Crystal structure of [1,8-bis(quinoliniumoxy)-3,6-dioxaoctane·$(H_2O)_2$]$(BF_4)_2$: hydrated quinolinium podand salt or hydronium ion complex?

Steven J. Archer, Klaus R. Koch* and Cheryl Sacht
Department of Chemistry, University of Cape Town, Private Bag Rondebosch, Cape Town 7700 (South Africa)

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Abstract

Structure of diprotonated, hydrated podand cation or hydronium ion complex? The title compound **2** represents the first example of a possible hydronium ion complex with an acyclic bis(quinolyl)-terminated oligoether. The molecule assumes a helical conformation, stabilized, in addition to intra- and intermolecular base stacking interactions, by two sets of bridging hydrogen bonds. The latter cannot unequivocally be formulated as either $N\cdots H{-}OH_2^+$ or $N{-}H^+\cdots OH_2$.

Introduction

In view of the well known proton solvating ability of macrocyclic polyethers [1, 2], structural details of such systems are of growing interest, as exemplified by the molecular structure of a hydronium ion complex of a tetracarboxy-18-crown-6 ether [3]. On the other hand, the proton solvating capacity of linear oligo- and polyethers (glymes) has been found to be considerably less pronounced than that for certain of the cyclic analogues [2, 4]. The incorporation of a variety of rigid terminal groups into acyclic oligoethers leads to enhanced complex stability (the 'terminal group' concept [5]), as is adequately demonstrated by the numerous crystal structures of alkali metal cations, and neutral organic guest molecule complexes [6, 7]. Clearly, basic terminal groups (e.g. quinolyl), may be expected to profoundly influence the proton binding affinity of these podands. This prediction is remarkably confirmed by the reaction of 1,8-bis(quinolyloxy)-3,6-dioxaoctane (**1**) with $[Co(H_2O)_6](BF_4)_2$ in acetone/chloroform mixtures, to yield the title compound **2**, the crystal and molecular structure of which is described here.

Experimental

Preparative methods

The podand **1** was prepared by published methods [8], while suitable, iridescent yellow crystals of **2** were obtained on slow evaporation of a chloroform–acetone (10+4 vol./vol.) solution containing **1** and a slight excess of $[Co(H_2O)_6](BF_4)_2$. *Anal.* Calc. for $C_{24}H_{30}N_2O_6B_2F_8$: C, 46.8; H, 4.9; N, 4.6. Found for **2**: C, 46.5; H, 4.8; N, 4.6%. Melting point 87–89 °C.

X-ray crystal structure determination

X-ray analysis was carried out on an Enraf-Nonius CAD4 diffractometer, using Mo Kα ($\lambda = 0.7107$ Å) radiation. Cell parameters were obtained from least-squares analysis of the setting angles of 24 reflections in the range $16° < \theta < 17°$. During data collection, intensities of 3 reference reflections were monitored every hour, while re-centering was checked after every 100 measured reflections. Lorentz–polarization and empirical absorption corrections (program EAC Enraf-Nonius) were applied. Crystal and other relevant experimental data are given in Table 1.

Structure determination

The structure was determined using the direct methods routine of SHELXS-86 [9] and refined by full-matrix least-squares techniques (SHELX-76 [10]), to $R = 10\%$. The disordered BF_4^- anions were

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*Author to whom correspondence should be addressed.

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TABLE 1. Summary of crystal data, experimental and final refinement parameters for compound **2**

