Inorganica Chimica Acta, 45 (1980) L35–L36
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

The Crystal Structure of Tris-[(2-methyl-8-quinolyloxy)ethyl] amine Rubidium Iodide

GABRIELA WEBER* and GEORGE M. SHELDRICK

Anorganisch-Chemisches Institut der Universität Göttingen, Tammannstrasse 4, D-3400 Göttingen, F.R.G.

Received March 17, 1980

Introduction

During the last decade, macrocyclic, macropolycyclic and acylic ligands have been designed which coordinate alkali metal ions well [1–3]. Recently reported polypod ligands may be considered 'noncyclic cryptands' [4–6] and indeed some of their complexes with alkali and earth metal ions are more stable than the respective linear oligoether and cyclic crown ether complexes [6].

Structural details of complexes of alkali cations and macrocylic, macropolycyclic and acyclic ethers are known [*e.g.* 2, 7]; it seemed, therefore, worthwhile to study a complex of an alkali cation with a tripod ether.

Experimental

Yellow, cube-shaped crystals were grown from a mixture of ethyl acetate and methanol. *Crystal data:* $C_{36}H_{36}N_4O_3RbI$, molecular weight 785.09, monoclinic space group $P2_1/n$, $a = 9.736(3)$ Å, $b = 15.931(5)$ Å, $c = 23.888(8)$ Å, $\beta = 92.20(3)^\circ$, $d_{\text{calc.}} = 1.408$ g cm^{-3}, $Z = 4$, $\mu(\text{MoK}_\alpha) = 2.16$ mm^{-1}.

The three dimensional intensity data were collected from a crystal of dimensions 0.2 × 0.3 × 0.3 mm^3, with an automated STOE four-circle X-ray diffractometer using monochromated MoK_α radiation ($\lambda = 0.71069$ Å) for θ values between 3° and 25°. 4801 independent reflections were measured, of which 2563 were considered as observed ($F > 4\sigma(F)$). Data were corrected for Lp and absorption effects.

The heavy atoms were located from a three-dimensional Patterson function, and a Fourier synthesis then revealed all the non-hydrogen atoms. In order to avoid a poor ratio of the number of refined parameters to the number of observed reflections, the three quinolyl nuclei and attached H atoms were refined as rigid groups after idealising their geometries (interatomic distances 1.395 Å and 0.96 Å, respectively, bond angles 120.0°). For the refinement of H atoms of secondary methylene groups a riding model was employed. All thermal parameters of H atoms were fixed at values 1.2 times the U values of attached C atoms. Several cycles of blocked cascade least-squares refinement including anisotropic thermal parameters only for the heavy atoms resulted in a residual factor, R_w, of 0.076 ($w = 1/\sigma^2$).

TABLE I. Fractional Atom Coordinates (× 10^4) and Isotropic Temperature Factors (Å^2 × 10^3).

