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The Crystal Structure of N,N′-Bis(cyanomethyl)-1,10-diaza-4,7,13,16-tetraoxa-cyclooctadecane Rubidium Iodide Hydrate

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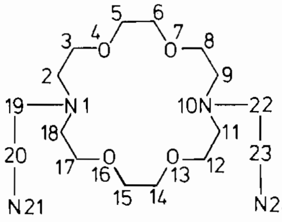
Introduction

Monocyclic crown ethers with additional hetero atoms (*i.e.* electron-donors) in the side chains ('Lariat'-ethers) display interesting cation-binding properties [1–3]; some of their metal complexes are much more stable than those of the respective unsubstituted crowns [1]. The title ligand *1* contains relatively short and hence inflexible $-CH_2-CN$ substituents [4]. The present X-ray study was undertaken to investigate the coordination geometry about Rb^+ and, in particular, the contribution from the cyano groups.



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Experimental

212 mg (1.00 mmol) RbI in 1 ml methanol were added dropwise to 340 mg (1.00 mmol) ligand *1* in 9 ml ethyl acetate and the warm solution was then concentrated to 5 ml. The colourless complex (yield 63%, m.p. 157–158 °C) precipitated on cooling; it was washed with diethyl ether. A sample for X-ray analysis was recrystallised from methanol/ethyl acetate.

Crystal data: $C_{16}H_{28}N_4O_4 \cdot RbI \cdot H_2O$, $M_r = 570.82$, orthorhombic space group $Pna2_1$, $a = 13.222(4)$, $b = 12.752(4)$, $c = 13.517(4)$ Å, $D_{calc.} = 1.663$ mg m^{-3} for $Z = 4$, $\mu(MoK_\alpha) = 3.48$ mm^{-1}.

2563 unique profile-fitted [5] diffractometer data to $2\theta_{max.} = 47°$ with $F > 3\sigma(F)$ were collected at 291 K from a prism *ca.* 0.15 × 0.2 × 0.45 mm with monochromated MoK_α-radiation ($\lambda = 0.71069$ Å); an empirical absorption correction based on ψ-scans was applied.

The structure was solved by Patterson and subsequent Fourier syntheses and refined anisotropically [6] to a final R of 0.042 [$R_w = 0.039$, $w^{-1} = \sigma^2(F) + 0.00015\ F^2$], with ligand H atoms included in calculated positions [C–H = 0.96 Å; $U_{iso}(H_i) = 1.2\ U_{eq}(C_i)$].

Atom parameters are listed in Table I, further information is available from GW on request.

TABLE I. Atomic Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters (Å^2 × 10^3).

	x	*y*	*z*	*U*
Rb	6743(1)	−1112(1)	7500[a]	58(1)
I	6239(1)	−6253(1)	7503(2)	70(1)
O(water)	2912(7)	−6447(6)	2528(15)	196(5)
N(1)	7465(7)	429(6)	9194(8)	60(5)
C(2)	6542(8)	613(10)	9757(8)	92(7)
C(3)	5683(8)	1056(10)	9186(11)	111(8)
O(4)	5338(7)	262(10)	8545(7)	83(4)
C(5)	4451(6)	387(8)	7898(6)	68(4)
C(6)	4691(7)	1026(7)	7002(6)	61(3)
O(7)	5410(7)	387(7)	6490(7)	79(4)
C(8)	5762(8)	1097(8)	5754(7)	86(6)
C(9)	6595(6)	641(11)	5160(8)	66(5)
N(10)	7501(7)	444(6)	5751(7)	52(4)
C(11)	8211(7)	−209(7)	5183(7)	59(4)
C(12)	9029(7)	−725(9)	5766(8)	121(6)
O(13)	8592(8)	−1397(9)	6478(8)	107(6)
C(14)	9203(7)	−2126(6)	7020(5)	104(4)
C(15)	9541(5)	−1567(8)	7917(5)	108(5)
O(16)	8654(4)	−1350(5)	8523(4)	98(3)
C(17)	9002(6)	−664(5)	9269(5)	60(3)
C(18)	8094(10)	−255(12)	9805(7)	95(7)
C(19)	8047(10)	1360(7)	8887(6)	63(5)
C(20)	8289(11)	2091(8)	9708(7)	61(5)
N(21)	8553(6)	2487(5)	10417(6)	79(3)
C(22)	7915(10)	1462(7)	6085(6)	54(4)
C(23)	8361(11)	2070(9)	5258(7)	63(5)
N(24)	8581(6)	2637(5)	4645(5)	84(3)

[a] Fixed to define the origin on the polar axis.

