

Fig. 2. A stereoscopic view of the packing for the bicyclic ether along the *b* axis.

methoxybromination step and formal loss of hydrogen. The presence of the double bond can be verified from two signals at  $\delta = 134.4$  [C(4)] and  $128.9$  [C(5)] in the  $^{13}\text{C}$  NMR spectrum.

The conformation results in some intramolecular contacts (keeping in mind the calculated C—H distances,  $1.03 \text{ \AA}$ ) which are noticeably shorter than the sum of van der Waals radii ( $d_w$ ): H(6)—O(1) =  $2.36$  (3), H(9)—O(1) =  $2.41$  (3),  $d_w = 2.60 \text{ \AA}$ ; H(4)—H(6) =  $2.02$  (5),  $d_w = 2.40 \text{ \AA}$ . The molecules are packed in planes parallel to the *ac* plane with two planes in a unit cell and are held together by van der Waals forces. Due to the packing there are also some

intermolecular contacts shorter than the sum of van der Waals radii: Br(2)—O(2) =  $3.197$  (7),  $d_w = 3.35 \text{ \AA}$ ; Br(1)—H(2) =  $2.89$  (2), Br(3)—H(19) =  $2.85$  (2),  $d_w = 3.15 \text{ \AA}$ .

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## SHORT-FORMAT PAPERS

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*Acta Cryst.* (1989). **C45**, 1619–1621

### Dipotassium Sodium Tris[dicyanoargentate(I)]

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(Received 30 March 1989; accepted 1 June 1989)

**Abstract.**  $\text{K}_2\text{Na}[\text{Ag}(\text{CN})_2]_3$ ,  $M_r = 580.91$ , trigonal,  $P\bar{3}1m$ ,  $a = 7.0509$  (7),  $c = 8.5766$  (8)  $\text{\AA}$ ,  $V = 369.26 \text{ \AA}^3$ ,  $Z = 1$ ,  $D_x = 2.614 \text{ Mg m}^{-3}$ ,  $\lambda(\text{Mo K}\alpha)$

$= 0.71073 \text{ \AA}$ ,  $\mu = 4.375 \text{ mm}^{-1}$ ,  $F(000) = 268$ ,  $T = 298 \text{ K}$ . The structure was refined to  $R = 0.0504$ ,  $wR = 0.0156$  for 410 absorption-corrected observed reflections. Ag atoms of linear NC—Ag—CN groups are arranged in Kagomé nets parallel to (001). The

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potassium and sodium ions occupy different octahedral holes between trigonal nitrogen layers with a sequence *ABAB*.

**Experimental.** The very stable compound forms easily by the reaction of a stoichiometric mixture of NaCN, KCN and AgCN in aqueous suspension. In contrast to the difficulty in growing crystals of  $K[Ag(CN)_2]$  and  $Na[Ag(CN)_2]$ , good-quality single crystals of  $K_2Na[Ag(CN)_2]_3$  were obtained simply by crystallization from the original solution using the evaporation method. After inspection of the crystals by microscopy and film methods a clear individual ( $190 \times 60 \times 60 \mu\text{m}$ ) could be isolated, which proved suitable for a structure determination. Gandolfi and Guinier patterns showed the individual to be the same phase as the other crystals and the bulk material.

For data collection an Enraf-Nonius CAD-4 diffractometer was used (Mo  $K\alpha$ , graphite monochromator). Lattice parameters were refined from 2 $\theta$  values of 25 reflections in the range  $6.2\text{--}15.2^\circ$ . Intensities measured for  $2 \leq \theta \leq 30^\circ$ ;  $\omega$ - $2\theta$ -scan technique [scan width  $(0.9 + 0.34 \tan \theta)^\circ$ ]. Three standard reflections indicated a 0.8% loss of intensity during data collection. An experimental correction for absorption based on  $\psi$  scans was applied; transmission factors varied between 86 and 99%. Merging of the 2478 collected intensities [ $(\sin \theta)_{\text{max}}/\lambda = 0.729 \text{ \AA}^{-1}$ ,  $-9 \leq h \leq 9$ ,  $-9 \leq k \leq 9$ ,  $0 \leq l \leq 24$ ] gave 410 unique reflections ( $R_{\text{int}} = 0.0096$ ) with  $I > 0.5\sigma(I)$ , which were used for all calculations (program system *SHELX76*; Sheldrick, 1976).

