

Crystal Circular Dichroism Spectra of Cobalt(III) Complexes with Mixed Ethylenediamine – Trimethylenediamine Coordination Spheres

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Crystal circular dichroism spectra of $(+)_D$ - $[\text{Co}(\text{tn}_3)\text{Br}_3]$ and $(+)_D$ - $[\text{Co}(\text{en}_2\text{tn})\text{Br}_3]$ have been measured and interpreted to give information of rotatory strengths and relative energy positions of the trigonal components of the $T_{1g} \leftarrow A_{1g}$ octahedral transitions at the metal ion centre. It is generally found, for the series of complexes $[\text{Co}(\text{en}_{3-x}\text{tn}_x)]^{3+}$, that the transition to the E excited level occurs at lower energy than the transition to the A_2 excited level. Furthermore the estimated rotatory strengths are in accordance with the interpretation of the solution circular dichroism spectra as arising from extensive cancellation between the respective components of the two trigonal transitions.

Tris(diamine)cobalt(III) complexes have been intensively studied in this laboratory, particularly complexes with mixed ethylenediamine – trimethylenediamine coordination spheres ($[\text{Co}(\text{en}_{3-x}\text{tn}_x)]^{3+}$).

Tris(1,3-propanediamine)cobalt(III) ($[\text{Co}(\text{tn}_3)]^{3+}$) was originally resolved by Woldbye through fractional crystallization with $(+)_D$ -nitrocamphor, the $(-)_D$ -enantiomer of the complex forming the less soluble diastereoisomer.^{1,2} For various reasons the $(-)_D$ - $[\text{Co}(\text{tn}_3)]^{3+}$ and the $(+)_D$ - $[\text{Co}(\text{en}_3)]^{3+}$ chromophores were thought to have the same absolute configuration (Λ) although the ligand field Cotton effects were of opposite sign.^{2–5} The configurations were finally confirmed by X-ray structural analysis.⁶

The complexes with mixed coordination spheres were isolated in this laboratory by a paper-chromatographic method and resolved in the form of their bromides by means of $(+)_D$ -nitrocamphor.^{7,8}

The less soluble $(+)_D$ -camphornitronates yield the $(+)_D$ -bromides of the two “mixed” complexes, and it was thus expected from the “solubility criterion” that $(+)_D$ - $[\text{Co}(\text{en}_2\text{tn})]^{3+}$ and $(+)_D$ - $[\text{Co}(\text{tn}_2\text{en})]^{3+}$ should have the same absolute configuration as $(-)_D$ - $[\text{Co}(\text{tn}_3)]^{3+}$ and $(+)_D$ - $[\text{Co}(\text{en}_3)]^{3+}$, i.e. Λ . This configuration was verified for the $(+)_D$ - $[\text{Co}(\text{en}_2\text{tn})]^{3+}$ chromophore by an X-ray determination.⁹

Recently our knowledge of the title complexes has been extended through determination of cumulative stability constants and it seems appropriate to suggest an intrinsic stability difference between five- and six-membered diamine chelate rings reasonably independent of the number of chelate rings.^{10,11} This was also demonstrated through infrared spectra, as those of the “mixed” complexes are additive in the spectra of $[\text{Co}(\text{en}_3)]^{3+}$ and $[\text{Co}(\text{tn}_3)]^{3+}$.^{12,13}

Finally it should be mentioned that $[\text{Co}(\text{tn}_3)]^{3+}$, among others, has been investigated by conformational analysis based on energy minimization.^{14–16}

One of the peculiar features of tris(diamine)-cobalt(III) complexes is the chirality and the optical activity of the compounds, and normally they exhibit two circular dichroism bands of opposite sign in the absorption region around 21.000 cm^{-1} . These bands are considered to correspond to transitions to the $E(D_3)$ and $A_2(D_3)$ excited levels of $T_{1g}(O_h)$ parentage in a D_3 environment.

The assignment has been the subject of much discussion in the literature and the two separate transitions have only recently been possible to identify by means of phase modulation spectroscopy.¹⁷ Thus it seems clear that the “random”

circular dichroism in the ligand field region of tris(diamine)cobalt(III) complexes is, as originally proposed by McCaffery and Mason,¹⁸ residual wing absorptions resulting from extensive cancellation of the rotatory strength under the two first D_3 spin allowed absorption bands.

