Inorganica Chimica Acta, 54 (1981) L185–L186

The Crystal Structure of N,N,N',N'-Tetrakis[2-(8-quinolyloxy)ethyl]ethylenediamine Rubidium Iodide

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Received April 30, 1981

Introduction

Annular, polycyclic and linear ethers containing $-CH_2CH_2O-$ moieties are well established ligands of alkali and alkaline earth metal cations [1–3]. The analogous tri- [4] and tetrapod [5] species also function as ligands. Tris[(2-methyl-8-quinolyloxy)ethyl]-amine has been reported to wrap around Rb^+ in the manner of a linear ether rather than a cryptand [6]. An investigation of a Rb^+ complex with a more intricate tetrapod thus seemed worthwhile.

Experimental

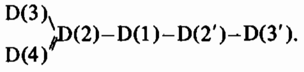
Brownish rods of the title compound containing disordered solvent (probably ethyl acetate) were grown from methanl/ethyl acetate [5]. Crystal data: $C_{46}H_{44}N_6O_4RbI \cdot C_4H_8O_2$, molecular weight 1045.38, monoclinic space group $C2/c$, a = 15.735(5) Å, b = 20.315(8) Å, c = 16.434(6) Å, β = 110.14(4)°, Z = 4, $d_{calc.}$ = 1.4077 g cm^{-3}, $d_{obs.}$ = 1.40 g cm^{-3} (flotation in bromobenzene/ethyl acetate), $\mu(MoK_\alpha)$ = 1.646 mm^{-1}.

Intensities for 1569 unique reflections were measured from a crystal *ca.* 0.4 × 0.2 × 0.2 mm³, with an automated four-circle X-ray diffractometer in the θ–2θ scan mode (BPB method) up to $\sin\theta/\lambda$ = 0.48 (monochromated MoK_α radiation, λ = 0.71069 Å). Data were corrected for Lp and for crystal decay (*ca.* 10%).

TABLE I. Atom Coordinates (×10⁴) and Isotropic Temperature Factors (Å² × 10³).

	x	y	z	U
Rb	0	4093(2)	7500	62(2)[a]
I	5705(3)	4315(2)	9954(2)	143(3)[a]
D(1)	0	1009(8)	7500	179(9)
D(2)	776	802	8096	197(9)
D(3)	1187	1300	8799	197(9)
D(4)	1076	273	8076	197(9)
D(2')	–518	541	6851	197(9)
D(3')	–1237	897	6171	197(9)
N(1)	–568(7)	3676(5)	5511(6)	73(6)
C(2)	–1243	3246	5256	110(9)
C(3)	–1205	2662	4836	157(12)
C(4)	–453	2510	4665	100(9)
C(5)	288	2954	4896	86(8)
C(6)	1081	2861	4704	85(8)
C(7)	1763	3304	4948	90(8)
C(8)	1685	3886	5393	94(9)
C(9)	923	3997	5590	72(7)
C(10)	191	3533	5332	58(7)
O(11)	743(8)	4543(6)	5981(8)	73(5)
C(12)	1436(12)	5045(9)	6208(12)	72(7)
C(13)	1074(13)	5601(9)	6591(12)	72(7)
N(14)	1067(11)	5419(7)	7527(10)	64(6)
C(15)	1998(13)	5368(9)	8182(13)	82(8)
C(16)	2073(13)	4810(9)	8776(12)	71(7)
O(17)	1872(8)	4175(6)	8386(8)	68(4)
C(18)	2522(7)	3870(4)	8140(5)	56(7)
C(19)	3357	4123	8243	82(7)
C(20)	3950	3778	7912	95(8)
C(21)	3691	3204	7481	81(8)
C(22)	2843	2926	7364	60(7)
C(23)	2526	2326	6923	72(7)
C(24)	1681	2119	6803	81(8)
C(25)	1129	2487	7127	85(8)
N(26)	1388	3044	7565	64(6)
C(27)	2236	3264	7681	51(7)
C(28)	510(10)	5915(9)	7767(13)	83(8)

[a] Equivalent isotropic U calculated from anisotropic U.
D(1) to D(3') stand for the solvent molecule



$$\begin{matrix} D(3) \diagdown \\ D(2)-D(1)-D(2')-D(3'). \\ D(4) /\!\!/ \end{matrix}$$

The structure was solved by direct methods and subsequent Fourier syntheses [7]. With only 1245 observed reflections [$F > 3\sigma(F)$], the two quinolyl nuclei per asymmetric unit were assigned geometries averaged from those reported earlier [8] and refined as rigid groups. For ligand H atoms in calculated positions (C–H = 0.96 Å) a riding model was employed; isotropic thermal parameters were fixed at U = 1.2 U of attached C atoms.

