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The Crystal Structure of $(-)_D$-Tris(trimethylenediamine)cobalt(III) Bromide Monohydrate*[1]

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The structure of $(-)_D$-$[Co(tn)_3]Br_3 \cdot H_2O$ (tn: H_2N–CH_2–CH_2–CH_2–NH_2) has been solved by the heavy atom method and refined to $R=0.11$ by least-squares analysis based on 1845 three-dimensional data. The substance crystallizes in the monoclinic space group $P2_1$ with unit cell dimensions: $a=16.274$, $b=9.863$, $c=9.489$ Å, $\beta=126.4°$ and $Z=2$. The complex ion in the structure has approximately a three-fold axis of rotation. The three six-membered Co-tn rings are nearly identical and take chair form. The chelate ring is rather flattened out, owing to the strong H-H repulsion. The absolute configuration of $(-)_D$-$[Co(tn)_3]^{3+}$ has been found to be the same as that of $(+)_D$-$[Co(en)_3]^{3+}$.

The absolute configuration of the complex ions, $(+)_D$-$[Co(en)_3]^{3+}$ and $(-)_D$-$[Co(l\text{-}pn)_3]^{3+}$ have been determined by means of X-rays.[1-3] They have five-membered chelate rings. No investigation has, however, been made on the absolute configurations of the complex ions with six-membered chelate rings. One of the simplest of those is tris(trimethylenediamine)cobalt(III) ion, $[Co(tn)_3]^{3+}$. The ORD and CD of $[Co(tn)_3]^{3+}$ have been measured by Woldbye.[4,5] The present investigation of the crystal structure of $(-)_D$-tris(trimethylenediamine)cobalt(III) bromide

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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, This Bulletin, **36**, 1543 (1963).

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

4) F. Woldbye, "Optical Rotatory Dispersion of Transition Metal Complexes," European Research Office, U. S. Army, Frankfurt a. M. (1959).

5) F. Woldbye, *Record of Chemical Progress*, **24**, 197 (1963).

monohydrate was undertaken with the purpose of contributing a better knowledge about the relation of the absolute configuration and optical properties of transition metal complexes.

Experimental

$(-)_D$-Tris(trimethylenediamine)cobalt(III) bromide monohydrate was kindly supplied by Professor Woldbye, Technical University of Denmark. Single crystals suitable for X-ray work were grown by slow evaporation of aqueous solution at room temperature. The specimens used for the collection of the intensity data were polished into cylinders of diameter 0.07 cm, the axes being parallel to the *b*- and *c*-axis, respectively. Using Cu$K\alpha$ radiation, equi-inclination Weissenberg photographs were taken of the zero to sixth levels for the crystal rotating about the *b*-axis and the zero to ninth level of the *c*-axis rotation. The intensities were measured visually using standard calibrated scales and were converted to structure amplitude values in the usual way. Correction was also made for absorption by assuming the crystal to be a perfect cylinder. It was soon found that the intensity data obtained with the *c*-axis rotation are not very accurate owing to the ill-formed shape of the specimen, so that they were eliminated from the final set of data used for the refinement. A total of 1845 independent pieces of intensity data were collected.

The crystal data are as follows: $[Co(H_2N\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}NH_2)_3]Br_3\cdot H_2O$, F.W.=538.6, Monoclinic, space group $P2_1$ (No. 4*[3]), $a=16.275(10)$, $b=7.863(15)$, $c=9.489(5)$ Å, $\beta=126.4(1)°$, $U=970$ Å^3, (Cu$K\alpha$ radiation, $\lambda=1.5418$ Å), $D_m=1.80$ g·cm^{-3}, $Z=2$, $D_x=1.79$ g·cm^{-3}. Linear absorption coefficient for Cu$K\alpha$ radiation $\mu=154.0$ cm^{-1}.

