

four corners, [two O(4) and two O(5), Table 1], with neighbouring MoO octahedra in the same plane perpendicular to the  $y$  direction. The Mo–O distances in such a plane can be divided in two classes, the first with bond lengths of *ca.* 1.75 Å and the second with bond lengths of *ca.* 2.24 Å. The other two apex ions of the MoO octahedra, [O(1) and O(6), Table 1], point towards a  $(\text{BiO}^+)_{2N}$  layer, one above and one below. These Mo–O bonds have intermediate lengths, 1.85 Å and 1.93 Å respectively (Table 2).

As all the bismuth ions have been shifted towards smaller  $a$  coordinates relatively to the oxygen ions in the BiO planes, [O(2) and O(3), Table 1], the Bi–O distances in that plane can be divided in two groups,

distances shorter than 2.3 Å and distances exceeding that value (Table 2). Each bismuth ion shares two more oxygen ions at approximate distances of 2.33 Å and 2.66 Å, [O(6) and O(1), Table 1] with two neighbouring MoO octahedra.

The authors want to thank the Smithsonian Institution, Washington D.C., for generously providing some crystals, Dr E. Keulen for collecting the X-ray data at the Philips Research Laboratories at Eindhoven, Dr A. S. Koster for conscientiously reading the manuscript and the Nederlandse Organisatie voor Zuiver Wetenschappelijk Onderzoek for a fellowship to A. F. van den Elzen.

Table 2. *Interatomic distances in koechlinite*

|            |          |            |          |
|------------|----------|------------|----------|
| Bi(1)–O(3) | 2.50 (8) | Bi(2)–O(1) | 2.72 (2) |
| Bi(1)–O(3) | 2.15 (8) | Bi(2)–O(1) | 2.29 (2) |
| Bi(1)–O(3) | 2.29 (8) | Bi(2)–O(2) | 2.21 (6) |
| Bi(1)–O(3) | 2.36 (7) | Bi(2)–O(2) | 2.50 (6) |
| Bi(1)–O(6) | 2.62 (3) | Bi(2)–O(2) | 2.33 (6) |
| Bi(1)–O(6) | 2.37 (3) | Bi(2)–O(2) | 2.25 (6) |
| Mo(1)–O(1) | 1.86 (3) |            |          |
| Mo(1)–O(4) | 2.24 (2) |            |          |
| Mo(1)–O(4) | 1.76 (2) |            |          |
| Mo(1)–O(5) | 2.24 (2) |            |          |
| Mo(1)–O(5) | 1.75 (3) |            |          |
| Mo(1)–O(6) | 1.93 (3) |            |          |

### References

- BATIST, P. A., BOUWENS, J. F. H. & SCHUIT, G. C. A. (1968). *J. Catal.* **12**, 45–60.
- JEFFERY, J. W. & ROSE, K. M. (1964). *Acta Cryst.* **17**, 343–350.
- RIETVELD, H. M. (1966). Fysica Memo No. 153. Stichting Reactor Centrum Nederland.
- SCHULZ, H. (1971). *Acta Cryst.* **A27**, 540–544.
- SCHULZ, H. & HUBER, P. J. (1971). *Acta Cryst.* **A27**, 536–539.
- Structure Reports for 1947–1948.* (1951). **11**, 305–310.
- ZEMANN, J. (1956). *Heidelb. Beitr. Miner. Petrogr.* **5**, 139–145.

*Acta Cryst.* (1973). **B29**, 2438

## The Crystal Structure of $(-)_589$ -Tris-(1,3-diaminopropane)cobalt(III) Chloride Monohydrate, $(-)_589$ - $[\text{Co}(\text{tn})_3]\text{Cl}_3 \cdot \text{H}_2\text{O}$

BY RUMIKA NAGAO, FUMIYUKI MARUMO\* AND YOSHIHIKO SAITO

*The Institute for Solid State Physics, The University of Tokyo, Roppongi-7, Minato-ku, Tokyo 106, Japan*

(Received 28 April 1973; accepted 13 June 1973)

Crystals of  $(-)_589$ - $[\text{Co}(\text{tn})_3]\text{Cl}_3 \cdot \text{H}_2\text{O}$  are monoclinic with space group  $P2_1$ . The cell dimensions are:  $a = 12.871$  (6),  $b = 7.545$  (2),  $c = 9.360$  (6) Å and  $\beta = 91.17$  (6)°, with two formula units in the unit cell. The structure was refined by anisotropic block-diagonal least-squares methods to an  $R$  value of 0.033 for 2806 observed reflexions collected by the diffractometer method. The structure is isotopic with its bromide analogue. The complex ion has an approximate threefold axis of rotation. The absolute configuration is  $\Lambda$ . The three six-membered chelate rings have the chair conformation. In one of the chelate rings the carbon atoms exhibit much greater thermal motion relative to those in the other chelate rings, suggesting a change in conformation in solution.

### Introduction

Six-membered chelate rings have been a subject of extensive study on coordination compounds by the method of strain-energy minimization. Calculated values of conformational energy, however, are different

according to the choice of potential function (Geue & Snow, 1971; Gollogly & Hawkins, 1972; Niketić & Woldbye, 1973). Thus we have to rely primarily on the results of structure determination. The tris-(1,3-diaminopropane)cobalt(III) ion represents a prototype of a tris(bidentate) complex with three saturated six-membered chelate rings. The geometry of this complex ion was determined by crystal-structure analysis of  $(-)_589$ - $[\text{Co}(\text{tn})_3]\text{Br}_3 \cdot \text{H}_2\text{O}$  (Nomura, Marumo & Sai-

\* Present address: Tokyo Institute of Technology, Ohokayama, Meguro-ku, Tokyo 152, Japan.