Results and Discussion

The structure of the complex between the unsubstituted aminopolyether 1,10-diaza-4,7,13,16-

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tetraoxa-cyclooctadecane (alternatively 1,7,10,16-tetraoxa-4,13-diaza-cyclooctadecane, hence 'tdco') and RbSCN is approximately the same [7] as that of KSCN/'tdco' [8] where potassium is located in the centre of the macrocycle and coordinated to all its hetero atoms and where these complex units are linked to give infinite chains *via* ··cation··(disordered)anion··cation·· interactions.

In the present compound (Fig. 1), rubidium is located +0.821(4) Å out of the plane of the four O(ether) atoms [co-planar to within ±0.07 Å, N(1) and N(10) deviating by −1.40(1) and −1.36(1) Å, respectively], but nevertheless coordinated to all ring hetero atoms and, additionally, to one water molecule which is in turn probably hydrogen-bonded to the bulky iodide anion.

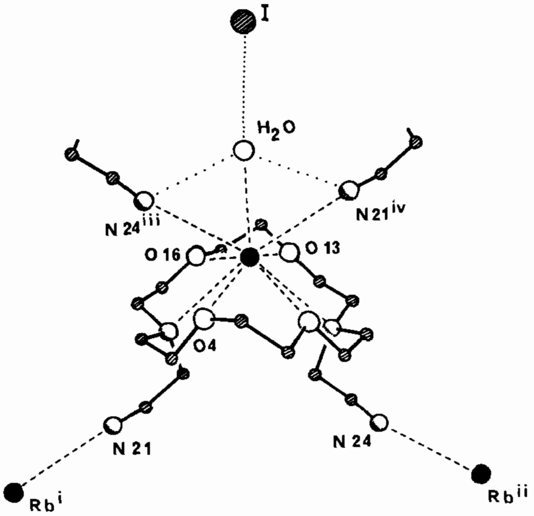

Fig. 1. A view of the title complex, showing interactions to symmetry-related atoms. Coordinates of O(water) as given in Table I, are to be transformed by $1 - x, -1 - y, 0.5 + z$. Rb^{i} is generated by $1.5 - x, 0.5 + y, 0.5 + z$; Rb^{ii} by $1.5 - x, 0.5 + y, -0.5 + z$; $N(24)^{iii}$ by $1.5 - x, -0.5 + y, 0.5 + z$; $N(21)^{iv}$ by $1.5 - x, -0.5 + y, -0.5 + z$. Relevant distances (Å) are: Rb··N(1) = 3.165(6), Rb··O(4) = 2.919(7), Rb··O(7) = 2.936(5), Rb··N(10) = 3.245(5), Rb··O(13) = 2.831(6), Rb··O(16) = 2.896(4), $Rb\cdot\cdot N(21)^{iv}$ = 3.358(8), $Rb\cdot\cdot N(24)^{iii}$ = 3.337(8), Rb··O(water) = 3.146(9), O(water)··I = 3.622(7), $O(water)\cdot\cdot N(21)^{iv}$ = 3.26(1), $O(water)\cdot\cdot N(24)^{iii}$ = 3.36(1).

The cyano substituents are involved in *inter*-molecular linkages to two symmetry-related cations whilst one Rb^+ accepts bonds from two symmetry-related $NC-\overset{|}{\underset{|}{C}}-$ groups. This arrangement results in an intricate system of interactions, probably stabilising the lattice more efficiently than would an *intra*-molecular $-CN\cdot\cdot Rb^+$ coordination (if possible at all from a steric point of view). Moreover, distances of about 3.3 Å (Fig. 1) between the water oxygen O_w and each of the two symmetry-related cyano groups might indicate some alternative N··H–O bonds (particularly when taking into account $N\cdot\cdot O_w\cdot\cdot I^-$ angles of about 110° and $N\cdot\cdot O_w\cdot\cdot N$ *ca.* 120°) which would be consistent with the high thermal motion of O(water) (Table I) and with the relatively weak linkages of Rb^+ to O_w (*ca.* 3.15 Å) and to N(21) and N(24) (*ca.* 3.3 Å) (Fig. 1).

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