There are, however, still details in the ligand field transitions of tris(diamine)cobalt(III) complexes which need further investigation. This is, *e.g.*, the general question of relative position on an energy scale of the E and A_2 excited levels, and the question concerning magnitude in general of rotatory strengths under the $A_2 \leftarrow A_1$ and $E \leftarrow A_1$ transitions. These points will be elucidated below through crystal circular dichroism spectra of $(+)_D-[Co en_2tn]Br_3$ and $(+)_D-[Co tn_3]Br_3$.

EXPERIMENTAL

Crystals of $(+)_D-[Co tn_3]Br_3$ and $(+)_D-[Co en_2tn]Br_3$ were grown by slow evaporation of aqueous solutions at room temperature.

Suitable crystals for the intended spectroscopic investigations were selected and mounted on microscope slides, and their thickness determined from absorption spectra. In order to obtain dichroism spectra the crystals were centered in the light beam of a microscope built into a phase modulation

spectrophotometer as described elsewhere.^{19,20} The signals obtained were processed and analyzed as in earlier papers in this series.^{17,19-23}

PREDICTIONS

From crystal structure data we may calculate the angular orientation of the molecular units with respect to the crystallographic axes. Such data are given for $[Co tn_3]Br_3$ in Table 1 and for $[Co en_2tn]Br_3$ in Table 2.

With the indicated choice of coordinate system the following expressions for the rotatory strengths are valid: (*cf.* Ref. 17)

$$R_{xy}(cr) = \frac{3}{2} R(E)$$

$$R_{yz}(cr) = R_{xz}(cr) = \frac{3}{2} (R(A_2) + \frac{1}{2} R(E))$$

the factor $\frac{3}{2}$ being due to the fixed orientation of the chromophores in the crystalline state.

Consulting Table 1 it is seen that in case we measure circular dichroism of $(+)_D-[Co tn_3]Br_3$ with light propagating along the crystallographic b

Table 1. Squares of inter-planar cosines in $(+)_D-[Co tn_3]Br_3$. Monoclinic crystals ($P2_1$),⁶ entrance face (010). The molecular coordinate system is defined as in Ref. 17, *i.e.* z along C_3 , x and y along mutual perpendicular C_2 axes.

Crystallographic planes	Molecular planes			% E	% A_2
	$(R(E))$ xy	$(R(A_2) + \frac{1}{2}R(E))$ xz	yz		
ab	0.167	0.003	0.830	58	83
bc	0.010	0.571	0.419	51	99
ac	0.802	0.045	0.153	90	20

Table 2. Squares of inter-planar cosines in $(+)_D-[Co en_2tn]Br_3$. Orthorhombic crystals ($P2_12_12_1$),⁹ entrance face (010). The molecular coordinate system is defined as indicated in Table 1.

Crystallographic planes	Molecular planes			% E	% A_2
	$(R(E))$ xy	$(R(A_2) + \frac{1}{2}R(E))$ xz	yz		
ab	0.944	0.044	0.012	97	6
ac	0.004	0.458	0.538	50	100
bc	0.052	0.498	0.450	53	95

axis, the spectrum should reflect 90% of the total rotatory strength from the transition to the E excited level and 20% of the total rotatory strength from the transition to the A_2 excited level.

Similarly it is seen from Table 2 that determination of circular dichroism from $(+)_D$ -[Co en₂tn]Br₃, light propagating along the b crystallographic axis, should give a spectrum reflecting 50% E and 100% A_2 rotatory strength, which by the way is the same as the expected ratio in a measurement on $2(+)_D$ -[Co en₃]Cl₃·NaCl·6H₂O, light propagating perpendicular to the c crystallographic axis in the hexagonal crystal.¹⁷

DISCUSSION

Generally it is assumed that the energy of the $A_2 \leftarrow A_1$ transition is higher than that of $E \leftarrow A_1$ in tris(1,2-diamine)cobalt(III) complexes.²⁴⁻²⁶ With tris(1,3-diamine)cobalt(III) complexes, however, the situation is not quite so clear. This problem is related to the old question of why the chromophores [Co en₃]³⁺ and [Co tn₃]³⁺, of the same absolute configuration, have virtually mirror-image Cotton effects.²⁻⁵

Earlier there seemed to be a tendency to believe that the energy relationship between the two transitions was the same for both 1,2- and 1,3-diamine complexes,^{2-5,24} but lately Judkins and Royer have suggested the opposite relationship,²⁷ *i.e.* $\Delta E(E) > \Delta E(A_2)$, a suggestion which has been followed by