Table 1. Atomic parameters

(a) Positional and thermal parameters of the non-hydrogen atoms ( $\times 10^4$ ), with their e.s.d.'s in parentheses.The  $\beta_{ij}$ 's are defined by:

$$\exp [-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})].$$

|       | <i>x</i> | <i>y</i>  | <i>z</i>  | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|-------|----------|-----------|-----------|--------------|--------------|--------------|--------------|--------------|--------------|
| Co    | 2362 (0) | 4566 (1)  | 1949 (0)  | 23 (0)       | 62 (1)       | 67 (0)       | 2 (1)        | 4 (0)        | -10 (1)      |
| Cl(1) | 629 (1)  | -30 (1)   | 287 (1)   | 51 (1)       | 113 (2)      | 134 (1)      | 28 (1)       | -57 (1)      | -45 (2)      |
| Cl(2) | 2681 (1) | -722 (1)  | 3950 (1)  | 84 (1)       | 84 (2)       | 139 (1)      | 3 (2)        | -36 (2)      | -30 (2)      |
| Cl(3) | 4138 (1) | 2118 (2)  | -1438 (1) | 51 (1)       | 283 (3)      | 125 (1)      | 96 (2)       | -5 (2)       | -106 (4)     |
| N(1)  | 1216 (2) | 6287 (4)  | 2063 (3)  | 34 (2)       | 95 (5)       | 76 (3)       | 15 (5)       | 20 (4)       | 14 (7)       |
| N(2)  | 1407 (2) | 2680 (4)  | 2581 (3)  | 37 (2)       | 84 (5)       | 86 (4)       | -23 (5)      | 19 (4)       | -11 (7)      |
| N(3)  | 2803 (2) | 4994 (4)  | 3943 (3)  | 35 (2)       | 85 (5)       | 81 (3)       | 2 (4)        | -19 (4)      | -16 (6)      |
| N(4)  | 3462 (2) | 2711 (4)  | 1783 (4)  | 34 (2)       | 94 (5)       | 119 (4)      | 29 (5)       | 20 (4)       | -10 (8)      |
| N(5)  | 3314 (2) | 6489 (4)  | 1391 (4)  | 30 (2)       | 103 (5)      | 120 (5)      | -10 (5)      | -1 (4)       | 34 (8)       |
| N(6)  | 1939 (2) | 4111 (4)  | -69 (3)   | 41 (2)       | 118 (6)      | 89 (4)       | 1 (5)        | 8 (4)        | -4 (7)       |
| C(1)  | 491 (3)  | 6302 (6)  | 3276 (5)  | 46 (2)       | 136 (7)      | 117 (5)      | 48 (7)       | 64 (6)       | 19 (11)      |
| C(2)  | -51 (4)  | 4542 (10) | 3399 (7)  | 81 (3)       | 199 (10)     | 274 (11)     | 46 (14)      | 207 (10)     | 118 (25)     |
| C(3)  | 554 (4)  | 2999 (7)  | 3572 (7)  | 63 (3)       | 158 (9)      | 244 (11)     | -54 (9)      | 148 (10)     | -24 (16)     |
| C(4)  | 3930 (3) | 5028 (5)  | 4372 (5)  | 42 (2)       | 126 (7)      | 115 (5)      | -25 (6)      | -62 (5)      | 10 (10)      |
| C(5)  | 4463 (3) | 3309 (6)  | 4029 (5)  | 35 (2)       | 150 (8)      | 155 (7)      | 14 (7)       | -45 (6)      | 70 (12)      |
| C(6)  | 4507 (3) | 2914 (6)  | 2475 (6)  | 28 (2)       | 136 (8)      | 176 (7)      | 37 (6)       | 11 (6)       | 61 (12)      |
| C(7)  | 3121 (3) | 7614 (5)  | 122 (5)   | 42 (2)       | 114 (7)      | 125 (6)      | -8 (6)       | 26 (6)       | 59 (10)      |
| C(8)  | 2921 (3) | 6544 (7)  | -1197 (5) | 55 (3)       | 185 (9)      | 104 (5)      | -2 (8)       | 55 (6)       | 54 (12)      |
| C(9)  | 1911 (3) | 5535 (6)  | -1164 (4) | 49 (3)       | 173 (9)      | 84 (5)       | 21 (8)       | 17 (5)       | 28 (10)      |
| O     | 2337 (3) | 2318 (5)  | 6256 (4)  | 73 (2)       | 191 (7)      | 130 (5)      | 28 (7)       | -25 (5)      | -17 (10)     |

to 1969). However, heavy bromide ions prevented us from obtaining accurate structural parameters. Accordingly the crystal structure of  $(-)\text{-}_{589}\text{-}[\text{Co}(\text{tn})_3]\text{Cl}_3 \cdot \text{H}_2\text{O}$  has been determined in order to obtain conformational details of the complex ion.

### Experimental

$(-)\text{-}_{589}\text{-}[\text{Co}(\text{tn})_3]\text{Br}_3 \cdot \text{H}_2\text{O}$  was converted to chloride by using Amberlite A.G. IRA-400. Crystals used for X-ray work were grown by slow evaporation of an aqueous solution. They are orange-red in colour and tabular. The cell dimensions were refined by a least-squares method, employing the data obtained on a single-crystal diffractometer with Mo  $K\alpha$  radiation ( $\lambda = 0.7107 \text{ \AA}$ ). The crystals are isostructural with  $[\text{Co}(\text{tn})_3]\text{Br}_3 \cdot \text{H}_2\text{O}$ ; the crystal data are:  $(-)\text{-}_{589}\text{-}[\text{Co}(\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_2)_3]\text{Cl}_3 \cdot \text{H}_2\text{O}$ , F.W.405.7, monoclinic;  $a = 12.871 (6)$ ,  $b = 7.545 (2)$ ,  $c = 9.360 (6) \text{ \AA}$  and  $\beta = 91.17 (6)^\circ$ ,  $U = 908.8 \text{ \AA}^3$ ;  $D_m = 1.48 \text{ g cm}^{-3}$ ,  $Z = 2$ ,  $D_x = 1.48 \text{ g cm}^{-3}$ , linear absorption coefficient for Mo  $K\alpha$ ,  $\mu = 14.2 \text{ cm}^{-1}$ , space group  $P2_1$  (No. 4).

