

SOLUTION CIRCULAR DICHROISM SPECTRA OF THE
COMPLEX ION, $(-)_546^{-\Delta}(1e1_3)-[Co(R,R-ptn)_3]^{3+}$

Reiko KURODA, Junnoske FUJITA* and Yoshihiko SAITO

Institute for Solid State Physics, The University
of Tokyo, Roppongi, Minato-ku, Tokyo 106

* Department of Chemistry, Faculty of Science,
Nagoya University, Chikusa-ku, Nagoya 464

The solution CD spectra of $(-)_546^{-\Delta}(1e1_3)-[Co(R,R-ptn)_3]^{3+}$ ion were found to be seriously affected by its counter ions. The CD change may be due to ion association between the complex and the counter ions.

Influence caused by the addition of various electrolytes on the solution CD spectra of tris-diamine complexes of Co(III) has been extensively investigated and the appreciable effect exerted by the addition of oxo anions such as SeO_3^{2-} or PO_4^{3-} is now one of the useful methods of assigning the symmetry of CD bands in the first d-d absorption region¹⁾. On the other hand, influence of the counter ions which comprise the complex salts has been considered to be negligibly small. The complex ion $\Delta(1e1_3)-[Co(R,R-ptn)_3]^{3+}$ affords an exception for this general observation. The solution CD spectra of this complex ion are seriously affected by its counter ions.

In the previous paper²⁾, one of the authors(J.F.) reported that the crystals of $(-)_546$ -tris(R,R-2,4-diaminopentane)cobalt(III) chloride were pseudoracemate, i.e., a mixture of 93% Δ -isomer and 7% Λ -isomer based on the different solution CD spectra observed for the chloride and the perchlorate. In fact, crystals of two different habits were recognized in the specimen prepared according to the method described in the previous paper: truncated tetragonal bipyramids and rhombic parallelepipeds. The two crystals were manually separated under a microscope and the CD spectra in aqueous solutions were measured separately. Both crystals showed exactly the same CD spectra: $\Delta\epsilon = -0.589$, 522 nm; $\Delta\epsilon = +0.104$, 462.5 nm, as shown in Fig. 1. Moreover these CD spectra were identical with those reported previously for the pseudoracemate. X-ray examination, however, at once revealed that the former crystal belonged to tetragonal system and the cell dimensions and the space group corresponded to optically pure $(-)_546^{-\Delta}(1e1_3)-[Co(R,R-ptn)_3]Cl_3 \cdot 2H_2O$, of

which the crystal structure had already been known³⁾. The crystal data for the latter are:

$(-)_546^-[\text{Co}(\text{R,R-ptn})_3]\text{Cl}_3$, orthorhombic, space group C222, $a = 19.89$, $b = 34.35$, $c = 16.30$ Å, $D_m = 1.263$, $D_x = 1.266$ g cm⁻³, $Z = 18$.

Accordingly the crystals of $(-)_546^-$ -tris(R,R-2,4-diaminopentane)cobalt(III) chloride are shown to be an optically pure mixture of dihydrate and anhydrate and not to be a pseudoracemate. Both crystals contain only one isomer, $\Delta(\text{lel}_3)-[\text{Co}(\text{R,R-ptn})_3]^{3+}$.

The crystals were then converted to perchlorate by the use of anion exchange resin(Dowex 1 X 8). The CD spectra of an aqueous solution showed a single negative peak ($\Delta\epsilon = -0.597$) at 518 nm (Fig. 1), which differed from those of the chloride and agreed with those previously reported for $(-)_546^-[\text{Co}(\text{R,R-ptn})_3](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$. These observations indicated that the solution CD spectra of this particular complex ion strongly depended upon the counter ions in the first absorption region, which comprised the complex salt. In order to interpret the effect, we have to admit an ion association between the complex and the counter ions. Owing to the smaller size, Cl^- ion is more liable to form an ion-pair than the bulky perchlorate, ClO_4^- . From conformational analyses six-membered chelate rings are known to be flexible i.e., the potential energy surface appears to have shallow minimum, and they can take more conformations than five-membered ring systems⁴⁾.

Such an ion association might affect the equilibrium among many conformers in solution. Details are now under investigation, which will be reported elsewhere.

It is recommended to record not only the complex cation but also the counter ion of the complex salt when the solution CD spectrum is reported.

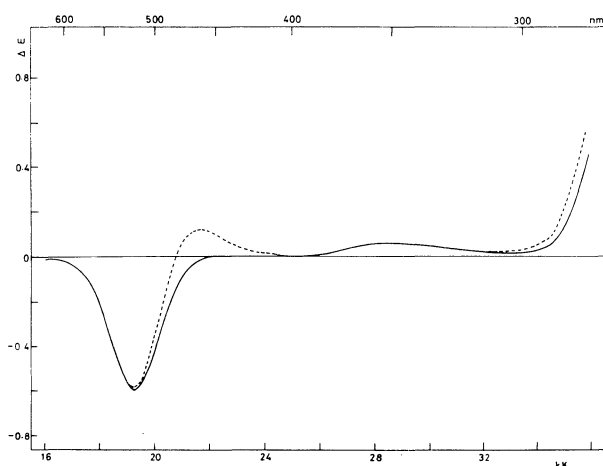


Fig. 1. The CD spectra of $\Delta(\text{lel}_3)-[\text{Co}(\text{R,R-ptn})_3]-\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ (-----) and $\Delta(\text{lel}_3)-[\text{Co}(\text{R,R-ptn})_3](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ (—) in water, 2.7×10^{-3} M.

REFERENCES

- 1) H. L. Smith, and B. E. Douglas, *Inorg. Chem.*, **5**, 784 (1966).
- 2) F. Mizukami, H. Ito, J. Fujita, and K. Saito, *Bull. Chem. Soc. Japan*, **45**, 2129 (1972).
- 3) A. Kobayashi, F. Marumo, and Y. Saito, *Acta Cryst.*, **B29**, 2443 (1973).
- 4) S. R. Niketić, and F. Woldbye, *Acta Chem. Scand.*, **27**, 621 (1973).

(Received January 13, 1975)