Potassium dicyanoargentate(I) 1,4,7,10,13,16-hexaoxacyclo-octadecane

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The crystal structure of the title compound, $K[Ag(CN)_2] \cdot C_{12}H_{24}O_6$, conventionally denoted $K(18\text{-crown-6})Ag(CN)_2$, where 18-crown-6 is 1,4,7,10,13,16-hexaoxacyclooctadecane, is characterized by closely packed linear chains formed by the coordination of the nitrile N atoms of the $[Ag(CN)_2]^-$ anions to the K^+ cations. The K atoms lie on centers of inversion and are additionally bound to the six O atoms of the crown ether.

Comment

The coordination chemistry of crown ethers has been studied extensively over the past 35 years (Izatt *et al.*, 1995), and recently much attention has been given to the structural aspects of their complexation (Belsky & Bulychev, 1999; Steed, 2001). To a lesser extent, these macrocycles have also been studied as molecular building blocks for solid-state structures with novel electronic and magnetic properties (Akutagawa *et al.*, 2002; Nishihara *et al.*, 2002). We are interested in building molecular solids of various dimensionalities, namely one-dimensional chains, two-dimensional sheets and three-dimensional networks. The $K(18\text{-crown-6})^+$ cation (18-crown-6 is 1,4,7,10,13,16-hexaoxacyclooctadecane) has the potential to act as a building block for one-dimensional chains, because additional coordination to the K^+ cation can occur both above and below the macrocyclic plane. We have recently investigated the use of the linear $[Ag(CN)_2]^-$ anion as a bidentate pseudohalide capable of forming polymeric structures, and we have shown that $KMn[Ag(CN)_2]_3$ forms a triply interpenetrating three-dimensional network (Geiser & Schlueter, 2003). The $K(18\text{-crown-6})^+$ cation should be capable of linking linear $[Ag(CN)_2]^-$ anions into infinite one-dimensional chains.

The $KAg(CN)_2$ salt, without the addition of crown ether, is characterized by layers of potassium cations separated by layers of linear $[Ag(CN)_2]^-$ anions (Hoard, 1933). The synthesis and IR spectroscopic characterization of $K(18\text{-crown-6})Ag(CN)_2$ was first reported by Poladyan *et al.* (1984), but no structural characterization has been reported until now.

The crystal structures of the related $Cs(18\text{-crown-6})Ag(CN)_2$ and $Rb(18\text{-crown-6})Ag(CN)_2$ salts have been published recently (Manskaya *et al.*, 1998). The $Cs(18\text{-crown-6})Ag(CN)_2$ structure is characterized by zigzag chains of $Cs(18\text{-crown-6})^+$ cations, which are coupled into two-dimensional layers through the coordination of the nitrile N atoms of the $[Ag(CN)_2]^-$ anions to Cs^+ cations in adjacent chains. $Rb(18\text{-crown-6})Ag(CN)_2$ forms zigzag chains that are regularly broken, because the $[Ag(CN)_2]^-$ anion is too short for the formation of a continuous chain. In both cases, the cavity of 18-crown-6 is too small to accommodate these alkali metal cations, forcing them to lie significantly out of the molecular plane and preventing the formation of linear chains of co-facially joined macrocycles. In this communication, we report that the potassium analog $K(18\text{-crown-6})Ag(CN)_2$, (I), forms a third distinct structural type characterized by the cofacial joining of macrocyclic $K(18\text{-crown-6})^+$ cations by bidentate anionic $[Ag(CN)_2]^-$ linkers to form a linear chain structure. This structure is related to that recently reported for $K(18\text{-crown-6})AuCl_2$ (Hossain *et al.*, 2003) and that of $K(18\text{-crown-6})CuI_2$ (Rath & Holt, 1986). However, in these salts, the $K-Cl$ and $K-I$ bonds are considerably weaker than the $K-N$ bond observed in (I), resulting in $Au-Cl-K$ and $Cu-I-K$ angles of 90.52 and 92.3°, respectively.

(1)
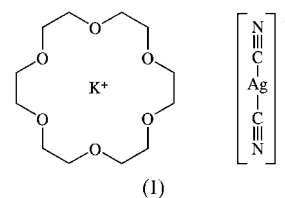
In the present structure, each K atom is coordinated to the nitrile N atoms of two $[Ag(CN)_2]^-$ anions, one above and one below the macrocyclic ring (Fig. 1), leading to the formation of a chain structure (–Ag–K1–Ag–K2–Ag–) that runs along the [201] direction (Fig. 2). These chains are essentially linear, with $K-N-C$ angles of 176.1 (2) and 175.6 (2)°. Along the chain, the macrocyclic planes are alternately tilted 4.36 (7)° with respect to one another, and the Ag atoms are alternately separated by 11.9687 (6) and 12.0049 (6) Å. The Ag⋯K distances are 5.9844 (3) and 6.0024 (3) Å, and the K⋯K separations are therefore 11.9867 (5) Å. The chains are approximately hexagonally packed, with interchain Ag⋯Ag interactions ranging from 8.1150 (3) to 8.2914 (5) Å.

