The Absolute Configuration of the Tris(trimethylenediamine)cobalt(III) Ion, $(-)_D$-$[\mathrm{Co\ tn_3}]^{3+}$

Yoshihiko SAITO, Teruo NOMURA and Fumiyuki MARUMO

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

(Received December 4, 1967)

In a series of our investigation on the absolute configurations of tris(bidentate)cobalt(III) complex ions,1-3) the absolute configuration of tris(trimethylenediamine)*1cobalt(III) ion, $[\mathrm{Co\ tn_3}]^{3+}$, has been determined. The crystal structure of $(-)_D$-tris(trimethylenediamine)cobalt(III) bromide monohydrate, $(-)_D$-$[\mathrm{Co\ tn_3}]\mathrm{Br_3}\cdot\mathrm{H_2O}$, has been determined by three-dimensional Fourier methods.4) The final R-value is 0.113 for 1890 observed reflections. The crystals were kindly supplied by Dr. Woldbye of the Technical University of Denmark. They are monoclinic with the space group $P2_1$: $a=16.274\pm0.009$ Å, $b=7.863\pm0.015$ Å, $c=9.489\pm0.005$ Å and $\beta=126.42°\pm0.06°$ ($\mathrm{Cu}K\alpha=1.5418$ Å). A perspective drawing of the complex ion is presented in Fig. 1. The complex ion has approximately a three-fold axis of rotation through the central cobalt atom. The three six membered Co-tn rings are nearly identical and take chair form. The chelate ring is rather flattened out, clearly owing to the strong H-H repulsion. Bond angles ∠CoNC are much larger than the normal tetrahedral angle, the average value being 117.4°. But the average value of ∠NCC and ∠CCC is 112.8°. The avarage ∠NCoN is 94.5°. The bond distances within the chelate ring are quite normal.

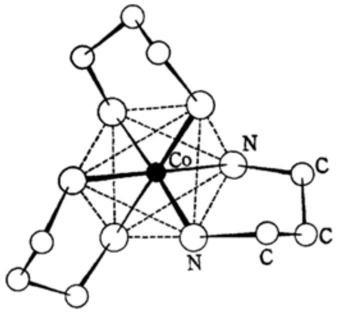

Fig. 1. A perspective drawing of the complex ion, $(-)_D$-$[\mathrm{Co\ tn_3}]^{3+}$.

The absolute configuration of the complex ion was determined by using absorption edge technique.5)

Some of the calculated intensities and observed relations between $I(hkl)$ and $I(h\bar{k}l)$, the latter being equivalent to $I(\bar{h}\bar{k}\bar{l})$ because of the symmetry of the space group, are compared in Table 1.

TABLE 1. DETERMINATION OF THE ABSOLUTE CONFIGURATION

Indices $h\ k\ l$	$F_c^2(hkl)$	obs.	$F_c^2(h\bar{k}l)$
$1\ 1\ \bar{2}$	2284	>	2174
$1\ 3\ 3$	380	>	369
$2\ 3\ 3$	374	>	310
$2\ 3\ \bar{3}$	394	>	319
$5\ 2\ \bar{5}$	576	<	654
$\bar{3}\ 1\ 2$	1287	<	1707
$\bar{4}\ 1\ 3$	331	<	534
$\bar{5}\ 1\ 4$	241	>	161

From these accordances in the table, it may be found that the complex ion, $[\mathrm{Co\ tn_3}]^{3+}$, shown in Fig. 1 corresponds to the laevorotatory form with respect to the Na D lines. Thus the absolute configuration of $(-)_D$-$[\mathrm{Co\ tn_3}]^{3+}$ can be represented by Δ according to the nomenclature proposed at the Meeting of the Commission on Inorganic Nomenclature of IUPAC, held at Beckenried, Switzerland in 1966. This configuration is enantiomeric to that assigned on the basis of the sign of the prominent Cotton effect.6) The ORD and CD of $[\mathrm{Co\ tn_3}]^{3+}$ have already been measured by Woldbye.8) A simple empirical rule8) relating the sign of the longer wavelength CD band and the absolute configuration of the chelate ring about the metal atom seems to hold in this case, too.

---

*1 tn: 1, 3 diaminopropane, $\mathrm{H_2N(CH_2)_3NH_2}$

1) Y. Saito, K. Nakatsu, M. Shiro and H. Kuroya, *Acta Cryst.*, **8**, 729 (1955), This Bulletin, **30**, 795 (1957).

2) Y. Saito, H. Iwasaki and H. Ota, *ibid.*, **36**, 1543 (1963).

3) H. Iwasaki and Y. Saito, *ibid.*, **39**, 92 (1966).

4) T. Nomura, F. Marumo and Y. Saito, *ibid.*, To be published.

5) J. M. Bijvoet, A. F. Peerdeman and A. J. van Bommel, *Nature*, **168**, 271 (1951).

6) R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, **1964**, 1368.

7) F. Woldbye, ORD of transition metal complexes, European Research Office, U. S. Army, Frankfurt a. M. (1959), Record of Chemical Progress, **24**, 197 (1963).

8) A. J. McCaffery, S. F. Mason and B. J. Norman, *Chem. Commn.*, **1965**, 49.