A crystal of dimensions  $0.4 \times 0.4 \times 0.4 \text{ mm}$  was mounted on a Rigaku automated four-circle diffractometer. Mo  $K\alpha$  radiation monochromated by a graphite crystal was used. 3014 reflexions were measured up to  $2\theta = 55^\circ$ , of which 2806 reflexions with  $|F| > 3\sigma$  were regarded as 'observed'. Three standard reflexions were measured every 50 reflexions. The intensities were corrected for Lorentz and polarization factors. No corrections for absorption or extinction were made.

Table 1 (cont.)

(b) Positional ( $\times 10^3$ ) and isotropic thermal parameters of the hydrogen atoms.

|        | <i>x</i> | <i>y</i> | <i>z</i> | <i>B</i> |
|--------|----------|----------|----------|----------|
| H(N1)  | 93 (3)   | 615 (7)  | 128 (5)  | 2.3      |
| H'(N1) | 157 (3)  | 759 (8)  | 204 (5)  | 2.0      |
| H(N2)  | 183 (4)  | 183 (8)  | 296 (5)  | 2.8      |
| H'(N2) | 105 (4)  | 214 (9)  | 162 (6)  | 4.1      |
| H(N3)  | 251 (3)  | 423 (7)  | 462 (4)  | 1.1      |
| H'(N3) | 257 (3)  | 593 (7)  | 423 (5)  | 1.3      |
| H(N4)  | 346 (3)  | 256 (7)  | 84 (5)   | 2.2      |
| H'(N4) | 312 (4)  | 169 (8)  | 214 (6)  | 3.7      |
| H(N5)  | 387 (4)  | 607 (7)  | 142 (5)  | 2.7      |
| H'(N5) | 329 (3)  | 724 (7)  | 219 (5)  | 1.9      |
| H(N6)  | 116 (3)  | 357 (7)  | -4 (5)   | 2.5      |
| H'(N6) | 234 (4)  | 337 (9)  | -12 (7)  | 5.7      |
| H(C1)  | 85 (4)   | 661 (10) | 416 (7)  | 6.1      |
| H'(C1) | -6 (4)   | 716 (8)  | 307 (5)  | 2.2      |
| H(C2)  | -51 (3)  | 486 (8)  | 430 (5)  | 2.7      |
| H'(C2) | -52 (5)  | 437 (11) | 244 (7)  | 8.0      |
| H(C3)  | 99 (4)   | 321 (8)  | 474 (6)  | 4.0      |
| H'(C3) | 20 (4)   | 187 (8)  | 350 (6)  | 3.1      |
| H(C4)  | 422 (3)  | 612 (7)  | 375 (5)  | 1.5      |
| H'(C4) | 396 (3)  | 519 (6)  | 546 (5)  | 1.3      |
| H(C5)  | 515 (4)  | 337 (8)  | 442 (5)  | 3.4      |
| H'(C5) | 419 (3)  | 244 (7)  | 452 (5)  | 1.8      |
| H(C6)  | 486 (3)  | 378 (7)  | 198 (5)  | 2.3      |
| H'(C6) | 487 (3)  | 192 (7)  | 232 (5)  | 1.9      |
| H(C7)  | 252 (3)  | 841 (7)  | 53 (5)   | 2.3      |
| H'(C7) | 365 (3)  | 839 (7)  | 4 (5)    | 2.2      |
| H(C8)  | 278 (4)  | 744 (9)  | -207 (6) | 4.2      |
| H'(C8) | 337 (4)  | 541 (7)  | -138 (5) | 3.0      |
| H(C9)  | 144 (3)  | 629 (6)  | -99 (4)  | 0.8      |
| H'(C9) | 179 (3)  | 491 (8)  | -218 (5) | 2.8      |
| H(O)   | 245 (4)  | 125 (9)  | 584 (6)  | 4.3      |
| H'(O)  | 284 (4)  | 247 (9)  | 697 (6)  | 4.1      |

### Structure determination

Initial positional parameters for the non-hydrogen atoms were taken from the final parameters of the bro-

\* The choice of the *a* axis of this compound is different from that of the isomorphous bromide: **a-c** corresponds to the *a* axis of the bromide.

amide (Nomura, Marumo & Saito, 1969). The usual  $R$  index was 0.22 at this stage. The atomic positions and isotropic thermal parameters were refined by the least-squares method with the block-diagonal program *HBL5-4* written by Dr Ashida. With the introduction of anisotropic temperature factors further cycles of least-squares refinement reduced the  $R$  index to 0.11. A difference Fourier synthesis showed all the hydrogen atoms in plausible positions. Further refinement cycles were carried out with anisotropic temperature factors for non-hydrogen atoms and with isotropic temperature factors for hydrogen atoms. The final  $R$  index was 0.033 for the 2806 observed reflexions. At the final stage of the refinement, all the parameter shifts of non-hydrogen atoms were less than one tenth of their standard deviations. Unit weight was given to all the observed reflexions. The scattering factors for Co, N, C

Table 2 (cont.)

