

Table 5. Comparison of dihedral angles

Ring A	I	II	Ring B	I	II
C(1)–C(2)	–6.2	–49.1	C(5)–C(6)	–11.5	–9.0
C(2)–C(3)	–12.7	22.1	C(6)–C(7)	–2.3	–1.7
C(3)–C(4)	14.1	2.6	C(7)–C(8)	–16.3	–17.7
C(4)–C(5)	4.9	0.5	C(8)–C(9)	47.3	46.6
C(5)–C(10)	–22.8	–26.6	C(9)–C(10)	–59.2	–56.2
C(1)–C(10)	23.0	50.0	C(5)–C(10)	40.5	37.0
Ring C			Ring D		
C(8)–C(9)	–56.3	–57.7	C(13)–C(14)	46.6	46.1
C(9)–C(11)	55.2	56.5	C(14)–C(15)	–36.4	–35.9
C(11)–C(12)	–54.3	–53.3	C(15)–C(16)	11.4	11.0
C(12)–C(13)	54.7	52.5	C(16)–C(17)	16.7	16.8
C(13)–C(14)	–58.4	–58.6	C(13)–C(17)	–38.1	–38.0
C(14)–C(8)	59.3	60.2			

Table 5 (cont.)

Side chain	I	II
C(13)–C(17)–C(20)–O(23)	96.0	97.6
C(16)–C(17)–C(20)–O(23)	–21.2	–21.5
C(13)–C(17)–O(24)–C(25)	178.5	179.5
C(16)–C(17)–O(24)–C(25)	–70.4	–69.7
C(17)–O(24)–C(25)–O(27)	5.6	2.9
C(17)–O(24)–C(25)–C(26)	–171.8	–174.9
C(13)–C(17)–C(20)–C(21)	–83.1	–78.5
C(16)–C(17)–C(20)–C(21)	159.7	162.3

References

- BRENNAN, D. M. & KRAAY, R. J. (1963). *Acta Endocrinol.* **44**, 367–379.
 CHANDROSS, R. J. & BORDNER, J. (1974). *Acta Cryst.* **B30**, 1581–1585.

Acta Cryst. (1975). **B31**, 931

(–)₅₈₉-Tris-(*R*-propylenediamine)cobalt(III) Bromide

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Abstract. (–)₅₈₉-[Co(*R*-pn)₃]Br₃, *M. W.* 518.0, hexagonal, *P*6₃, *a* = 11.012 (2), *c* = 8.582 (1) Å, *Z* = 2, *D*_m = 1.911, *D*_x = 1.908 g cm^{–3}, *U* = 901.4 Å³, *μ*(Mo *Kα*, λ = 0.7107 Å) = 80.0 cm^{–1}. The crystal structure was redetermined on the basis of the intensity data collected by diffractometry in order to obtain more accurate information on the conformational details. The results are essentially the same as those previously reported; however, the standard deviations of the atomic parameters were reduced to about one third of the previous values. Methyl groups were revealed to take two alternative azimuthal orientations around the C–CH₃ bonds.

Introduction. *A*(*le*₃)-[Co(*R*-pn)₃]³⁺ ion is one of the most familiar and fundamental complex ions in coordination chemistry and has been extensively studied, including the absolute configuration (Iwasaki & Saito, 1966). Recently the *A*(*ob*₃) isomer of this complex ion was isolated and the crystal structure of the hexacyanocobaltate was determined accurately by diffractometer methods (Kuroda & Saito, 1974).

The crystal structure of the *A*(*le*₃)-[Co(*R*-pn)₃]Br₃ was redetermined by the diffractometer method, since the previous work was based on the intensity data collected by the photographic method. The redetermination will enable us to compare the detailed conformations of the two isomeric complex ions and, moreover, such accurate knowledge of the crystal struc-

ture would be of a great help in constructing a theoretical model for optical activity.

Crystals were prepared according to the method described by Iwasaki & Saito (1966). They are dark-red hexagonal prisms elongated along the *c* axis. Unit-cell dimensions were determined from Weissenberg photographs and were later refined on a diffractometer. The crystal specimen was shaped into a sphere with a radius of 0.15 mm. The intensity data were measured on a Rigaku automated four-circle diffractometer using Mo *Kα* radiation monochromated by a graphite plate. The ω–2θ scan technique was employed. The data were corrected for Lorentz and polarization factors but not for absorption and extinction. Among 1067 accessible reflexions below 2θ = 60°, 888 with |*F*_o| ≥ 3σ were used for structure determination.

The atomic coordinates previously reported by Iwasaki & Saito (1966) were used as a starting set in the least-squares refinement. After several cycles of least-squares refinement with isotropic thermal parameters, the *R* value became 0.099. A difference Fourier map at this stage showed some of the hydrogen atoms. Successive difference Fourier synthesis and least-squares refinement with anisotropic thermal parameters for non-hydrogen atoms finally revealed all the hydrogen atoms in an asymmetric unit. The *R* value decreased to 0.037 for 888 independent reflexions. At the final stage all the positional shifts of non-hydrogen atoms were less than one half of the standard deviations of the positional parameters. The weighting scheme used was *w* = 1.0 for |*F*_o| ≥ 19.67, *w* = 0.5 for 0 ≤ |*F*_o| ≤ 19.67. The scattering factors for the atoms apart from hydro-

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Table 2. *Positional and thermal parameters*

(a) Fractional atomic coordinates ($\times 10^4$) and thermal parameters for the non-hydrogen atoms, with estimated standard deviations. The U_{ij} 's are defined by: $\exp[-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{12}hka^*b^* + \dots) \times 10^{-3}]$.