Crystal data	
Molecular formula	$C_{24}H_{30}N_2O_6B_2F_8$
Molecular weight (g mol^{-1})	616.12
Crystal system	monoclinic
Space group	$P2_1$
a (Å)	7.014(2)
b (Å)	12.260(3)
c (Å)	16.657(2)
β (°)	97.08(1)
V (Å^3)	1421(1)
Z	2
D_c (g cm^{-3})	1.44
μ (Mo Kα) (cm^{-1})	1.46
F(000)	636
Data collection	
Crystal dimensions (mm)	0.23 × 0.38 × 0.38
Scan mode	ω–2θ
Scan width in ω (°)	$(0.90 + 0.35\tan\theta)$
Aperture width (mm)	$(1.12 + 1.05\tan\theta)$
θ Range scanned (°)	1–25
Intensity decay (%)	1.2
No. unique reflections collected	2252
No. observed reflections, N, with $I_{rel} > 2\sigma(I_{rel})$	1674
Final refinement	
Residual electron density, max./min. (e Å^{-3})	0.48/−0.38
No. parameters	252
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.105
$R_w = \Sigma w^{1/2}\|\|F_o\| - \|F_c\|\|/\Sigma w^{1/2}\|F_o\|$	0.100
Weighting scheme, w	$(\sigma^2 F)^{-1}$

modelled as two offset rigid tetrahedra (site occupancy factor 0.6 and 0.4) with the boron atoms superimposed (site occupancy 1). The disorder displayed by the BF_4^- anions is responsible for the high temperature factors of the B and F atoms, the residual electron density near the BF_4^- groups ($\sim\frac{1}{2}$ e Å^{-3}) and also the high overall residual of the structure. The available number of data points allowed only the atoms in the ethyleneoxy chain to be treated anisotropically. Other details of the final refinement are given in Table 1. The fractional atomic coordinates and thermal parameters for all non-hydrogen atoms are listed in Table 2. Complex neutral atom scattering factors were taken from Cromer and Mann [11], while dispersion corrections were according to Cromer and Liberman [12]. Drawings were generated using PLUTO [13].

Results and discussion

The structure of **2** is remarkable in that the molecule is stabilized in the observed helical conformation by two sets of bridging hydrogen bonds, in addition to significant intramolecular base stacking interactions. As is evident from Fig. 1, three distinct sets of hydrogen bonds (N···O, O···O, F···O < 2.9 Å) appear to lock the molecule into the observed

TABLE 2. Fractional atomic coordinates (× 10^4) and thermal parameters (Å^2 × 10^3) for non-hydrogen atoms with e.s.d.s. in parentheses for compound **2**

Atom	x/a	y/b	z/c	U_{iso}/U_{eq}[a]
N(11)	5642(13)	6008(11)	7865(6)	50(3)
C(11)	6183(20)	6721(13)	8460(9)	71(4)
C(12)	6279(22)	7850(15)	8238(10)	85(5)
C(13)	5861(21)	8167(16)	7510(10)	86(5)
C(14)	5295(20)	7442(14)	6860(9)	69(4)
C(15)	5170(17)	6319(12)	7073(7)	48(3)
C(16)	4773(22)	7747(15)	6043(10)	88(5)
C(17)	4297(21)	6965(16)	5453(11)	94(5)
C(18)	4163(21)	5860(15)	5690(9)	82(5)
C(19)	4598(18)	5552(11)	6466(8)	51(3)
O(11)	4466(11)	4520(0)	6752(5)	52(3)[a]
C(1)	3842(22)	3675(12)	6203(9)	72(6)[a]
C(2)	3578(19)	2675(12)	6692(9)	67(6)[a]
O(3)	5448(12)	2311(9)	7054(6)	69(4)[a]
C(4)	5378(21)	1452(12)	7605(9)	76(7)[a]
C(5)	7282(18)	1204(13)	7985(9)	71(6)[a]
O(6)	8059(12)	2184(10)	8401(6)	68(4)[a]
C(7)	10005(20)	2093(14)	8655(10)	78(7)[a]
C(8)	10747(18)	3199(14)	8952(8)	68(7)[a]
O(21)	10517(12)	3921(9)	8259(6)	62(4)[a]
N(21)	9855(14)	5131(11)	6941(7)	54(3)
C(21)	9423(21)	5702(15)	6247(9)	79(5)
C(22)	9790(22)	6833(16)	6318(11)	89(5)
C(23)	10368(19)	7337(14)	6968(9)	71(4)
C(24)	10705(20)	6793(14)	7695(9)	67(4)
C(25)	10440(17)	5631(12)	7659(8)	49(3)
C(26)	11360(20)	7235(15)	8423(10)	79(5)
C(27)	11608(21)	6670(15)	9089(10)	80(5)
C(28)	11430(19)	5499(13)	9086(8)	60(4)
C(29)	10855(18)	4983(13)	8355(8)	55(4)
O(1)	8672(13)	3070(10)	6461(5)	70(3)
O(2)	5662(12)	4030(10)	8520(6)	70(3)
B(1)	6434(18)	4900(13)	543(8)	76(5)
F(11)	6481(19)	4782(13)	1364(6)	67(4)
F(12)	5445(22)	4057(13)	151(8)	98(5)
F(13)	5836(21)	5933(12)	367(9)	97(5)
F(14)	8274(23)	4710(17)	354(11)	137(7)
F(11A)[b]	4538(23)	4578(21)	391(15)	118(9)
F(12A)	7478(35)	4284(29)	50(14)	163(14)
F(13A)	7411(30)	4884(18)	1314(8)	79(7)
F(14A)	6759(30)	5824(16)	129(11)	87(7)
B(2)	9902(21)	5125(13)	4056(8)	98(7)
F(21)	9927(22)	6142(12)	4395(9)	79(5)
F(22)	9798(26)	4340(14)	4649(8)	109(6)
F(23)	8581(20)	4950(15)	3405(8)	102(5)
F(24)	11705(21)	4880(18)	3823(11)	153(8)
F(21A)[b]	10865(30)	4347(15)	4484(10)	81(7)
F(22A)	9750(29)	5046(19)	3237(8)	81(7)
F(23A)	8039(28)	5013(22)	4292(14)	137(10)
F(24A)	10554(30)	6157(14)	4249(15)	82(9)