Table 2. Observed and calculated structure amplitudes

| h   | k | l | observed | calculated |
|-----|---|---|----------|------------|
| 1   | 0 | 0 | 100      | 100        |
| 2   | 0 | 0 | 100      | 100        |
| 3   | 0 | 0 | 100      | 100        |
| 4   | 0 | 0 | 100      | 100        |
| 5   | 0 | 0 | 100      | 100        |
| 6   | 0 | 0 | 100      | 100        |
| 7   | 0 | 0 | 100      | 100        |
| 8   | 0 | 0 | 100      | 100        |
| 9   | 0 | 0 | 100      | 100        |
| 10  | 0 | 0 | 100      | 100        |
| 11  | 0 | 0 | 100      | 100        |
| 12  | 0 | 0 | 100      | 100        |
| 13  | 0 | 0 | 100      | 100        |
| 14  | 0 | 0 | 100      | 100        |
| 15  | 0 | 0 | 100      | 100        |
| 16  | 0 | 0 | 100      | 100        |
| 17  | 0 | 0 | 100      | 100        |
| 18  | 0 | 0 | 100      | 100        |
| 19  | 0 | 0 | 100      | 100        |
| 20  | 0 | 0 | 100      | 100        |
| 21  | 0 | 0 | 100      | 100        |
| 22  | 0 | 0 | 100      | 100        |
| 23  | 0 | 0 | 100      | 100        |
| 24  | 0 | 0 | 100      | 100        |
| 25  | 0 | 0 | 100      | 100        |
| 26  | 0 | 0 | 100      | 100        |
| 27  | 0 | 0 | 100      | 100        |
| 28  | 0 | 0 | 100      | 100        |
| 29  | 0 | 0 | 100      | 100        |
| 30  | 0 | 0 | 100      | 100        |
| 31  | 0 | 0 | 100      | 100        |
| 32  | 0 | 0 | 100      | 100        |
| 33  | 0 | 0 | 100      | 100        |
| 34  | 0 | 0 | 100      | 100        |
| 35  | 0 | 0 | 100      | 100        |
| 36  | 0 | 0 | 100      | 100        |
| 37  | 0 | 0 | 100      | 100        |
| 38  | 0 | 0 | 100      | 100        |
| 39  | 0 | 0 | 100      | 100        |
| 40  | 0 | 0 | 100      | 100        |
| 41  | 0 | 0 | 100      | 100        |
| 42  | 0 | 0 | 100      | 100        |
| 43  | 0 | 0 | 100      | 100        |
| 44  | 0 | 0 | 100      | 100        |
| 45  | 0 | 0 | 100      | 100        |
| 46  | 0 | 0 | 100      | 100        |
| 47  | 0 | 0 | 100      | 100        |
| 48  | 0 | 0 | 100      | 100        |
| 49  | 0 | 0 | 100      | 100        |
| 50  | 0 | 0 | 100      | 100        |
| 51  | 0 | 0 | 100      | 100        |
| 52  | 0 | 0 | 100      | 100        |
| 53  | 0 | 0 | 100      | 100        |
| 54  | 0 | 0 | 100      | 100        |
| 55  | 0 | 0 | 100      | 100        |
| 56  | 0 | 0 | 100      | 100        |
| 57  | 0 | 0 | 100      | 100        |
| 58  | 0 | 0 | 100      | 100        |
| 59  | 0 | 0 | 100      | 100        |
| 60  | 0 | 0 | 100      | 100        |
| 61  | 0 | 0 | 100      | 100        |
| 62  | 0 | 0 | 100      | 100        |
| 63  | 0 | 0 | 100      | 100        |
| 64  | 0 | 0 | 100      | 100        |
| 65  | 0 | 0 | 100      | 100        |
| 66  | 0 | 0 | 100      | 100        |
| 67  | 0 | 0 | 100      | 100        |
| 68  | 0 | 0 | 100      | 100        |
| 69  | 0 | 0 | 100      | 100        |
| 70  | 0 | 0 | 100      | 100        |
| 71  | 0 | 0 | 100      | 100        |
| 72  | 0 | 0 | 100      | 100        |
| 73  | 0 | 0 | 100      | 100        |
| 74  | 0 | 0 | 100      | 100        |
| 75  | 0 | 0 | 100      | 100        |
| 76  | 0 | 0 | 100      | 100        |
| 77  | 0 | 0 | 100      | 100        |
| 78  | 0 | 0 | 100      | 100        |
| 79  | 0 | 0 | 100      | 100        |
| 80  | 0 | 0 | 100      | 100        |
| 81  | 0 | 0 | 100      | 100        |
| 82  | 0 | 0 | 100      | 100        |
| 83  | 0 | 0 | 100      | 100        |
| 84  | 0 | 0 | 100      | 100        |
| 85  | 0 | 0 | 100      | 100        |
| 86  | 0 | 0 | 100      | 100        |
| 87  | 0 | 0 | 100      | 100        |
| 88  | 0 | 0 | 100      | 100        |
| 89  | 0 | 0 | 100      | 100        |
| 90  | 0 | 0 | 100      | 100        |
| 91  | 0 | 0 | 100      | 100        |
| 92  | 0 | 0 | 100      | 100        |
| 93  | 0 | 0 | 100      | 100        |
| 94  | 0 | 0 | 100      | 100        |
| 95  | 0 | 0 | 100      | 100        |
| 96  | 0 | 0 | 100      | 100        |
| 97  | 0 | 0 | 100      | 100        |
| 98  | 0 | 0 | 100      | 100        |
| 99  | 0 | 0 | 100      | 100        |
| 100 | 0 | 0 | 100      | 100        |