Ignoring the crown ether groups, the chain packing derives from an idealized rhombohedral prototype ($a \simeq b \simeq c \simeq 8.2$ Å, $\alpha \simeq \beta \simeq \gamma \simeq 98°$; space group $R\bar{3}m$). The trigonal axis corresponds to the chain direction. This high-symmetry lattice is distorted, leading to a monoclinic intermediate structure ($a = 10.719$ Å, $b = 12.219$ Å, $c = 8.241$ Å and $\beta = 102.79°$; space group $C2/m$) whose symmetry is further broken by the mutual orientation of the crown ether rings with concomitant doubling of the c axis. Because of the presence of this hypersymmetry (K at $0, \frac{1}{2}, 0$ and $0, \frac{1}{2}, 0$; Ag near $\frac{1}{2}, \frac{1}{2}, \frac{1}{4}$), a large number of reflections are weak; only those with both $l = 2n$ and $h + 2l = 2n$ are strong.

The $[Ag(CN)_2]^-$ anion in (I) is essentially linear, with a C—Ag—C angle of 179.80 (8)° and Ag—C—N angles of 179.0 (3) and 179.5 (2)°. The bond distances are also similar to those previously reported in $K_2Na[Ag(CN)_2]_3$ (Zabel *et al.*, 1989) and $Na[Ag(CN)_2]$ (Range *et al.*, 1989). The nitrile N atoms of the anion are coordinated to one K atom each, with K—N bond lengths of 2.860 (2) and 2.856 (2) Å. The K atoms are eight-coordinate, including the six K—O bonds to the crown ether, which range from 2.7926 (13) to 2.8283 (14) Å (Table 1). The K atoms lie on inversion centers and are thus entirely in the plane of the six coordinating O atoms. Around the periphery of the macrocycle, the O atoms lie alternately above and below this plane. The O atoms in the crown ether associated with atom K1 lie above or below the molecular plane by 0.1950 (8)–0.1968 (8) Å, while those associated with atom K2 deviate from their molecular plane by 0.1964 (9)–0.1991 (9) Å. Both of the 18-crown-6 macrocycles in (I) are largely ordered. The C—C bond lengths range from 1.487 (3) to 1.501 (3) Å, while the C—O bond lengths are between 1.407 (3) and 1.421 (3) Å, and the geometry of the K(18-crown-6)$^+$ cation in all respects is consistent with previously reported results (*e.g.* Dunitz *et al.*, 1974).
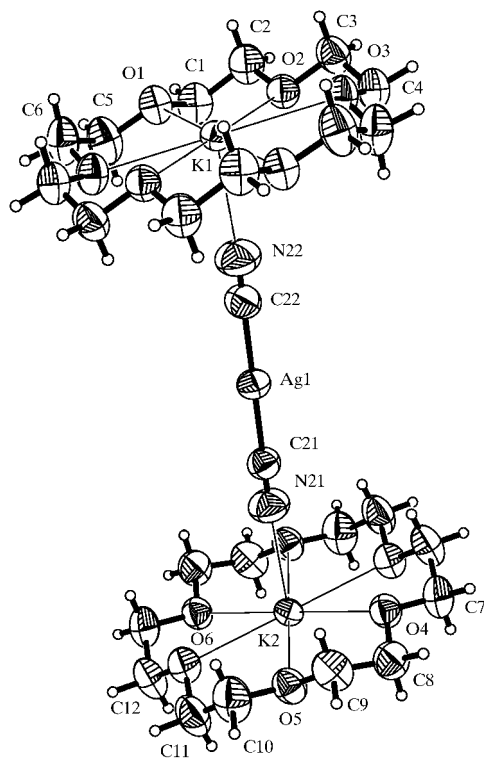