Determination of the Structure

A three-dimensional Patterson synthesis was calculated, in order to seek the heavy atom-heavy atom vectors. This normal Patterson synthesis was, however, found to be inadequate for this purpose since rather serious overlappings of peaks were observed. To reduce the overlappings a Patterson synthesis was calculated with only the reflections, of which $\sin\theta/\lambda \gtrsim 0.45$. These reflections were supposed to consist mainly of the contributions of the heavy atoms. The peaks were sharpened to a good extent. The interpretation of the Patterson synthesis was not so straightforward because there exist as many as eight heavy atoms in the unit cell (6 Br and 2 Co). After several trials positions of the heavy atoms could be assigned. The coordinates of these atoms were refined by a block-diagonal least-squares method. The discrepancy factor, $R=\sum||F_o|-|F_c||/\sum|F_o|$, decreased to 0.27. A three-dimensional Fourier synthesis with phases determined by the heavy atoms allowed the six nitrogen atoms to be located around the cobalt atom. After further refinements a Fourier synthesis of electron density and a difference synthesis revealed the positions of the rest of all the lighter atoms except those of hydrogen atoms and also indicated that anisotropic temperature factors were required for all the atoms. After several cycles of least-squares refinement with anisotropic thermal parameters, the discrepancy factor was 0.11. The absolute configuration of the complex ion was automatically determined when dispersion corrections were taken into account during the course of the refinement. Part of observed and calculated relations between hkl and $h\bar{k}l$ are compared in Table 1. A final difference Fourier synthesis gave no significant indications of the positions of hydrogen atoms. Atomic scattering factors were taken from International Tables for X-ray Crystallography.[6] Dispersion corrections were also taken from the International Tables. The Fourier synthesis program used is ANSFR-1 written by Dr. H. Iwasaki, in which the anomalous scattering is taken into consideration. The least-squares program is HBLS-III written by Dr. T. Ashida. The weights were assumed as 1 for all

TABLE 1. CALCULATED AND OBSERVED INTENSITY RELATIONS BETWEEN hkl AND $h\bar{k}l$

$h\ k\ l$	$Fc^2(hkl)/4$	Obsd	$Fc^2(h\bar{k}l)/4$
$1\ 1\ \bar{2}$	2284	>	2174
$3\ 1\ \bar{2}$	1287	<	1707
$3\ 1\ \bar{4}$	38.1	>	30.9
$4\ 1\ \bar{3}$	330.5	<	533.6
$5\ 1\ \bar{4}$	240.9	>	160.8
$5\ 1\ \bar{9}$	8.4	>	3.4
$6\ 1\ \bar{5}$	170.8	<	199.1
$6\ 1\ \bar{9}$	8.5	<	9.9
$7\ 1\ \bar{6}$	206.8	<	238.1
$8\ 1\ \bar{3}$	634.0	>	448.2
$9\ 1\ \bar{3}$	377.1	<	507.6
$10\ 1\ \bar{3}$	124.3	<	196.0
$11\ 1\ \bar{3}$	173.7	>	110.7
$12\ 1\ \bar{3}$	56.4	<	72.1
$2\ 2\ 3$	98.8	>	92.7
$2\ 2\ \bar{9}$	1.9	<	2.3
$3\ 2\ \bar{4}$	500.0	>	462.3
$4\ 2\ \bar{3}$	390.1	<	411.3
$4\ 2\ \bar{8}$	9.9	>	6.6
$4\ 2\ \bar{9}$	7.8	<	9.5
$5\ 2\ \bar{5}$	576.0	<	653.8
$6\ 2\ \bar{8}$	6.7	<	14.2
$7\ 2\ \bar{7}$	17.4	>	15.0
$1\ 3\ 3$	379.9	>	368.6
$2\ 3\ \bar{3}$	393.6	>	318.6
$2\ 3\ 3$	374.4	>	310.1

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*[3] $P2_1/m$ is excluded since the crystal is optically active.

[6] International Tables for X-ray Crystallography, Vol. III, Kynoch Press, Birmingham (1962).

reflections in the least-squares refinements. The final three dimensional electron density map is shown in Fig. 1. The final parameters are given in Tables 2 and 3. Agreement between the observed and calculated structure amplitudes is reasonable.*4 The standard deviations of the coordinates, estimated from least-squares results, are 0.005 Å for the bromine and cobalt atoms and 0.03 Å (mean) for others.