[a] $U_{eq} = 1/3$ (trace of the orthogonalized U_{ij} matrix). [b] A refers to alternative orientations of BF_4^-.

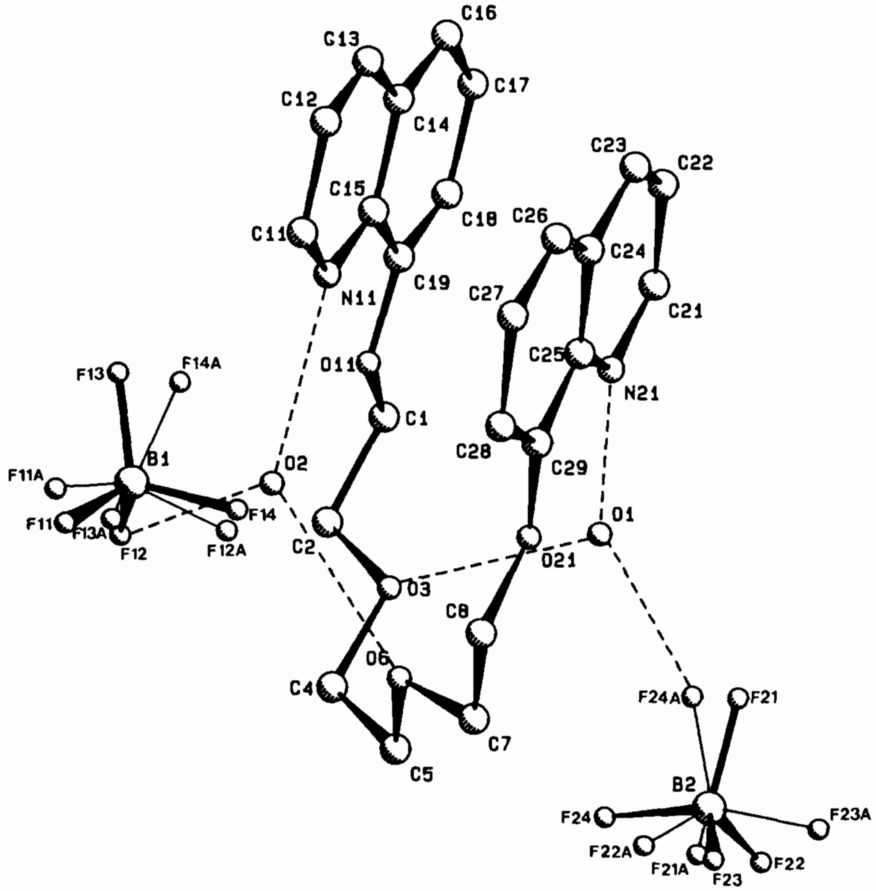

Fig. 1. Structure of 2 including two disordered BF_4^- anions; hydrogen bonds indicated by dashed lines (H atoms omitted for clarity).

conformation. These observations raise the pertinent question of whether it is more appropriate to consider 2 to be a bis(hydronium ion)–podand complex or simply a hydrated diprotonated tetrafluoroborate salt of 1. In the case of N(11)···H···O(2) (2.66(2) Å), N(21)···H···O(1) (2.75(2) Å), O(2)···H···O(6) (2.84(2) Å) and O(1)···H···O(3) (2.74(1) Å), approximate positions for the H atoms have been located by means of difference Fourier maps. Nevertheless, in view of the unfortunate disorder displayed by the BF_4^- anions, attempts to refine the model including these H atoms proved fruitless. Furthermore, it was not possible to locate the H atoms inferred to exist between the definite oxygen–fluorine interactions O(2)···H···F(12) (2.74 Å) and O(1)···H···F(24A) (2.71 Å). Thus given the present data, it is not possible to unequivocally formulate the bridging hydrogen bonds as either $N\cdots H–OH_2^+$ or $N–H^+\cdots OH_2$.

Inspection of the conformation of the ethyleneoxy fragments shows that the C–C–O–C and C–O–C–C torsion angles are *trans* (mean 173°, range 169–178°), while the O–C–C–O fragments assume a *gauche* configuration (mean 64°, range 60–69°). These torsion angles compare well with previously observed values in analogous linear oligoether alkali metal cation complexes [14], as well as in the bis[(8-quinolyloxy)ethoxyethyl]ether–thiourea complex [7]. Evidently such an arrangement represents a favoured, strainfree conformation. All other bond lengths and bond angles fall within the expected ranges (Table 3).