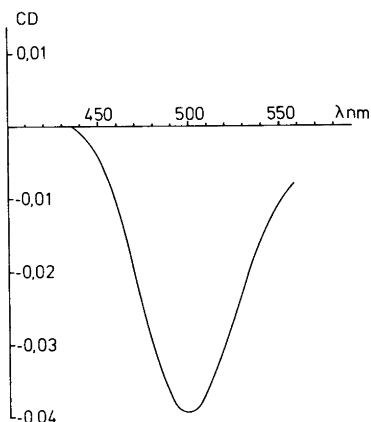


Fig. 1. Crystal circular dichroism in the ac plane of $(+)_D$ -[Co tn₃]Br₃. Thickness of the crystal: 0.025 mm.

Mason and Seal in their recent calculations of rotatory strengths using a dynamic-coupling ligand-polarization model.²⁸

Considering Fig. 1, which is the single crystal circular dichroism of $(+)_D$ -[Co tn₃]Br₃ light propagating along the crystallographic b axis, we know from Table 1 that we should expect to collect 90% of the rotatory strength connected with transition to the E excited level and only 20% of that connected with transition to the A_2 excited level. As we experimentally observe (Fig. 1) a negative peak with maximum at 499 nm, *i.e.* above the absorption maximum at 488 nm, it is demonstrated that in [Co tn₃]³⁺, as in [Co en₃]³⁺, and thus also in the "mixed" complexes, the relative position of the two trigonal transitions is the same, *i.e.* $\Delta E(A_2) > \Delta E(E)$.

Using the formulas given in Ref. 17 we may calculate the rotatory strength of the $E \leftarrow A_1$ transition in $(+)_D$ -[Co tn₃]³⁺ on basis of the measured crystal circular dichroism. Thus we have, disregarding that the spectrum also reflects 20% A_2 rotatory strength:

$$\Delta \epsilon_{\text{mol}}(\text{max}) = \frac{-0.04 \cdot 2}{0.9 \cdot 0.0025 \cdot 3 \cdot 3.32} = -3.6 \frac{\text{dm}^3}{\text{mol cm}}$$

This value should be compared with a maximum molar circular dichroism in solution of approx. -0.1 at 525 nm,^{2,5,7} and thus we have support for the assumption that the solution circular dichroism results from extensive cancellation of rotatory strength from two trigonal components. The experimental rotatory strength $R(E)$ may from the molar circular dichroism and Fig. 1 be estimated to -10.5×10^{-40} (cgsu), a value which is numerically in agreement with the one found by Judkins and Royer,²⁷ and that calculated by Mason and Seal for the chloride.²⁸

We may now turn our attention to the crystal circular dichroism of $(+)_D$ -[Co en₂tn]Br₃, light propagating along the crystallographic b axis (Fig. 2). The spectrum reflects mainly the rotatory strength of the transition to the E excited level, since the peak is positive and positioned on the low energy site of the absorption maximum. There is also a small negative peak with maximum around 425 nm. As we from Table 2 expect the crystal circular dichroism of the ac plane to reflect 100% of the rotatory strength connected with the A_2 transition, but only 50% of that connected to the E transition, there seems at first glance to be a

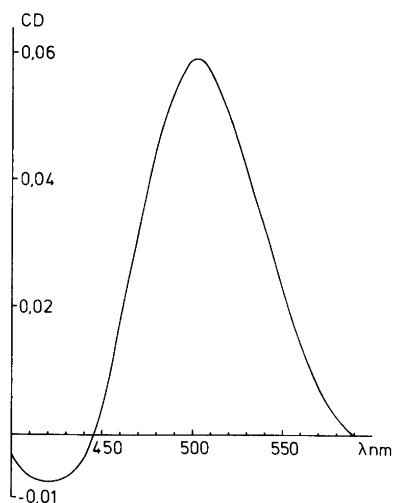


Fig. 2. Crystal circular dichroism in the *ac* plane of (+)_P-[Co en₂tn]Br₃. Thickness of the crystal: 0.035 mm.

contradiction between the prediction and the experiment. It should, however, be remembered that the visible solution circular dichroism of (+)_P-[Co en₂tn]³⁺, reflecting $R(E) + R(A_2)$,^{17,18,25-28} shows no negative peak at all.⁸ This means obviously that $R(E) > R(A_2)$, an inequality which as a matter of fact is also taken into account in the calculations by Mason and Seal.²⁸