| h   | k | l | observed | calculated |
|-----|---|---|----------|------------|
| 1   | 1 | 0 | 100      | 100        |
| 2   | 1 | 0 | 100      | 100        |
| 3   | 1 | 0 | 100      | 100        |
| 4   | 1 | 0 | 100      | 100        |
| 5   | 1 | 0 | 100      | 100        |
| 6   | 1 | 0 | 100      | 100        |
| 7   | 1 | 0 | 100      | 100        |
| 8   | 1 | 0 | 100      | 100        |
| 9   | 1 | 0 | 100      | 100        |
| 10  | 1 | 0 | 100      | 100        |
| 11  | 1 | 0 | 100      | 100        |
| 12  | 1 | 0 | 100      | 100        |
| 13  | 1 | 0 | 100      | 100        |
| 14  | 1 | 0 | 100      | 100        |
| 15  | 1 | 0 | 100      | 100        |
| 16  | 1 | 0 | 100      | 100        |
| 17  | 1 | 0 | 100      | 100        |
| 18  | 1 | 0 | 100      | 100        |
| 19  | 1 | 0 | 100      | 100        |
| 20  | 1 | 0 | 100      | 100        |
| 21  | 1 | 0 | 100      | 100        |
| 22  | 1 | 0 | 100      | 100        |
| 23  | 1 | 0 | 100      | 100        |
| 24  | 1 | 0 | 100      | 100        |
| 25  | 1 | 0 | 100      | 100        |
| 26  | 1 | 0 | 100      | 100        |
| 27  | 1 | 0 | 100      | 100        |
| 28  | 1 | 0 | 100      | 100        |
| 29  | 1 | 0 | 100      | 100        |
| 30  | 1 | 0 | 100      | 100        |
| 31  | 1 | 0 | 100      | 100        |
| 32  | 1 | 0 | 100      | 100        |
| 33  | 1 | 0 | 100      | 100        |
| 34  | 1 | 0 | 100      | 100        |
| 35  | 1 | 0 | 100      | 100        |
| 36  | 1 | 0 | 100      | 100        |
| 37  | 1 | 0 | 100      | 100        |
| 38  | 1 | 0 | 100      | 100        |
| 39  | 1 | 0 | 100      | 100        |
| 40  | 1 | 0 | 100      | 100        |
| 41  | 1 | 0 | 100      | 100        |
| 42  | 1 | 0 | 100      | 100        |
| 43  | 1 | 0 | 100      | 100        |
| 44  | 1 | 0 | 100      | 100        |
| 45  | 1 | 0 | 100      | 100        |
| 46  | 1 | 0 | 100      | 100        |
| 47  | 1 | 0 | 100      | 100        |
| 48  | 1 | 0 | 100      | 100        |
| 49  | 1 | 0 | 100      | 100        |
| 50  | 1 | 0 | 100      | 100        |
| 51  | 1 | 0 | 100      | 100        |
| 52  | 1 | 0 | 100      | 100        |
| 53  | 1 | 0 | 100      | 100        |
| 54  | 1 | 0 | 100      | 100        |
| 55  | 1 | 0 | 100      | 100        |
| 56  | 1 | 0 | 100      | 100        |
| 57  | 1 | 0 | 100      | 100        |
| 58  | 1 | 0 | 100      | 100        |
| 59  | 1 | 0 | 100      | 100        |
| 60  | 1 | 0 | 100      | 100        |
| 61  | 1 | 0 | 100      | 100        |
| 62  | 1 | 0 | 100      | 100        |
| 63  | 1 | 0 | 100      | 100        |
| 64  | 1 | 0 | 100      | 100        |
| 65  | 1 | 0 | 100      | 100        |
| 66  | 1 | 0 | 100      | 100        |
| 67  | 1 | 0 | 100      | 100        |
| 68  | 1 | 0 | 100      | 100        |
| 69  | 1 | 0 | 100      | 100        |
| 70  | 1 | 0 | 100      | 100        |
| 71  | 1 | 0 | 100      | 100        |
| 72  | 1 | 0 | 100      | 100        |
| 73  | 1 | 0 | 100      | 100        |
| 74  | 1 | 0 | 100      | 100        |
| 75  | 1 | 0 | 100      | 100        |
| 76  | 1 | 0 | 100      | 100        |
| 77  | 1 | 0 | 100      | 100        |
| 78  | 1 | 0 | 100      | 100        |
| 79  | 1 | 0 | 100      | 100        |
| 80  | 1 | 0 | 100      | 100        |
| 81  | 1 | 0 | 100      | 100        |
| 82  | 1 | 0 | 100      | 100        |
| 83  | 1 | 0 | 100      | 100        |
| 84  | 1 | 0 | 100      | 100        |
| 85  | 1 | 0 | 100      | 100        |
| 86  | 1 | 0 | 100      | 100        |
| 87  | 1 | 0 | 100      | 100        |
| 88  | 1 | 0 | 100      | 100        |
| 89  | 1 | 0 | 100      | 100        |
| 90  | 1 | 0 | 100      | 100        |
| 91  | 1 | 0 | 100      | 100        |
| 92  | 1 | 0 | 100      | 100        |
| 93  | 1 | 0 | 100      | 100        |
| 94  | 1 | 0 | 100      | 100        |
| 95  | 1 | 0 | 100      | 100        |
| 96  | 1 | 0 | 100      | 100        |
| 97  | 1 | 0 | 100      | 100        |
| 98  | 1 | 0 | 100      | 100        |
| 99  | 1 | 0 | 100      | 100        |
| 100 | 1 | 0 | 100      | 100        |

and O atoms were those listed in *International Tables for X-ray Crystallography* (1962). The final positional and thermal parameters of atoms, together with their standard deviations, are listed in Table 1. The final calculated structure amplitudes are compared with the observed values in Table 2.

#### Determination of the absolute configuration

Equi-inclination Weissenberg photographs of the first and second layers around the  $a$  axis were taken with  $\text{Cu K}\alpha$  radiation. Table 3 lists some of the observed relations between  $hkl$  and  $h\bar{k}l$  and the calculated values. Comparison of the observed and calculated differences shows that the complex ion has the absolute configuration  $A$ , in accordance with our previous results (Nomura *et al.*, 1969).

Table 3. Observed and calculated intensity relations between some  $hkl$  and  $h\bar{k}l$  reflexions

| $h$ | $k$ | $l$ | $F_c(hkl)$ | Obs. | $F_c(h\bar{k}l)$ |
|-----|-----|-----|------------|------|------------------|
| 1   | 1   | 1   | 36.4       | >    | 31.5             |
| 1   | 2   | 1   | 19.6       | <    | 32.1             |
| 1   | 3   | 1   | 23.3       | <    | 28.7             |
| 1   | 4   | 1   | 29.6       | <    | 33.9             |
| 1   | 3   | 2   | 11.5       | >    | 9.5              |
| 1   | 4   | 2   | 0.9        | <    | 7.4              |
| 2   | 1   | 1   | 3.2        | <    | 11.4             |
| 2   | 2   | 2   | 28.7       | >    | 25.1             |
| 2   | 3   | 2   | 39.0       | >    | 36.4             |
| 2   | 4   | 2   | 14.8       | >    | 9.0              |
| 2   | 2   | 3   | 49.8       | >    | 42.5             |
| 2   | 3   | 3   | 11.2       | <    | 16.7             |
| 2   | 4   | 3   | 13.0       | >    | 9.5              |
| 2   | 1   | 4   | 25.7       | <    | 29.8             |
| 2   | 2   | 4   | 15.7       | >    | 14.4             |
| 2   | 4   | 4   | 14.3       | >    | 10.6             |

