₄ (OH) ₂] ₃ Co ⁶⁺ ⁵	14,700	(- 4) ^a	16,500	(+ 16) ^a	20,000	(- 14) ^a	25,500	(+ 1) ^a

^a Data estimated from figure.

greater extent, restricting access by solvent molecules. The (-)-isomer is much more soluble than the (+)-isomer and one might expect the more soluble one to have the wide, flat arrangement which offers more opportunities for solvation.

If the isomers of the (+)-pn complex are $\Delta(\Lambda\Lambda\Lambda)$ and $\Lambda(\Lambda\Lambda\Lambda)$, adding their CD curves (Figure 1) should give a resultant curve for the contribution of six Λ -[Co(+)-pn₂(OH)₂]⁺ units, since the contributions of the Δ - and Λ -[Co(OH)₆] units should cancel. If the CD peak at 20,000 cm⁻¹ for the resultant curve is E_a, its positive sign is consistent with the Λ configuration for Co(+)-pn₂(OH)₂⁺, expected for (+)-pn. The opposite signs of the CD peaks at 20,100 cm⁻¹ for the two isomers do not require opposite configurations for the Co(+)-pn₂(OH)₂⁺ groups. CD peaks of comparable intensities and opposite signs are also observed in this region for the two isomers of the corresponding ammonia complex(I), so that the same dominant factor will determine the sign of this peak for the NH₃, en, and pn complexes.

The CD peaks of the resultant curve in the CoO₆ absorption region are the result of the induced activity from the presence of the three active

Co(+)-pn₂(OH)₂⁺ ligands. Using the assignment E₂ at lower energy than A₂, the greater intensity of the A₂ peak (16,300 cm⁻¹) is not unexpected for a "vicinal effect" curve.¹³

If the 14,500 cm⁻¹ CD peak is the E_a component, its negative sign for the (-)-isomer indicates the Δ configuration for the Co(OH)₆ or, from the assignment of the Λ -configuration to the Co(+)-pn₂(OH)₂⁺ groups, this would be the $\Delta(\Lambda\Lambda\Lambda)$ isomer. This assignment is consistent with the greater solubility expectation for the wide, flat configuration, as already noted. On the same basis the less soluble (+)-isomer would have the $\Lambda(\Lambda\Lambda\Lambda)$ configuration.

Earlier assignments of the two CD peaks in the first band region (CoO₆) were based upon relative intensities, even though the intensities for the complexes I, II and III are very unusual. It seems more reasonable to expect the usual order, E_a at lower energy than A₂, for complexes with significant trigonal compression. On this basis, the sign of the E_a component (20,000 cm⁻¹) of the Co(NH₃)₄(OH)₂⁺ groups for I (Table I) is the same as that of the Co(OH)₆ group, which is the center of the optical activity of I. Variations in the intensity of

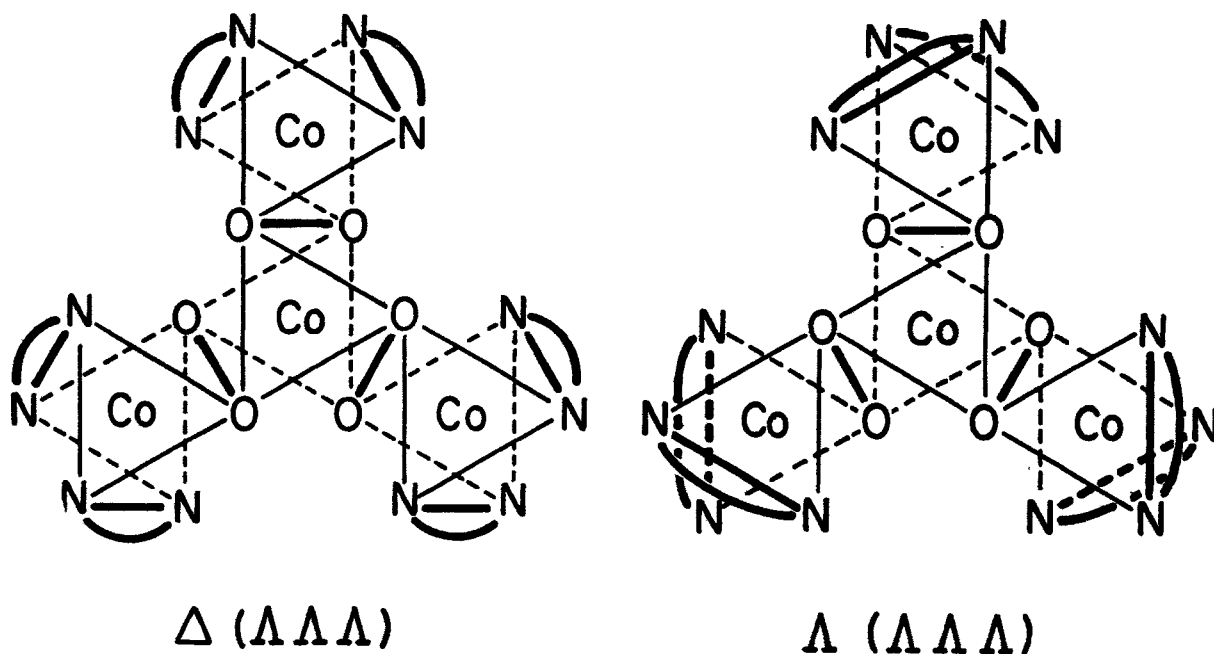


FIGURE 2. Views of the $\Delta(\Lambda\Lambda\Lambda)$ and $\Lambda(\Lambda\Lambda\Lambda)$ isomers of the [Co(diamine)₂(OH)₂]₃Co³⁺ ion looking down the C₃ axis of the central Co(OH)₆ group. The diamine chelate rings project outward horizontally for $\Delta(\Lambda\Lambda\Lambda)$ and upward or downward for $\Lambda(\Lambda\Lambda\Lambda)$.

the 20,000 cm^{-1} peak for the active pn complex (III) are consistent with the expected contribution from the preferred Λ configuration of the $\text{Co}(+)\text{-pn}_2(\text{OH})_2^+$ groups.

REFERENCES

1. Work supported by grant GM 10829 from the U.S. Public Health. I. M., Research Associate, University of Pittsburgh, 1966-7.
2. A. Werner, *Ber*, **47**, 3087 (1914).
3. A. Werner, *ibid*, **40**, 2103 (1907).
4. A. Werner, *ibid*, **40**, 2121 (1907).
5. S. F. Mason and J. W. Wood, *Chem Commun*, 1967, 209.
6. H. A. Goodwin, E. C. Gyarfas, and D. P. Mellor, *Austral. J. Chem.* **11**, 426 (1958).
7. R. D. Kern and R. A. D. Wentworth, *Inorg. Chem.* **6**, 1018 (1967).
8. Y. Sasaki, J. Fujita, and K. Saito, *Bull. Chem. Soc. Japan* **40**, 2206 (1967); **42**, 146 (1969).
9. F. P. Dwyer, F. L. Garvan, and A. Shulman, *J. Am. Chem. Soc.* **81**, 290 (1959).
10. R. R. Judkins and D. J. Royer, *Inorg. Nucl. Chem. Letters* **6**, 305 (1970).
11. T. S. Piper and R. L. Carlin, Jr., *J. Chem. Phys.* **35**, 1809 (1961).
12. T. S. Piper, *ibid.*, **35**, 1240 (1961).
13. K. Ogino, K. Murano, and J. Fujita, *Inorg. Nucl. Chem. Letters* **4**, 351 (1968).
14. For notation see *Inorg. Chem.* **9**, 1 (1970).