TABLE 2. FINAL FRACTIONAL COORDINATES AND THEIR e. s. d.'s

Atom	$x(\sigma(x))\times10^4$	$y(\sigma(y))\times10^4$	$z(\sigma(z))\times10^4$
Co	2373(3)	4587(7)	4293(5)
Br(1)	0683(3)	0000(6)	0958(4)
Br(2)	2704(3)	0730(6)	6770(5)
Br(3)	4111(3)	2083(8)	2622(5)
N(1)	1969(19)	4005(47)	2007(33)
N(2)	2783(16)	5030(36)	6806(28)
N(3)	1305(16)	6401(34)	3412(27)
N(4)	1446(16)	2712(35)	4081(30)
N(5)	3392(15)	2706(35)	5232(29)
N(6)	3386(17)	6386(37)	4913(31)
C(1)	0751(25)	3133(51)	4532(55)
C(2)	0647(22)	6380(52)	3981(43)
C(3)	0060(25)	4692(58)	3524(54)
C(4)	3868(21)	5053(63)	8283(37)
C(5)	4387(20)	3354(46)	8444(36)
C(6)	4415(20)	2978(48)	6882(39)
C(7)	3151(22)	7485(55)	3486(37)
C(8)	1969(21)	5398(46)	0973(34)
C(9)	2972(25)	6419(59)	1964(44)
O	2192(15)	2397(41)	8406(26)

Description of the Structure and Discussion

A projection of the contents of an asymmetric unit onto the plane (010) is presented in Fig. 2. The bond lengths and bond angles with their

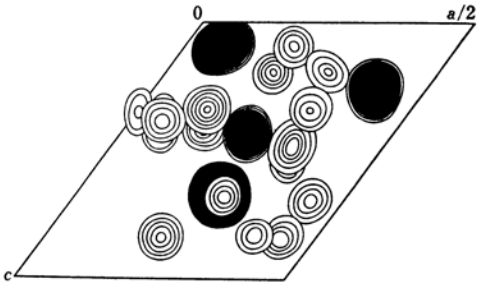

Fig. 1. The final three-dimensional electron density map composed of sections through the atomic centers parallel to (010). The contours are drawn at intervals of $1.0\,\mathrm{e.Å}^3$, starting with $1.0\,\mathrm{e.Å}^{-3}$.

TABLE 3. FINAL THERMAL PARAMETERS AND THEIR e. s. d.*
Temperature factors are of the form: $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$.

Atom	$\beta_{11}\times10^5$	$\beta_{22}\times10^5$	$\beta_{33}\times10^5$	$\beta_{12}\times10^5$	$\beta_{13}\times10^5$	$\beta_{23}\times10^5$
Co	00695(0)	02987(2)	02962(1)	00021(0)	00892(0)	−00143(2)
Br(1)	01011(0)	03502(2)	03136(1)	00253(0)	00720(0)	−00089(1)
Br(2)	01293(0)	03155(2)	03779(1)	−00065(0)	01267(0)	−00212(1)
Br(3)	01040(0)	05566(2)	03438(1)	00820(0)	01128(0)	−00032(2)
N(1)	01076(1)	04938(16)	03509(11)	00121(4)	01278(2)	−00120(11)
N(2)	00965(1)	02758(10)	02073(8)	00086(3)	00958(1)	−00152(9)
N(3)	00848(1)	03257(11)	02771(8)	−00277(3)	00975(1)	−00447(8)
N(4)	00924(1)	02729(10)	03554(10)	00035(3)	01263(2)	−00168(8)
N(5)	00726(1)	02986(10)	03197(9)	00098(2)	00906(1)	−00200(8)
N(6)	00897(1)	03835(13)	03401(10)	00167(3)	01165(2)	00612(9)
C(1)	01172(2)	03358(16)	07166(23)	−00042(4)	02239(3)	00726(16)
C(2)	00926(1)	04254(17)	04093(14)	00000(4)	01326(2)	00079(13)
C(3)	01247(2)	03262(17)	07320(23)	00353(5)	02133(3)	00586(18)
C(4)	00958(1)	05319(20)	02964(11)	00497(5)	00797(2)	−00036(15)
C(5)	00828(1)	03242(14)	02801(10)	00157(3)	00651(2)	00384(10)
C(6)	00807(1)	03522(14)	03356(12)	00116(3)	00940(2)	00310(11)
C(7)	01007(1)	04382(17)	03028(11)	00202(4)	01035(2)	−00103(13)
C(8)	01059(1)	03407(14)	02631(10)	−00284(4)	01002(2)	00089(10)
C(9)	01284(2)	05415(22)	03954(14)	−00456(5)	01644(3)	−00189(15)
O	01170(1)	05049(13)	03278(8)	00317(3)	01162(1)	00016(10)

[*4] A complete list of the observed and calculated structure factors has been submitted to and is kept as Document No. 6902 at the office of the Bulletin of the Chemical Society of Japan, 1—5 Kanda-Surugadai, Chiyoda-ku, Tokyo. A copy may be secured by citing the Doument number and by remitting, in advance, ¥ 1,600 for photo prints. Pay by check or money order, payable to: Chemical Society of Japan.

e.s.d.'s are listed in Table 4, and pertinent intermolecular contacts (*i. e.,* those less than 4.5 Å) are given in Table 5.