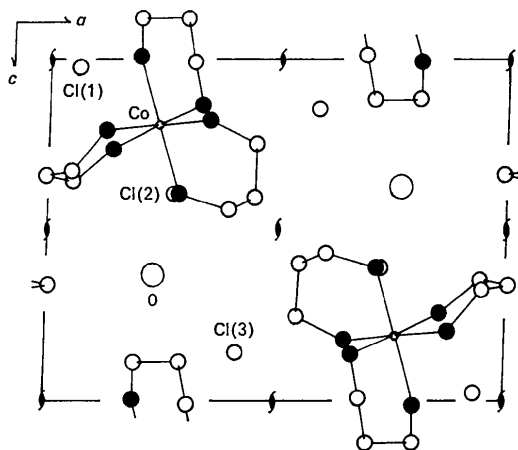
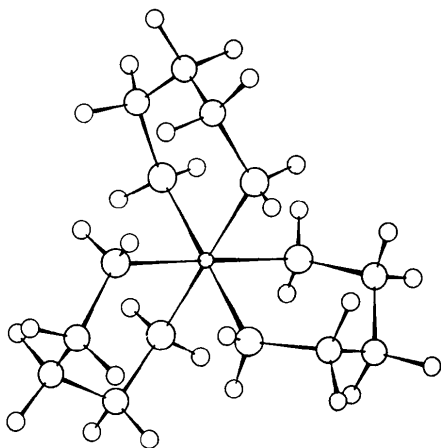
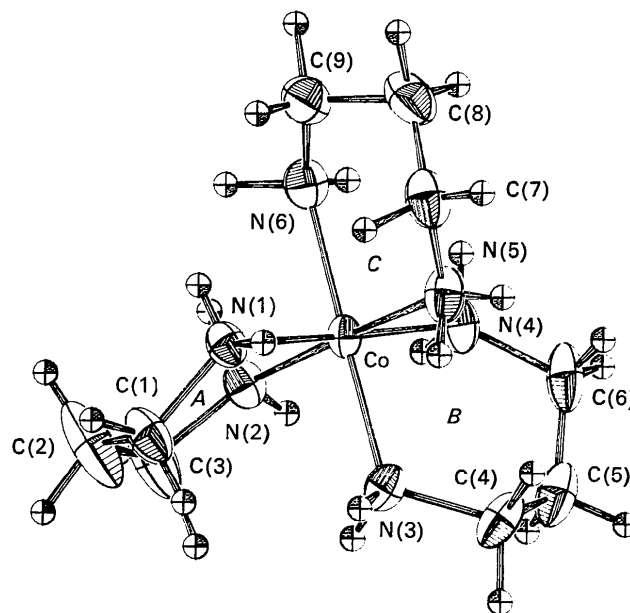
Fig. 1. A projection of the structure along the  $b$  axis. The numbering scheme for the chelate rings is given in Fig. 3.Fig. 2. A perspective drawing of the complex ion  $(-)_{589}[\text{Co}(\text{tn})_3]^{3+}$ .

Fig. 3. Ellipsoids of thermal motion of the complex ion with numbering scheme.

### Description of the structure and discussion

The overall structure is the same as that of the isostructural bromide,  $(-)_{589}[\text{Co}(\text{tn})_3]\text{Br}_3 \cdot \text{H}_2\text{O}$ . A projection of the structure along the  $b$  axis is shown in Fig. 1. Fig. 2 gives a perspective drawing of the complex ion,  $(-)_{589}[\text{Co}(\text{tn})_3]^{3+}$ , as viewed down the pseudo-threefold axis. In Fig. 3 are shown the ellipsoids of thermal motion with numbering scheme. Interatomic distances and bond angles within the complex ion are given in Table 4. The nitrogen atoms of the three 1,3-diaminopropane ligands form a slightly distorted octahedron around the cobalt atom. The displacement of the nitrogen atoms from a regular octahedral position is much less than that observed in the bromide analogue. This was to be expected because of the presence of heavy bromide ions. The three chelate rings have stable chair conformations. The complex ion has a pseudo-threefold axis of rotation. The Co-N distances range from 1.966 to 1.999 Å. The three N-Co-N angles in the chelate rings are closer to  $90^\circ$  than those in the bromide analogue. The chelate rings are flattened out by interactions between non-bonded hydrogen atoms of adjacent chelate rings. The Co-N-C angles are much larger than the normal tetrahedral angle. Other C-C and C-N distances are normal apart from the C(2)-C(3) distance of 1.408 Å, which is unusually shorter than the normal C-C bond. In Fig. 3 the much greater thermal motion in the carbon atoms C(2) and C(3) is particularly striking. The short C(2)-C(3) distance seems to be due to the error introduced by the high correlation of the positional parameters with the large thermal motion of the carbon atoms. Little or no significance can be attached to the highly distorted C(1)-

C(2)–C(3) angle of 118.8° and the N(2)–C(3)–C(2) angle of 118.7° for the same reason. The shape and size of the chelate ring closely resemble those of *cis*-[Co(tn)<sub>2</sub>CO<sub>3</sub>]<sup>+</sup> (Geue & Snow, 1971). They may also be compared with those observed in the Cr–tn ring with chair conformation in crystals of [Cr(tn)<sub>3</sub>] [Ni(CN)<sub>5</sub>]·2H<sub>2</sub>O (Jurnack & Raymond, to be published). The observed geometry of the chelate ring averaged for *B* and *C* assuming mirror symmetry is compared with the minimized conformation in Table 5. The agreement is very good except for the dihedral angles Co–N–C–C and N–C–C–C. The disagreement may be due to the deformation of the complex ion by packing forces in the crystal. The geometry calculated by Niketić & Woldbye (1973) is based on Liquori's nonbonded parameters (Liquori, Damiani & Elefante, 1968).

