Cryptates with Macrotricyclic Ligands: the Crystal and Molecular Structure of the Silver [3]-Cryptates, $C_{24}H_{48}N_4O_6,3AgNO_3$

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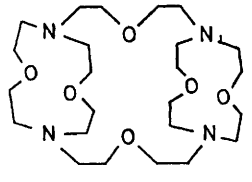
Summary A single-crystal *X*-ray diffraction study of the [3]-cryptate, $C_{24}H_{48}N_4O_6,3AgNO_3$ shows that the macrotricyclic ligand encloses two metal cations; the crystal structure consists of $(C_{24}H_{48}N_4O_6Ag_2)$ and $Ag(NO_3)_3$ units connected by bridging oxygen atoms from nitrato-groups to form chains which are parallel to the [001] direction.

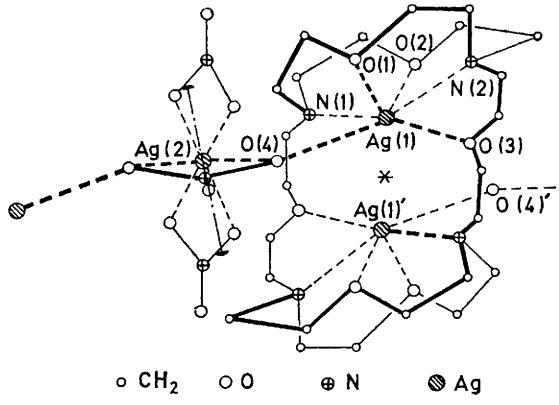
IN continuation of our investigations of macrocyclic metal cation complexes[1] we now report the structure of a novel cryptate with the macrotricyclic ligand (I).

(I)



Ligand (I) forms complexes with various metal salts.[2] Suitable crystals of (I),$3AgNO_3$ were obtained by slow evaporation of a methanol–butanol solution of the ligand and silver nitrate.

(I),$3(AgNO_3)$ crystals are monoclinic, $a = 24{\cdot}942(4)$, $b = 10{\cdot}134(2)$, $c = 15{\cdot}882(2)$ Å, $\beta = 121{\cdot}86(2)°$, $D_m = 1{\cdot}95 \pm 0{\cdot}05$, $D_c = 1{\cdot}945$ g cm^{-3} based on $Z = 4$, space group $C2/c$, 3612 diffractometer observations with Mo-K_α radiation, $R = 0{\cdot}038$.



FIGURE

The structure was solved by Patterson and Fourier techniques and refined by least-squares methods with anisotropic thermal factors for all non-hydrogen atoms.

In (I),3($AgNO_3$), two silver cations are located inside the molecular cavity of the macrotricyclic ligand (I). They give rise to (I)Ag_2 units located at a centre of symmetry of the cell. Each silver atom of these units is bound to five heteroatoms of (I) and to an oxygen atom of a nitrato-group which is also co-ordinated to a third silver atom. This silver atom is located outside ligand (I) on a crystallographic twofold symmetry axis and engaged in $Ag(NO_3)_3$ units.

The Figure shows the structures of the (I)Ag_2 and $Ag(NO_3)_3$ units which are linked together in chains through the Ag(1)–O(4) bond. These chains are parallel to the [001] direction of the crystal.

The Ag(1)–N(1), Ag(1)–N(2), Ag(1)–O(1), Ag(1)–O(2), and Ag(1)–O(3) bond lengths are 2·333(2), 2·558(2), 2·501(3), 3·022(2), and 2·382(2) Å respectively. Similar distances have been found in the silver complexes of the antibiotic X537(A)[3] and of grisorixin.[4] The Ag(1)–O(4) and Ag(1)–Ag(1′) bond lengths are 2·604(2) and 3·876(1) Å respectively. The C–C, C–O, and C–N bonds within ligand (I) have the expected values.

One nitrato-group in the $Ag(NO_3)_3$ units is unsymmetrically bidendate,[5] the other one is symmetrically bidentate and bridging as shown in the Figure. The Ag(2)–O(4) bond length is 2·474(3) Å.

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