Location of the Ag atom from a Patterson synthesis, all remaining atoms found in successive difference Fourier maps. In least-squares refinement  $|F|$  magnitudes were used to refine atomic coordinates and anisotropic temperature factors.

Final  $R = 0.050$ ,  $wR = 0.016$ .  $w = 0.0113/\sigma^2(F)$ .  $(\Delta/\sigma)_{\text{max}} < 0.002$  in final refinement cycle, 21 parameters. Max. features in the final  $\Delta\rho$  map  $+1.5$ ,  $-1.6 \text{ e \AA}^{-3}$ . Atomic scattering factors and  $f'$ ,  $f''$  values were taken from *International Tables for X-ray Crystallography* (1974). Bond distances and angles were calculated using the program *SADIAN* (Baur & Wenninger, 1969). Final atomic coordinates and equivalent isotropic temperature factors are given in Table 1, derived bond distances and angles in Table 2.\*

The structure (Fig. 1) comprises layers of linear NC—Ag—CN groups. The Ag atoms form a regular

Table 1. Atomic coordinates and equivalent isotropic temperature factors ( $\text{\AA}^2$ )

The equivalent isotropic  $U$  values are defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

	x	y	z	$U_{\text{eq}}$
Ag	$\frac{1}{2}$	0	0	0.0445 (2)
K	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.0337 (5)
Na	0	0	$\frac{1}{2}$	0.0218 (10)
C	0	0.3631 (4)	0.2117 (3)	0.0322 (20)
N	0	0.2962 (4)	0.3316 (3)	0.0323 (20)

Table 2. Interatomic distances ( $\text{\AA}$ ) and bond angles ( $^\circ$ )

Ag—C	2.056 (2) (2 ×)	C—Ag—C	180.0
Ag—N	3.186 (2) (2 ×)	N—C—Ag	176.65 (21)
Ag—Ag	3.525 (4 ×)	N—Na—N	90.84 (7)
			89.16 (7)
C—N	1.131 (4)		180.0
			90.84 (7)
Na—N	2.539 (2) (6 ×)		89.16 (7)
K—N	2.880 (2) (6 ×)	N—K—N	76.48 (6)
			90.06 (6)
			97.06 (6)
			97.05 (6)
			170.98 (5)

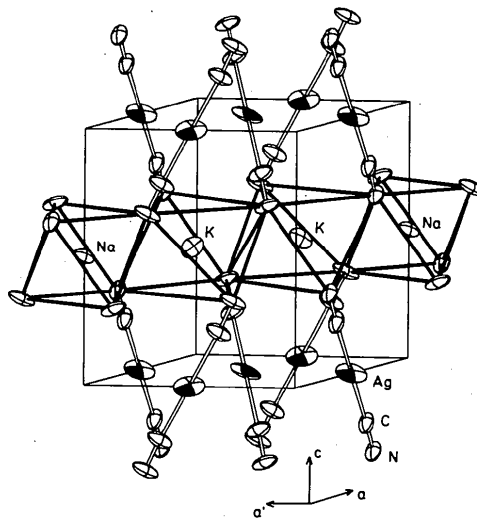


Fig. 1. The crystal structure of  $K_2Na[Ag(CN)_2]_3$  (ORTEP; Johnson, 1976).

Kagomé (3.6.3.6) net. As the NC—Ag—CN groups are canted by about  $28^\circ$  with respect to the  $c$  axis, the terminal N atoms form a trigonally distorted close-packed layer, stacked with a sequence *ABAB*. This distortion causes two kinds of octahedral holes in the ratio 2:1, which have different size and are occupied by the potassium and sodium ions, respectively.

**Related literature.** The same layered arrangement of the NC—Ag—CN groups, based on Kagomé nets, is found in  $K[Au(CN)_2]$  (Rosenzweig & Cromer, 1959) and supposed for  $K[Ag(CN)_2]$  (Hoard, 1933). The stacking sequences, however, are different. Another layer type is verified in  $Na[Ag(CN)_2]$  (Range, Kühnel & Zabel, 1989).

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51965 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

We thank Dr U. Klement for the collection of diffractometer data. The generous support given by the Fonds der Chemischen Industrie and the Degussa AG is gratefully acknowledged.