Table 4. *Interatomic distances and bond angles within the complex ion with their standard deviations in parentheses*

| Chelate ring <i>A</i> |             |                |           |
|-----------------------|-------------|----------------|-----------|
| Co—N(1)               | 1.969 (3) Å | N(1)—Co—N(2)   | 89.3 (1)° |
| Co—N(2)               | 1.979 (3)   | Co—N(1)—C(1)   | 122.0 (2) |
| N(1)—C(1)             | 1.484 (5)   | Co—N(2)—C(3)   | 123.2 (2) |
| N(2)—C(3)             | 1.471 (6)   | N(1)—C(1)—C(2) | 110.6 (2) |
| C(1)—C(2)             | 1.505 (8)   | N(2)—C(3)—C(2) | 118.7 (4) |
| C(2)—C(3)             | 1.408 (9)   | C(1)—C(2)—C(3) | 118.8 (4) |
| Chelate ring <i>B</i> |             |                |           |
| Co—N(3)               | 1.966 (3)   | N(3)—Co—N(4)   | 89.9 (1)  |
| Co—N(4)               | 1.999 (3)   | Co—N(3)—C(4)   | 121.1 (2) |
| N(3)—C(4)             | 1.498 (5)   | Co—N(4)—C(6)   | 122.0 (2) |
| N(4)—C(6)             | 1.488 (5)   | N(3)—C(4)—C(5) | 111.8 (2) |
| C(4)—C(5)             | 1.505 (6)   | N(4)—C(6)—C(5) | 113.2 (3) |
| C(5)—C(6)             | 1.487 (7)   | C(4)—C(5)—C(6) | 114.1 (3) |
| Chelate ring <i>C</i> |             |                |           |
| Co—N(5)               | 1.976 (3)   | N(5)—Co—N(6)   | 92.0 (1)  |
| Co—N(6)               | 1.984 (3)   | Co—N(5)—C(7)   | 122.6 (2) |
| N(5)—C(7)             | 1.477 (6)   | Co—N(6)—C(9)   | 122.3 (2) |
| N(6)—C(9)             | 1.485 (5)   | N(5)—C(7)—C(8) | 112.2 (2) |
| C(7)—C(8)             | 1.492 (6)   | N(6)—C(9)—C(8) | 111.8 (3) |
| C(8)—C(9)             | 1.507 (6)   | C(7)—C(8)—C(9) | 113.0 (3) |

Table 5. *Observed and calculated geometry of the Co–tn ring in [Co(tn)<sub>3</sub>]<sup>3+</sup>*

| Bond angles     | Observed                      | Calculated |       |
|-----------------|-------------------------------|------------|-------|
|                 |                               | (a)        | (b)   |
| N—Co—N          | 91.0°                         | 89.4°      | 95.0° |
| Co—N—C          | 122.0                         | 120.3      | 119.5 |
| N—C—C           | 112.4                         | 112.0      | 112.0 |
| C—C—C           | 113.6                         | 110.5      | 109.5 |
| Dihedral angles |                               |            |       |
| Co—N—C—C        | 56.1 (chelate ring <i>B</i> ) | 60.0       |       |
|                 | 51.9 (chelate ring <i>C</i> ) |            |       |
| N—C—C—C         | 63.5 (chelate ring <i>B</i> ) | 70.0       |       |
|                 | 67.6 (chelate ring <i>C</i> ) |            |       |

(a) Niketić & Woldbye (1973).  
 (b) Gollogly & Hawkins (1972).

Table 6 lists some of the important distances outside the complex ion. The closest approach occurs between nitrogen atoms of the complex cation and the chloride ions. The distances between each chloride ion and its nearest neighbour are generally shorter than the corresponding distances in the bromide and may be compared with those observed in  $(+)_S89$ -[Co(en)<sub>3</sub>]Cl<sub>3</sub>·H<sub>2</sub>O (Iwata, Nakatsu & Saito, 1969). Hydrogen bonds of the type N–H···Cl probably exist between N(4)···Cl(3) and N(2)···Cl(1), the N–H···Cl angles being 158.2 and 151.4° respectively. The oxygen atom of the water molecule is associated with two chloride ions at distances of 3.139 and 3.186 Å. It is also linked to N(3) by an N–H···O hydrogen bond of 3.029 Å.

Table 6. *Interatomic distances less than 3.5 Å outside the complex ions*

Key to symmetry operations:

| Superscript                 | <i>x</i>   | <i>y</i>          | <i>z</i>      |
|-----------------------------|------------|-------------------|---------------|
| None                        | <i>x</i>   | <i>y</i>          | <i>z</i>      |
| i                           | – <i>x</i> | $\frac{1}{2} + y$ | – <i>z</i>    |
| ii                          | <i>x</i>   | –1 + <i>y</i>     | <i>z</i>      |
| iii                         | <i>x</i>   | <i>y</i>          | –1 + <i>z</i> |
| N(2)···Cl(1)                |            |                   | 3.116 (3) Å   |
| N(2)···Cl(2)                |            |                   | 3.291 (3)     |
| N(4)···Cl(2)                |            |                   | 3.452 (3)     |
| N(4)···Cl(3)                |            |                   | 3.186 (4)     |
| N(6)···Cl(3)                |            |                   | 3.473 (3)     |
| N(1)···Cl(1 <sup>i</sup> )  |            |                   | 3.354 (3)     |
| N(6)···Cl(1 <sup>i</sup> )  |            |                   | 3.370 (3)     |
| Cl(1)···N(1 <sup>ii</sup> ) |            |                   | 3.318 (3)     |
| Cl(2)···N(1 <sup>ii</sup> ) |            |                   | 3.410 (3)     |
| Cl(2)···N(3 <sup>ii</sup> ) |            |                   | 3.236 (3)     |
| Cl(2)···N(5 <sup>ii</sup> ) |            |                   | 3.303 (4)     |
| O···Cl(2)                   |            |                   | 3.186 (4)     |
| Cl(3)···O <sup>iii</sup>    |            |                   | 3.139 (3)     |
| N(3)···O                    |            |                   | 3.029 (5)     |

The largest amplitude of thermal vibration of the carbon atoms C(2) and C(3) is primarily perpendicular to the plane formed by the two C–C or C–N bonds for each atom. In fact the chelate ring *A* is most loosely packed in the crystal. The C···C distances between the two adjacent chelate rings related by a twofold screw axis are longer than 4.5 Å. This large thermal motion of the carbon atoms is consistent with the results of conformational analyses of the six-membered chelate rings and it suggests a conformational equilibrium involving significant amounts of two or more conformers in solution at room temperature. Such a conformational equilibrium in aqueous solution was evidenced by the measurements of the solution and solid-state circular dichroism of  $(+)_S89$ -[Co(tn)<sub>3</sub>]Br<sub>3</sub>·H<sub>2</sub>O (Beddoe, Harding, Mason & Peart, 1971).