	x/a	*y/b*	*z/c*	*U*
I	8037(2)	2811(1)	1258(1)	94(1)*
Rb	5251(2)	3876(1)	2041(1)	66(1)*
N(1)	4838(8)	2260(5)	2772(3)	49(4)
C(2)	3985(8)	1629(5)	2550(3)	54(5)
C(3)	3247(8)	1121(5)	2907(3)	63(5)
C(4)	3361(8)	1244(5)	3485(3)	87(7)
C(5)	4213(8)	1875(5)	3707(3)	65(6)
C(6)	4327(8)	1998(5)	4285(3)	79(6)
C(7)	5179(8)	2629(5)	4506(3)	105(8)
C(8)	5918(8)	3137(5)	4150(3)	63(6)
C(9)	5804(8)	3015(5)	3571(3)	64(6)
C(10)	4952(8)	2383(5)	3350(3)	54(5)
C(11)	3977(17)	1531(11)	1963(7)	80(7)
O(12)	6480(10)	3445(7)	3189(5)	68(4)
C(13)	7533(16)	4018(11)	3403(7)	68(6)
C(14)	8266(15)	4392(11)	2908(7)	62(6)
N(15)	7479(12)	4966(7)	2549(6)	48(4)
N(16)	4131(9)	4667(5)	913(3)	72(5)
C(17)	3032(9)	4268(5)	631(3)	84(7)
C(18)	2373(9)	4655(5)	171(3)	87(7)
C(19)	2812(9)	5441(5)	−7(3)	95(7)
C(20)	3910(9)	5840(5)	275 (3)	81(7)
C(21)	4349(9)	6626(5)	96(3)	86(7)
C(22)	5447(9)	7026(5)	378(3)	85(7)
C(23)	6107(9)	6638(5)	838(3)	90(7)
C(24)	5668(9)	5853(5)	1017(3)	74(6)
C(25)	4570(9)	5453(5)	735(3)	70(6)
C(26)	2570(17)	3448(11)	851(8)	95(7)
O(27)	6354(11)	5366(7)	1408(5)	73(4)
C(28)	7650(17)	5689(12)	1635(8)	90(7)
C(29)	8255(15)	5097(10)	2069(6)	53(5)
N(30)	2829(8)	4148(5)	2890(3)	57(4)
C(31)	1891(8)	3492(5)	2937(3)	60(6)
C(32)	1439(8)	3261(5)	3462(3)	65(6)
C(33)	1923(8)	3687(5)	3940(3)	86(7)
C(34)	2860(8)	4343(5)	3893(3)	70(6)
C(35)	3344(8)	4768(5)	4372(3)	85(7)
C(36)	4281(8)	5425(5)	4325(3)	86(7)
C(37)	4734(8)	5655(5)	3800(3)	68(6)
C(38)	4250(8)	5230(5)	3321(3)	48(5)
C(39)	3313(8)	4574(5)	3368(3)	52(5)
C(40)	1416(16)	3189(11)	2393(7)	89(7)
O(41)	4666(10)	5364(7)	2805(4)	55(3)
C(42)	5655(15)	6011(10)	2695(7)	66(6)
C(43)	7117(14)	5729(9)	2832(7)	54(5)

*Equivalent isotropic *U* calculated from anisotropic *U*.

Final atom parameters are listed in Table I, the structure of the complex is shown in Fig. 1.**

Results and Discussion

The cation is coordinated by the iodide and also cradled by the three chains of the ligand so that all

---

*Author to whom correspondence should be sent.

**Lists of bond lengths and angles, H atom parameters and observed and calculated structure factors may be obtained from the authors on request.

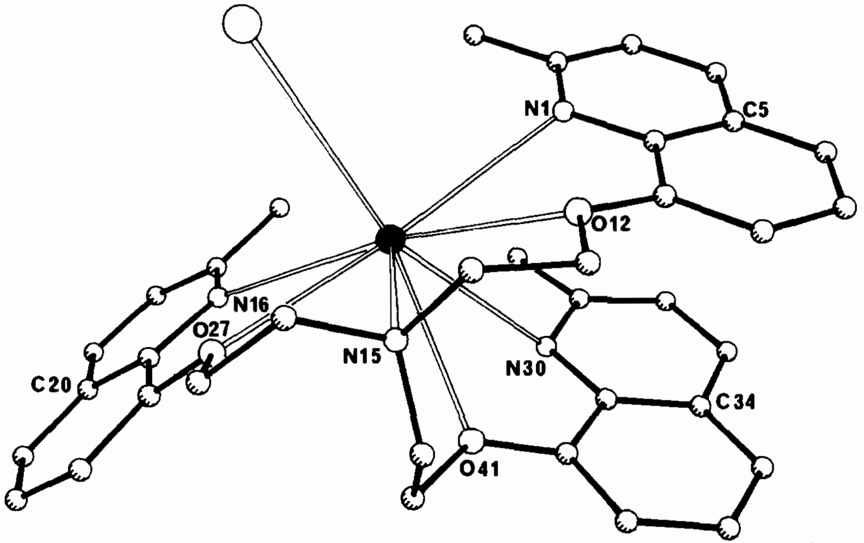

Fig. 1. The Structure of the Complex. Radii are arbitrary. Coordination distances [Å] are: to I^- = 3.758(2), to N(1) = 3.144(8), to O(12) = 3.029(11), to N(15) = 2.999(12), to N(16) = 3.133(9), to O(27) = 3.034(12), to N(30) = 3.198(8), and to O(41) = 3.059(11).

its seven hetero-atoms are brought into coordinating positions with distances slightly longer than the respective sum of van der Waals and ionic radii (see Fig. 1).