Figure 1
The atomic numbering scheme for (I), illustrating a dumb-bell-like fragment of the linear cofacially joined macrocyclic chain. Displacement ellipsoids are drawn at the 50% probablility level.
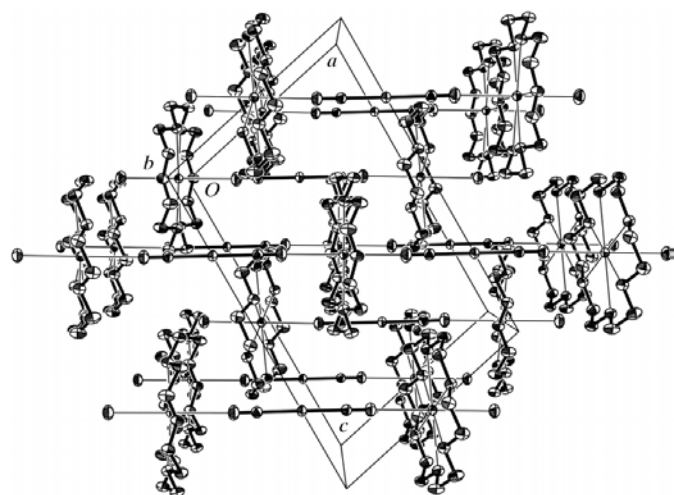

Figure 2
The chain structure of (I), which runs along the [201] direction. Displacement ellipsoids are drawn at the 20% probability level and H atoms have been omitted for clarity.

Experimental

Potassium dicyanoargentate(I) (Aldrich, 1.194 g, 6 mmol) was dissolved in water (15 ml) and combined with an ethanol solution (10 ml) containing 18-crown-6 (Aldrich, 2.378 g, 9 mmol). In a futile attempt to produce a ternary salt, this mixture was then added to a solution of tetrapropylammonium bromide (Aldrich, 0.532 mg, 2 mmol) in ethanol (10 ml). The resulting colorless solution was layered on top of an aqueous solution (10 ml) containing manganese(II) nitrate hydrate (Aldrich, 358 mg, 2 mmol). The solution was allowed to evaporate slowly at room temperature. After one month, clear colorless block-like crystals of (I) were collected from the concentrated solution by gravity filtration. Decomposition began near 525 K as the colorless crystals began to darken.

Crystal data

$K[Ag(CN)_2] \cdot C_{12}H_{24}O_6$	$D_x = 1.462$ Mg m^{-3}
$M_r = 463.32$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 2038
$a = 10.7189$ (5) Å	reflections
$b = 12.2191$ (5) Å	$\theta = 2.5–30.5°$
$c = 16.4816$ (7) Å	$\mu = 1.18$ mm^{-1}
$\beta = 102.795$ (2)°	$T = 298$ (2) K
$V = 2105.08$ (16) Å^3	Block, colorless
$Z = 4$	$0.50 \times 0.44 \times 0.40$ mm

Data collection

Siemens SMART CCD area-detector diffractometer	6428 independent reflections
ω scans	3178 reflections with $I > 2\sigma(I)$
Absorption correction: by	$R_{int} = 0.031$
integration (Sheldrick, 2001)	$\theta_{max} = 30.5°$
$T_{min} = 0.604$, $T_{max} = 0.694$	$h = -15 \rightarrow 15$
26 868 measured reflections	$k = -17 \rightarrow 17$
	$l = -23 \rightarrow 23$

Table 1
Selected geometric parameters (Å, °).

K1—O3	2.8081 (14)	K2—O6	2.8283 (14)
K1—O1	2.8142 (14)	K2—N21	2.856 (2)
K1—O2	2.8203 (13)	Ag1—C21	2.043 (2)
K1—N22	2.860 (2)	Ag1—C22	2.061 (3)
K2—O4	2.7926 (13)	C21—N21	1.106 (3)
K2—O5	2.8050 (15)	C22—N22	1.066 (3)
O3—K1—N22	99.16 (6)	C21—Ag1—C22	179.80 (8)
O1—K1—N22	91.54 (6)	N21—C21—Ag1	179.5 (2)
O2—K1—N22	88.78 (6)	C21—N21—K2	176.1 (2)
O4—K2—N21	79.18 (5)	N22—C22—Ag1	179.0 (3)
O5—K2—N21	96.27 (6)	C22—N22—K1	175.6 (2)
O6—K2—N21	95.08 (5)		

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0272P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.026$	$+ 0.5054P]$
$wR(F^2) = 0.086$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} = 0.049$
6428 reflections	$\Delta\rho_{max} = 0.28$ e Å^{-3}
221 parameters	$\Delta\rho_{min} = -0.19$ e Å^{-3}
H-atom parameters constrained	Extinction correction: *SHELXL*97
	Extinction coefficient: 0.0173 (4)

H atoms were placed geometrically at C—H distances of 0.97 Å and were refined as riding. The H-atom U_{iso} values were constrained to be 1.2 times the U_{eq} values of their respective methylene C atoms.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1429). Services for accessing these data are described at the back of the journal.

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