It is noteworthy that the conformation assumed by 2 allows for significant intra- and intermolecular stacking interactions between the quinolyl moieties (3.4 Å). This results in the formation of chains of either left or right-handed helices interspersed with BF_4^- anions as is evident in Fig. 2. (The absolute configuration of the helices could not be determined unambiguously.) The pronounced intra- and intermolecular stacking observed in 2 has not to our knowledge been previously reported for similar quinolyl podand complexes [6, 7, 14]. A certain degree

TABLE 3 Bond distances (Å), bond angles (°) and torsion angles (°) along the oligoether chain of compound **2**

A	B	C	D	B–C (Å)	A–B–C (°)	A–B–C–D[a] (°)
C(11)	N(11)	C(15)	C(19)	1 37(2)	123(1)	− 180(1)
N(11)	C(15)	C(19)	O(11)	1 40(2)	121(1)	4(2)
C(15)	C(19)	O(11)	C(1)	1 36(1)	113(1)	178(1)
C(19)	O(11)	C(1)	C(2)	1 42(2)	119(1)	− 172(1)
O(11)	C(1)	C(2)	O(3)	1 50(2)	107(1)	− 69(1)
C(1)	C(2)	O(3)	C(4)	1 45(2)	108(1)	173(1)
C(2)	O(3)	C(4)	C(5)	1 40(2)	114(1)	− 175(1)
O(3)	C(4)	C(5)	O(6)	1 44(2)	110(1)	60(2)
C(4)	C(5)	O(6)	C(7)	1 46(2)	108(1)	− 169(1)
C(5)	O(6)	C(7)	C(8)	1 38(2)	112(1)	171(1)
O(6)	C(7)	C(8)	O(21)	1 51(2)	108(1)	− 64(2)
C(7)	C(8)	O(21)	C(29)	1 45(2)	107(1)	173(1)
C(8)	O(21)	C(29)	C(25)	1 33(2)	120(1)	− 175(1)
O(21)	C(29)	C(25)	N(21)	1 41(2)	116(1)	− 0(2)
C(29)	C(25)	N(21)	C(21)	1 36(2)	119(1)	180(1)