In the section of the ligand containing equatorially coordinating hetero-atoms this is achieved without violating the usual stereochemical constraints [2], *i.e.* the C–X–C–C and X–C–C–X moieties are *trans* and *gauche* respectively along the linear chain. Additional coordination of apical hetero-atoms N(30) and O(41), however, requires considerable deviations from the strain-free conformation which is reflected by the torsion angles: C(14)–N(15)–(C43)–C(42) = −138(1)°, C(29)–N(15)–C(43)–C(42) = 100(2)°, C(38)–O(41)–C(42)–C(43) = 81(2)°; in addition C(13)–C(14)–N(15)–C(43) and C(28)–C(29)–N(15)–C(43) are *gauche* instead of *trans*. A 50% overlap of aromatic nuclei N(1) to C(10) and N(30) to C(39) (distance and angle between ring planes 3.17(2) Å, 3(2)° respectively) probably stabilises this configuration *via* intramolecular $\pi\cdots\pi$ interactions. Furthermore, there are short intermolecular contacts between parallel aromatic systems N(16) to C(25) related by a crystallographic centre of inversion. In view of their inert gas electronic structures alkali metal ions can be considered as spherical e^--acceptors and might not require distinct geometries upon complex formation as do transition metals. However, a 'spherical' *i.e.* helical wrapping by ligands mentioned above is not always observed. Especially with cyclic or short acyclic ethers, the coordination geometry is as close to a regular polyhedron as the stereochemistry of the ligand allows [2, 7]. This also holds for the compound under study where the five hetero-atoms N(1) to O(27) are coplanar with Rb^+ within 0.2 Å and form an incomplete hexagon. The remaining two hetero-atoms and I^- complete the coordination bipyramid.

From the coordination geometries of Rb^+ in complexes with comparable ligands, namely (*1*) the cyclic 2,3,11,12-dibenzo-1,4,7,10,13,16-hexaoxocyclo-octadeca-2,11-diene ('dibenzo-18-crown-6') [8], (*2*) the acyclic bis-(8-quinolyloxyethyl)ether [9], and (*3*) the bicyclic 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo-[8.8.8]hexacosane ('[2.2.2]') [10] it appears that the tripod wraps around the cation in the manner of a linear ligand rather than a cryptand.

Acknowledgement

The authors are indebted to Prof. F. Vögtle and his co-workers, Bonn (FRG) for providing the title compound. All calculations and plots were performed with programs written by Prof. G. M. Sheldrick.

References

1 Review: J. M. Lehn, a) *Struct. Bonding (Berlin), 16,* 1 (1973) and b) *Acc. Chem. Res., 11,* 49 (1978).
2 Review: M. Truter, *Struct. Bonding (Berlin), 16,* 71 (1973).
3 Review: F. Vögtle and E. Weber, *Angew. Chem. Int. Ed., 18,* 753 (1979).
4 U. Heinmann, M. Herzhoff and F. Vögtle, *Chem. Ber., 112,* 1392 (1979).
5 F. Vögtle, W. M. Müller, E. Buhleier and W. Wehner, *Chem. Ber., 112,* 899 (1979).
6 F. Vögtle, W. M. Müller, W. Wehner and E. Buhleier, *Angew. Chem. Int. Ed., 16,* 548 (1977).
7 W. Saenger, I.-H. Suh and G. Weber, *Isr. J. Chem.,* in press.
8 D. Bright and M. R. Truter, *J. Chem. Soc. (B),* 1544 (1970).
9 W. Saenger and B. S. Reddy, *Acta Cryst., B35,* 56 (1979).
10 D. Moras, B. Metz and R. Weiss, *Acta Cryst., B29,* 388 (1973).