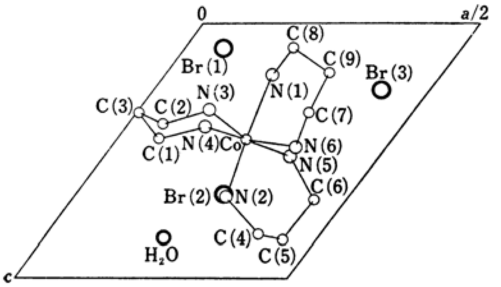

Fig. 2. The structure in an asymmetric unit, viewed along the *b*-axis.

TABLE 4. THE BOND LENGTHS AND BOND ANGLES IN THE COMPLEX ION, $(-)_D$-$[Co(tn)_3]^{3+}$

Their e. s. d.'s are given in parentheses.

Co–N (1)	2.00(3) Å	Co–N (4)	2.00(3) Å
Co–N (2)	2.00(3)	Co–N (5)	2.00(3)
Co–N (3)	2.00(3)	Co–N (6)	2.00(3)
N (1)–C (8)	1.47(5)	N (2)–C (4)	1.47(3)
N (6)–C (7)	1.45(5)	N (4)–C (1)	1.47(7)
N (5)–C (6)	1.48(3)	N (3)–C (2)	1.46(6)
C (8)–C (9)	1.54(5)	C (5)–C (4)	1.54(6)
C (9)–C (7)	1.54(6)	C (1)–C (3)	1.55(5)
C (6)–C (5)	1.54(6)	C (2)–C (3)	1.54(6)
∠N(1)CoN(6)	96(1)°	∠N(1)C(8)C(9)	114(2)°
∠N(2)CoN(5)	92(1)	∠N(6)C(7)C(9)	110(3)
∠N(3)CoN(4)	95(1)	∠N(5)C(6)C(5)	113(3)
		∠N(2)C(4)C(5)	111(3)
∠CoN(1)C(8)	117(2)	∠N(4)C(1)C(3)	114(4)
∠CoN(6)C(7)	118(2)	∠N(3)C(2)C(3)	112(3)
∠CoN(5)C(6)	118(2)		
∠CoN(2)C(4)	119(2)	∠C(7)C(9)C(8)	114(4)
∠CoN(4)C(1)	116(3)	∠C(4)C(5)C(6)	114(3)
∠CoN(3)C(2)	117(2)	∠C(1)C(3)C(2)	114(3)

TABLE 5. INTERMOLECULAR CONTACTS LESS THAN 4.5 Å AND THEIR e. s. d.'s IN PARENTHESES

The following superscripts are used for this table.

′	x,	$y+1/2$,	z
″	$-x$,	$y+1/2$,	$1-z$
‴	$1-x$,	$y+1/2$,	$1-z$

Co–Br(1)	4.533(9) Å	Br(1)–N(1)	3.58(4) Å
Co–Br(2)	4.627(11)	Br(1)–N(4)	3.24(3)
Co–Br(3)	4.510(9)	Br(2)–N(3)	3.44(3)
Co–Br(1″)	4.544(9)	Br(2)–N(5)	3.55(3)
Co–Br(2′)	4.183(9)	Br(3)–N(1)	3.52(3)
		Br(3)–N(5)	3.34(3)
O–Co	4.35(3)	Br(1′)–N(3)	3.41(3)
O–Br(2)	3.27(3)	Br(2′)–N(2)	3.43(3)
O–N(2)	3.04(4)	Br(2′)–N(3)	3.44(3)
O–N(4)	3.53(4)	Br(2′)–N(6)	3.33(3)
O–N(5)	4.46(5)	Br(3‴)–N(6)	3.33(3)

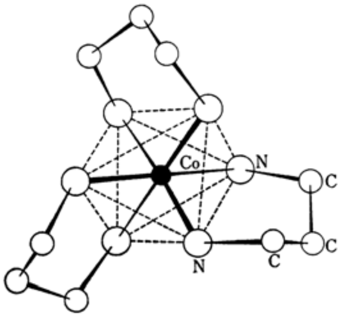

Fig. 3. A drawing of the complex ion, $(-)_D$-$[Co(tn)_3]^{3+}$, viewed along the approximate three-fold axis through the cobalt atom.