From Fig. 2 we may calculate the molar circular dichroism and the rotatory strength connected with the *E* transition, disregarding the smaller, but existing, *A*₂ contribution to the experimental spectrum:

$$\Delta\epsilon_{\text{mol}}(\text{max}) = \frac{0.06 \times 2}{0.5 \times 0.0035 \times 3 \times 4.06} = 5.6 \frac{\text{dm}^3}{\text{mol cm}}$$

This value should be compared with a value for $\Delta\epsilon_{\text{mol}}(\text{max})$ in solution of appr. 1.⁸

From the molar circular dichroism and Fig. 2 we estimate $R(E)$ to 20×10^{-40} (cgsu), which is a reasonable value as it falls in the interval between $R(E)$ for [Co en₃]³⁺ of $\sim 50 \times 10^{-40}$ and for [Co tn₃]³⁺ of $\sim 10 \times 10^{-40}$.²⁸

Acknowledgements. My sincere thanks are due to Professor J. A. Schellman, Institute of Molecular Biology, University of Oregon, for the opportunity to visit his laboratory and use his equipment. Also I would like to thank Professor F. Woldbye of this university for samples of optically pure compounds.

Grants from Danish Natural Science Research Council and NATO are highly appreciated.

REFERENCES

1. Woldbye, F. *US Army Report* DA-91-508-EUC-246 (1959).
2. Woldbye, F. *Studier over Optisk Aktivitet*, Polyteknisk Forlag, Copenhagen 1969.
3. Woldbye, F. In Snatzke, G., Ed., *Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry*, Heyden, London 1967, p. 101.
4. Woldbye, F. *Proc. R. Soc. London A* 297 (1967) 79.
5. Woldbye, F. *Rec. Chem. Prog.* 24 (1963) 197.
6. Nomura, T., Marumo, F. and Saito, Y. *Bull. Chem. Soc. Jpn.* 42 (1969) 1016.
7. Bang, O., Engberg, A., Rasmussen, K. and Wolbye, F. *Proc. 3rd. Symp. Coord. Chem. Vol. I*, Akadémiai Kiadó, Budapest 1970, p. 63.
8. Bang, O., Engberg, A., Rasmussen, K. and Wolbye, F. *Acta Chem. Scand. A* 29 (1975) 749.
9. Schousboe-Jensen, H. V. F. *Acta Chem. Scand.* 26 (1972) 3413.
10. Bang, O., Rasmussen, K. and Woldbye, F. *Acta Chem. Scand. A* 31 (1977) 192.
11. Bang, O. *Diss.*, Chemistry Department A, The Technical University of Denmark, Lyngby 1976.
12. Rasmussen, K. *Diss.*, Chemistry Department A, The Technical University of Denmark, Lyngby 1970.
13. Rasmussen, K. *Spectrochim. Acta A* 30 (1974) 1763.
14. Niketic, S. R. and Woldbye, F. *Acta Chem. Scand.* 27 (1973) 621.
15. Niketic, S. R. and Woldbye, F. *Acta Chem. Scand. A* 28 (1974) 248.
16. Niketic, S. R., Rasmussen, K., Woldbye, F. and Lifson, S. *Acta Chem. Scand. A* 30 (1976) 485.
17. Jensen, H. P. and Galsbøl, F. *Inorg. Chem.* 16 (1977) 1294.
18. McCaffery, A. J. and Mason, S. F. *Mol. Phys.* 6 (1963) 359.
19. Jensen, H. P., Schellman, J. A. and Troxell, T. *Appl. Spectrosc.* 32 (1978) 192.
20. Jensen, H. P. *Acta Chem. Scand. A* 30 (1976) 137.
21. Jensen, H. P. *Chem. Phys. Lett.* 52 (1977) 559.
22. Jensen, H. P. *Acta Chem. Scand. A* 32 (1978) 153.
23. Jensen, H. P. *Acta Chem. Scand. A* 33 (1979) 563.
24. Bürer, T. *Helv. Chim. Acta* 46 (1963) 2388.
25. Toftlund, H. and Pedersen, E. *Acta Chem. Scand.* 26 (1972) 4019.
26. Kuroda, R. and Saito, Y. *Bull. Chem. Soc. Jpn.* 49 (1976) 433.
27. Judkins, R. R. and Royer, D. J. *Inorg. Chem.* 13 (1974) 945.
28. Mason, S. F. and Seal, R. H. *Mol. Phys.* 31 (1976) 755.

Received May 14, 1979.