A head-to-tail disordered molecule of ethyl acetate, with dimensions taken from the literature [9], was fitted to the residual electron density around the two-fold axis; this procedure reduced R from 0.18 to 0.12 and the maximum difference density from 2.0 to 0.5 e$^-$ Å^{-3}. Omission of 10 low-angle reflections and application of an empirical extinction correction led to final R_w = 0.093 ($w = 1/\sigma^2$) with anisotropic temperature factors for the heavy atoms only.

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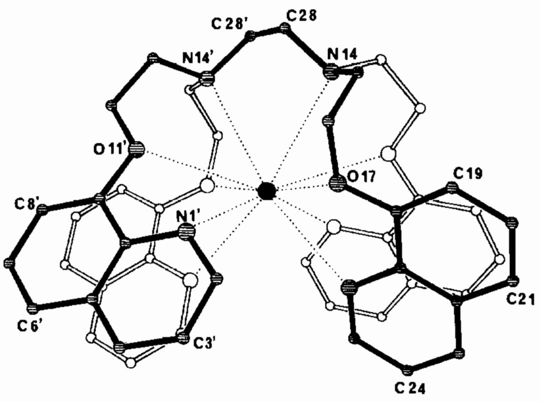

Fig. 1. The structure of the complex and the numbering scheme adopted. Primed atoms are related by the two-fold axis (−x, y, 1.5 − z) running through Rb$^+$ and bisecting the C(28)–C(28') bond. Coordination distances (Å) are: to N(1) = 3.191(10), to O(11) = 3.231(16), to N(14) = 3.165(17), to O(17) = 2.806(12) and to N(26) = 3.026(11).

Atom parameters are listed in Table I, a view of the complex is given as Fig. 1.[†]

Results and Discussion

A ten-fold coordination of Rb$^+$ has been reported with a linear [10] and with a cyclic oligoether [11]; in both cases the cation is totally shielded by the ligand, with the hetero-atoms forming a rather irregular polyhedron at distances slightly longer than the respective sum of ionic and van der Waals radii.

This also holds for the present compound: N(14), O(17), N(26), N(14'), O(17'), N(26') and Rb$^+$ are approximately co-planar (within ±0.64 Å), and the apical atoms N(1) and O(11) deviate by 3.00(3) and 2.77(3) Å from this 'plane'; thus the wrapping of the tetrapod is probably better described as spherical, rather than hexagonal bi-apical-bipyramidal as observed in the tripod complex [6]. Bringing all the hetero-atoms into coordinating positions obviously induces some conformational strain in the ligand. This is particularly reflected in the torsion angles C(13)–N(14)–C(15)–C(16) = −140(2)° and C(28–N(14)–C(15)–C(16) = 99(2)°. Moreover, the shortest ion··dipole contact Rb$^+$··O(17) = 2.806(12) Å is accompanied by an unusual gauche torsion [1] of 79(2)° along C(16)–O(17).

The configuration of the complex cation is possibly further stabilised by a *ca.* 35% overlap of neighbouring quinolyl nuclei N(1) to C(10) and C(18) to C(27) (distance and angle between ring planes 3.37(2) Å, 3(2)°, respectively). This geometry precludes, however, an additional Rb$^+$··I$^-$ contact and leaves the anion in hydrophobic environment which is consistent with its two-fold disorder and high thermal motion. The lack of strong intermolecular interactions in the lattice may be responsible for the poor crystal quality and hence for the relatively high *R* factor in this study.

Acknowledgement

The authors thank Prof. F. Vögtle and his coworkers, Bonn (F.R.G.), for providing the title compound. Except MULTAN, all programs used were home-spun.

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[†] Lists of bond lengths and angles, torsion angles, H atom parameters and observed and calculated structure factors may be obtained from G.W. on request.