[a] The torsion angles are defined as follows in a molecular fragment –A–B–C–D–, the torsion angle about the B–C bond is the dihedral angle between the planes defined by A–B–C and B–C–D The strain free values of these angles are ± 180° (*trans*) or ± 60° (*gauche*)

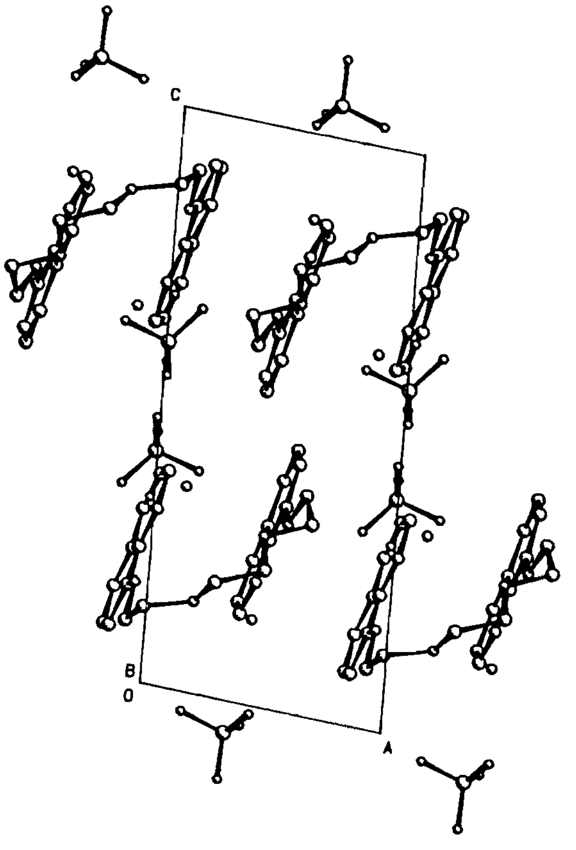

Fig 2 A projection of the molecular packing of **2** viewed along the *b* axis, showing the inter- and intramolecular base stacking interactions between the quinoline groups Only the BF_4^- groups of higher occupancy are shown for clarity

of intramolecular stacking does however occur in the bis[(2-methyl-8-quinolyloxy)ethoxyethyl]ether–RbI complex [15], while intermolecular stacking (3 4 Å) involving the quinoline heterocycles of adjacent molecules, is evident in the structure of bis[(8-quinolyloxy)ethoxyethyl]ether–RbI complex [16]

The unexpected isolation of **2** on attempting to prepare Co(II) complexes with the podand **1**, clearly highlights a consequence of the introduction of a relatively basic terminal group We suggest that the quinolyl moiety induces hydrolysis of the hexaaquocobaltous ion to yield *inter alia*, **2** In contrast, we have found that the analogous podand, 1,8-bis(quinolyloxy)-3,6-dithiaoctane (**3**), readily forms stable cobalt(II) and copper(II) complexes under similar conditions, despite our finding that the Brønsted basicity of the quinolyl groups of **1** and **3** are essentially indistinguishable in dimethyl sulfoxide (log $K_1 = 11\ 72$, 11 69 and log $K_2 = 4\ 22$, 4 15, respectively) [17] We shall report on these details elsewhere

Supplementary material

Additional crystallographic data, bond lengths and angles are available from one of the authors (K R K) on request Arrangements to deposit this material at the Cambridge Crystallographic Data Centre will also be made

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