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*Acta Cryst.* (1989). **C45**, 1621–1623

## A Carbonato(optically active cyclen)cobalt(III) Complex\*

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(Received 20 April 1989; accepted 7 June 1989)

**Abstract.** *cis*-(*SSSR*)- $\beta_1$ -Carbonato[(2*R*,5*R*,8*R*,11*R*)-2,5,8,11-tetraethyl-1,4,7,10-tetraazacyclododecane]cobalt(III) perchlorate trihydrate, [Co(CO<sub>3</sub>)-(C<sub>16</sub>H<sub>36</sub>N<sub>4</sub>)]ClO<sub>4</sub>·3H<sub>2</sub>O,  $M_r = 556.93$ , monoclinic,  $P2_1$ ,  $a = 18.936$  (3),  $b = 13.768$  (5),  $c = 9.419$  (2) Å,  $\beta = 100.70$  (2)°,  $V = 2413$  (1) Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.536$ ,  $D_x = 1.534$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 0.88$  mm<sup>-1</sup>,  $F(000) = 1184$ ,  $T = 296$  K, final  $R = 0.057$  for 3710 unique reflections with  $|F_o| > 3\sigma(|F_o|)$ . The asymmetric unit contains two virtually identical molecules. The Co<sup>III</sup> ion is surrounded by four N atoms of the macrocycle, and two O atoms of the bidentate carbonate group. The Co—O and Co—N distances agree with those found in related *cis*-carbonato(tetramine) complexes.

**Experimental.** During the reaction of racemic tyrosine and the optically active complex *cis*-(*SSSR*)-bromo(dibromo-aqua)[(2*R*,5*R*,8*R*,11*R*)-2,5,8,11-tetraethyl-1,4,7,10-tetraazacyclododecane]cobalt(III) (1) (Sakurai, Tsuboyama & Tsuboyama, 1980) under atmospheric conditions, the title compound (2) was obtained as a by-product. The reaction conditions are similar to those for the preparation of an (amino acidato) (chiral cyclen) complex (Tsuboyama, Sakurai & Tsuboyama, 1987). The characterization of complex (2) will be reported separately. The same crystal was obtained from an aqueous solution of (1)

when the pH was adjusted with Na<sub>2</sub>CO<sub>3</sub> to pH 8.0. The density was measured by flotation in CCl<sub>4</sub>-benzene. Crystals of the title compound are red plates. Unit-cell parameters by least-squares fit of 20 reflections in the range  $20 < 2\theta < 25^\circ$ . Crystal  $0.72 \times 0.30 \times 0.09$  mm, Rigaku AFC automated four-circle diffractometer, graphite-monochromatized Mo  $K\alpha$  radiation,  $\omega$  and  $\omega-2\theta$  ( $2\theta > 30^\circ$ ) scan mode at a scan rate of  $4.0^\circ \text{ min}^{-1}$ , 4420 reflections measured in the range  $2\theta < 55^\circ$ ,  $hkl$  range:  $h -24-24$ ,  $k 0-17$ ,  $l 0-12$ , 3710 unique reflections with  $|F_o| > 3\sigma(|F_o|)$ ; three standard reflections (212, 751 and 0.10.0) remeasured after every 150 reflections did not show any significant change in intensity during data collection. Lorentz-polarization correction, none for absorption. Structure solved by direct methods with *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Calculations performed using the program system *UNICSIII* (Sakurai & Kobayashi, 1979) on a FACOM M-780. The two independent molecules are labelled *A* and *B*. The H-atom coordinates were calculated assuming ideal geometry. Refinement was carried out using block-diagonal least-squares procedure with anisotropic thermal parameters for all non-H atoms and isotropic for H atoms. The absolute configurations of the complex cations were assigned from the known configurations of the ligand as an internal reference (Sakurai *et al.*, 1980). Scattering factors and corrections for anomalous dispersion from *International Tables for X-ray Crystallography* (1974).  $R = 0.057$ ,  $wR = 0.066$  (unit weight),  $S = 2.42$  for 856 refined

\* Metal Complexes of Chiral Cyclen. 13. Part 12: Tsuboyama, Miki, Chijimatsu, Tsuboyama & Sakurai (1989).

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