	<i>x</i>	<i>y</i>	<i>z</i>	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	6667	3333	0 (3)	15 (1)	15 (0)	10 (1)	0	0	0
Br	4519 (1)	1194 (1)	5089 (3)	47 (0)	31 (0)	28 (0)	16 (0)	2 (1)	-5 (1)
N(1)	4964 (6)	2693 (6)	-1288 (7)	24 (3)	27 (3)	18 (3)	14 (2)	0 (2)	2 (2)
N(2)	5495 (7)	1698 (7)	1334 (7)	32 (3)	31 (3)	19 (3)	14 (3)	7 (3)	6 (3)
C(1)	3907 (7)	1204 (7)	-829 (8)	19 (3)	18 (3)	21 (3)	4 (2)	5 (3)	-5 (3)
C(2)	4006 (10)	1143 (11)	997 (11)	36 (5)	41 (5)	39 (5)	10 (4)	13 (3)	6 (4)
C(3)	2417 (8)	807 (9)	-1406 (12)	19 (4)	34 (4)	59 (6)	6 (3)	-5 (4)	-6 (4)

Table 2 (cont.)

(b) Positional parameters for the hydrogen atoms with estimated standard deviations ($\times 10^3$). Mean isotropic temperature factor of the hydrogen atoms is 3.0 \AA^2 .

	<i>x</i>	<i>y</i>	<i>z</i>
H(1)	454 (10)	325 (9)	-127 (11)
H(2)	520 (8)	276 (9)	-243 (10)
H(3)	577 (9)	102 (9)	129 (10)
H(4)	568 (9)	200 (9)	243 (10)
H(5)	414 (10)	51 (10)	-151 (11)
H(6)	330 (9)	3 (9)	152 (10)
H(7)	355 (10)	172 (11)	169 (11)
H(8)*	220 (18)	140 (18)	-55 (17)
H(9)*	170 (17)	-30 (18)	-144 (20)
H(10)*	239 (18)	120 (20)	-243 (23)
H'(8)*	211 (18)	141 (18)	-104 (19)
H'(9)*	160 (17)	-20 (18)	-75 (18)
H'(10)*	220 (17)	60 (17)	-260 (22)

* Population 0.5.

gen and the corrections for anomalous scattering of Co and Br atoms were taken from *International Tables for X-ray Crystallography* (1962). Atomic scattering factors for the hydrogen atom were those given by Stewart, Davidson & Simpson (1965). Observed and calculated structure amplitudes are compared in Table 1.* Table 2 lists the final atomic parameters with their estimated standard deviations. The numbering scheme is the same as that previously reported (Iwasaki & Saito, 1966).

Discussion. The structure is essentially the same as that previously determined. However, the standard deviations of atomic parameters reduced to about one third, and consequently those of bond lengths and bond angles decreased to about one sixth and one tenth respectively, of the previous values. Bond distances and angles are given in Table 3. They are broadly similar to those of the *A(ob₃)* isomer except for the central C-C bond in the chelate ring. The C-C distance of $1.576 (12) \text{ \AA}$ in the *A(l₃)* isomer is longer than that of $1.506 (9) \text{ \AA}$ in the *A(ob₃)* isomer. The central C-C bond in the chelate ring is inclined at an angle of $5.7 (3)^\circ$ to the threefold axis of rotation.

The six coordinating nitrogen atoms are slightly

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Table 3. *Bond distances and angles*

Co—N(1)	1.978 (6) Å
Co—N(2)	1.973 (6)
N(1)—C(1)	1.513 (8)
N(2)—C(2)	1.464 (13)
C(1)—C(2)	1.574 (11)
C(1)—C(3)	1.551 (10)
N(1)—Co—N(2)	85.9 (2)°
Co—N(1)—C(1)	108.7 (4)
Co—N(2)—C(2)	110.5 (4)
N(1)—C(1)—C(2)	105.8 (5)
N(2)—C(2)—C(1)	105.5 (5)
N(1)—C(1)—C(3)	110.8 (7)
C(2)—C(1)—C(3)	113.1 (5)

distorted from a regular octahedral disposition. The upper triangle formed by the three nitrogen atoms is rotated clockwise by about 5.9° with respect to the lower triangle of the three remaining nitrogen atoms. This angle of azimuthal distortion is similar to that observed in the *A(ob₃)* isomer.

There are two independent Co-N bonds, since the complex ion has a threefold symmetry. The Co-N(1) bond formed by the nitrogen atom next to the asymmetric carbon atom is inclined at an angle of $56.0 (2)^\circ$ with respect to the threefold axis of the complex ion, while the bond Co-N(2) makes an angle of $54.5 (2)^\circ$. This angle is 54.75° for a regular octahedral disposition of the six nitrogen atoms. Such an unequal distortion might be due to the presence of the methyl groups.

The methyl hydrogen atoms seem to take two alternative sets of positions with equal probability. Hydrogen bonds are formed between nitrogen atoms and bromide ions: Br...H(4)-N(2) [Br...N(2) = $3.355 (6) \text{ \AA}$], Br...H(3)-N(2) [Br...N(2) = $3.351 (6) \text{ \AA}$], and Br...H(2)-N(1) [Br...N(1) = $3.439 (6) \text{ \AA}$]. The complex ions and the bromide ions are held together by these hydrogen bonds.

Calculations were carried out on the FACOM 270-30 of this Institute.

References

- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
 IWASAKI, H. & SAITO, Y. (1966). *Bull. Chem. Soc. Japan*, **39**, 92-100.
 KURODA, R. & SAITO, Y. (1974). *Acta Cryst.* **B30**, 2126-2130.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175-3187.