All the calculations were performed on the FACOM 270-30 of this Institute. The authors would like to thank Professor Flemming Woldbye for communicating the results of their conformational analysis prior

to its publication. Part of the cost of this research was met by a Scientific Research Grant from the Ministry of Education, to which the authors' thanks are due.

### References

BEDDOE, P. G., HARDING, M. J., MASON, S. F. & PEART, B. J. (1971). *Chem. Commun.* p. 1283.  
 GEUE, R. J. & SNOW, M. R. (1971). *J. Chem. Soc. (A)* pp. 2981–2987.

GOLLOGLY, J. R. & HAWKINS, C. J. (1972). *Inorg. Chem.* **11**, 156–161.  
*International Tables for X-ray Crystallography.* (1962). Vol. III. Birmingham: Kynoch Press.  
 IWATA, M., NAKATSU, K. & SAITO, Y. (1969). *Acta Cryst.* **B25**, 2562–2571.  
 LIQUORI, A. M., DAMIANI, A. & ELEFANTE, G. (1968). *J. Mol. Biol.* **33**, 439–444.  
 NIKETIĆ, S. Q. & WOLDBYE, F. (1973). *Acta Chem. Scand.* **27**, 621–642.  
 NOMURA, T., MARUMO, F., SAITO, Y. (1969). *Bull. Chem. Soc. Japan*, **42**, 1016–1020.

*Acta Cryst.* (1973). **B29**, 2443

## The Crystal Structure of $(-)_546$ -Tris- $(R,R$ -2,4-diaminopentane)cobalt(III) Chloride Dihydrate, $(-)_546$ -[Co( $R,R$ -ptn) $_3$ ]Cl $_3$ ·2H $_2$ O

BY A. KOBAYASHI,\* F. MARUMO† AND Y. SAITO

*The Institute for Solid State Physics, The University of Tokyo, Roppongi-7, Minato-ku, Tokyo 106, Japan*

(Received 15 May 1973; accepted 15 June 1973)

The structure of  $(-)_546$ -[Co( $R,R$ -ptn) $_3$ ]Cl $_3$ ·2H $_2$ O has been determined from three-dimensional X-ray data collected by the diffractometer method. The compound forms tetragonal crystals with  $a = 11.395$  (1),  $c = 20.242$  (1) Å and  $Z = 4$  in space group  $P4_32_12$ . The structure has been refined by least-squares methods with anisotropic temperature factors to an  $R$  value of 0.039 for 3016 observed reflexions. The complex cation has an approximate  $D_3$  symmetry. The six-membered chelate ring has a twisted-boat form. The two methyl groups are in equatorial positions with respect to the average plane of the chelate ring. The mean N–Co–N angle is  $89.1^\circ$ . The absolute configuration is  $\Delta$  and that of the three chelate rings is  $\lambda$ . The line joining the two asymmetric carbon atoms makes an angle of  $2^\circ$  with respect to the quasi-threefold axis of rotation.

### Introduction

$(-)_546$ -Tris- $(R,R$ -2,4-diaminopentane)cobalt(III) chloride dihydrate,  $(-)_546$ -[Co( $R,R$ -ptn) $_3$ ]Cl $_3$ ·2H $_2$ O is one of the two isomers of tris- $(R,R$ -2,4-diaminopentane)cobalt(III) salts (Mizukami, Ito, Fujita & Saito, 1970). This isomer was assigned as a  $\Delta$  isomer from the negative circular dichroism band in the first transition region. The crystal structure was determined in order to gain conformational details of the complex ion. The crystal structure of the other isomer has already been determined (Kobayashi, Marumo & Saito, 1972).

### Experimental

Crystals of  $(-)_546$ -[Co( $R,R$ -ptn) $_3$ ]Cl $_3$ ·2H $_2$ O were kindly supplied by Professor J. Fujita of Tohoku University. They are needle-like orange-red crystals. The unit-cell dimensions determined from higher-order reflexions recorded on Weissenberg photographs were later re-

fined by employing data obtained on a single-crystal diffractometer with Mo  $K\alpha$  radiation ( $\lambda = 0.7107$  Å).

Crystal data are:  $(-)_546$ -Co(C $_5$ H $_{14}$ N $_2$ ) $_3$ Cl $_3$ ·2H $_2$ O, F.W. 507.9; tetragonal,  $a = 11.395$  (1),  $c = 20.242$  (1) Å,  $U = 2630$  Å $^3$ ;  $D_m = 1.280$  g cm $^{-3}$ ,  $Z = 4$ ,  $D_x = 1.283$  g cm $^{-3}$ . Space group  $P4_32_12$  (No. 96). Linear absorption coefficient for Mo  $K\alpha$ ,  $\mu = 9.99$  cm $^{-1}$ .

The intensity data were collected on a Rigaku automated four-circle diffractometer. The specimen was ground into a sphere of about 0.23 mm diameter. The  $\omega$ - $2\theta$  scan technique was employed. Mo  $K\alpha$  radiation monochromated by a graphite crystal was used. A set of standard reflexions was measured every 50 reflexions during the data collection. A total of 3500 reflexions were measured up to  $2\theta = 55^\circ$ . Those reflexions which were non-equivalent as a result of anomalous dispersion were treated as independent reflexions. The reflexions of which the intensities were less than three times their standard deviations were regarded as 'unobserved' and were not included in subsequent calculations. Thus, 3016 independent reflexions were collected. The intensities were corrected for Lorentz and polarization effects, but corrections for absorption and extinction were not applied.

\* Present address: Department of Chemistry, Faculty of Science, The University of Tokyo, Tokyo 113, Japan.

† Present address: Tokyo Institute of Technology, Oh-okayama, Meguro-ku, Tokyo 152, Japan.