The complex cation, $[Co(tn)_3]^{3+}$, has approximately a three-fold symmetry. A projection of the complex ion along its approximate three-fold axis is shown in Fig. 3. The three chelate rings are nearly but not exactly identical and take chair forms, in contrast to a puckered form of the five-membered chelate rings formed by ethylenediamine. The six-membered ring seems to be more flexible than the five-membered ring. Its conformation may be easily affected by the specific intermolecular forces in the crystal. The chelate ring is rather flattened out due to non-bonded hydrogen interactions. Bond angles Co–N–C are larger than the normal tetrahedral angle, the mean value being 117.4°. This value does not differ significantly from those found in the six-membered ring in *trans*-dichloro(1,4,8,11-tetraazacyclotetradecane)nickel(II).[7] But the mean value of N–C–C and C–C–C angles is 112.8°, which is closer to the normal tetrahedral angle. The N–Co–N angle is larger than 90°, the mean value being 94.5°. The interatomic distances are normal as shown in Table 4. The displacement of the nitrogen atoms from the regular octahedral position is recognized in Fig. 3. The displacements are quite irregular. Distortions of the chelate rings described above and of octahedral coordination appear to make the complex less stable than that with five-membered chelate rings.[8] It is to be noted here that the chair conformation of the metal-trimethylenediamine ring is maintained in various complexes with multidentate chelating agents that contain these amines as their fragments.

A complex cation is surrounded by six bromide anions. Eight closest Br–N approaches occur at distances ranging from 3.24 Å to 3.44 Å. The

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[7] B. Bosnich, C. K. Poon and M. L. Tobe, *Inorg. Chem.,* **4**, 1102, 1109 (1965).

[8] J. C. Bailar, Jr., and J. B. Work, *J. Am. Chem. Soc.,* **68**, 232 (1946).

closest O–N contact occurs at a distance of 3.04 Å between O and N(2), whereas the van der Waals radii are 1.92 Å for Br, 1.50 Å for N and 1.40 Å for O. The molecule of water of crystallization has contact to Br(2) with a distance of 3.27 Å.

The absolute configuration of the complex ion, $(-)_D$-$[Co(tn)_3]^{3+}$, is represented in Fig. 3, which has the same absolute configuration as that of $(+)_D$-$[Co(en)_3]^{3+}$ and may be denoted by Λ.[9] The optical rotatory dispersion and circular dichroism spectra of the complex ion has been measured by Woldbye. Its absolute configuration is enantiomeric to that assigned on the basis of the sign of the prominent Cotton effect.[10,11] Woldbye has assigned correctly its absolute configuration by examining the behavior of CD spectra in the presence of phosphate ions.[12] The complex ions, $(-)_D$-$[Co(tn)_3]^{3+}$ and $(+)_D$-$[Co(en)_3]^{3+}$ have similar circular dichroism spectra and consequently the sign of the Cotton effect of a particular transition does not depend on the N–Co–N ring angle, as some workers suppose.[13]

A simple empirical rule 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.[14]

The rotatory strength of $[Co(tn)_3]^{3+}$ was found to be smaller than that of $[Co(en)_3]^{3+}$ by a factor of ten. This ring size effect seems natural in view of Moffit's model[15] for the tris(bidentate) complexes, in which he ascribed the optical activity to the crowding of the carbon chains of the ligands in space, the crowding becoming greater the shorter the chain. The difference in rotatory strength may also be attributable to the difference in the conformation of the chelate ring. In the cobalt-ethylenediamine ring the two carbon atoms are arranged symmetrically above and below the plane formed by the central metal atom and the two nitrogen atoms, while in the cobalt-trimethylenediamine ring the three methylene groups are located on one side of the plane of the cobalt and the two nitrogen atoms and each chelate ring has approximately a mirror symmetry.

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[9] IUPAC Information Bulletin, No. 33, p. 68 (1968).

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[14] A. G. McCaffery, S. F. Mason and B. J. Norman, *Chem. Commun.*, **1965**, 49.

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