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Crystal structure of diaqua[*N*,*N*′-bis(tetrafluoropyridyl)diaza-18-crown-6]lead(II) perchlorate: the effect of perfluoroaromatic groups on the stucture of the complex

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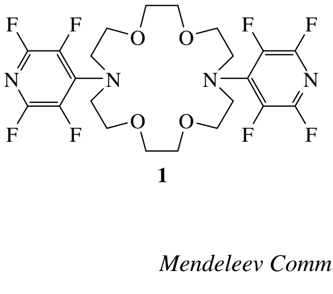
According to X-ray analysis data, in the $[PbL(H_2O)_2]^{2+}$ complex cation [L = *N*,*N*′-di(tetrafluoropyridyl)diaza-18-crown-6], the Pb atom is coordinated asymmetrically by four O(1)–O(4) atoms of the macrocycle and two O(5), O(6) atoms of water molecules, and, additionally, at longer distances, by the *ortho*-fluorine atoms F(4), F(5) of two perfluoropyridyl rings and the N(1), N(2) atoms of the macrocycle, thus demonstrating a partial localization of the lone electron pair of Pb. Using ^1H NMR, the stability of the complex of L with $Pb(ClO_4)_2$ in $[^2H_6]$acetone was estimated ($\log \beta = 0.9$).

Macrocyclic ligands such as crown ethers and cryptands can bind selectively various cations and neutral molecules and, possibly, are the most important class of complex-forming compounds introduced in the chemical practice in the last 30 years. However, there are practically no data on the structure of these complexes of macrocyclic ligands with polyfluorinated fragments in a macrocycle or side chains. A reason for this lack is a very low stability of complexes formed by these compounds, which is due to the strong –*I* effect of fluorine.[1] Particular interest in fluorine-containing ligands is related to the recently revealed capability of substituents, *i.e.*, F atoms, to participate in the coordination of metal cations and appreciation of the importance of such interactions for biological systems.[1,2]



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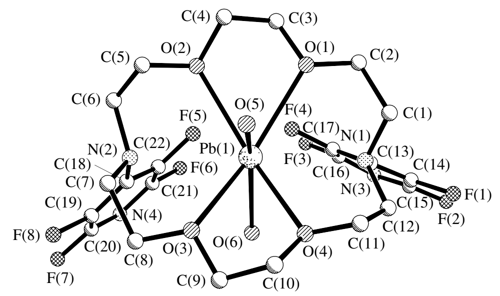

Figure 1 Molecular structure of complex **2**. Selected bond lengths (Å): Pb(1)–O(1) 2.719(6), Pb(1)–O(2) 2.727(6), Pb(1)–O(3) 2.608(6), Pb(1)–O(4) 2.558(6), Pb(1)–O(5) 2.450(8), Pb(1)–O(6) 2.704(8), Pb(1)–N(1) 2.978(8), Pb(1)–N(2) 3.108(8), Pb(1)–F(4) 2.890(10), Pb(1)–F(5) 3.123(9).

N,N'-bis(tetrafluoropyridyl)diaza-18-crown-6 **1** appeared incapable of forming complexes with Group I and II cations and lanthanides.[3] The analysis of published data[4] showed that the most stable complexes with the *N*-substituted diaza-18-crown-6 ethers are formed with Pb^{2+} cations. We have demonstrated that this regularity is also true for *N,N'*-diarylated diaza-18-crown-6 ethers. The stability constants of complexes of *N,N'*-diphenyl- and *N,N'*-bis(*para*-anisyl)diaza-18-crown-6 ethers with $Pb(ClO_4)_2$ in methanol (Table 1) were determined spectrophotometrically as described previously.[5,6] However, no evidence for the complexation of perfluoroarylated crown ether **1** with $Pb(ClO_4)_2$ in methanol was found: the UV and ^{1}H NMR spectra of crown ether **1** in methanol (0.005 mol dm^{-3}) remained unchanged until a $Pb(ClO_4)_2$ concentration of 0.2 mol dm^{-3}.

Nevertheless, the addition of a $Pb(ClO_4)_2\cdot3H_2O$ solution in acetone ($C \sim 0.18$ mol dm^{-3}) to an equal volume of a solution of crown ether **1** ($C \sim 0.15$ mol dm^{-3}) in methylene chloride resulted in the crystallization of complex $PbL(H_2O)_2(ClO_4)_2$ **2**,[†] the structure of which was studied by X-ray analysis.[‡]

In the complex cation $[PbL(H_2O)_2]^{2+}$ (Figure 1), the Pb atom contacts four O(1)–O(4) atoms of the macrocycle and two O(5), O(6) atoms of water molecules along with two N(1), N(2) atoms of the macrocycle and two *ortho* atoms F(4), F(5) of the perfluoroaryl substituents. The irregular ('one-side') coordination of the Pb^{2+} atom in the decahedron $PbO_6N_2F_2$[§] gives evidence for the partial localization of a lone electron pair (LEP) of Pb[10] on the side of seven atoms (3O + 2N + 2F), which are distant from the metal atom.

Table 1 Stability constants (β/dm^3 mol^{-1}) of the complexes of *N,N'*-diaryl-diaza-18-crown-6 ethers with $Pb(ClO_4)_2$, 20 °C.

Aryl	Solvent	log β
p-MeOC$_6$H$_4$	MeOH	4.7±0.1
Ph	MeOH	2.7±0.1
NC$_5$F$_4$	CD$_3$OD	< 0
NC$_5$F$_4$	(CD$_3$)$_2$O	0.9±0.1

The structures of the coordinated molecule L in complex **2** and a free molecule of **1**[11] differ principally. In complex **2**, both tetrafluoropyridyl substituents are located on one side of averaged plain of macrocycle (A); in the centrally symmetric molecule of **1**, they are located by both sides of the plane A. The *gauche* and *trans* conformations of **1** in relation to the bonds N(1)–C(1), N(2)–C(7) and C(1)–C(2), C(7)–C(8), respectively, transfer in **2** to the opposite *trans* and *gauche* conformations. The conformation formula of macrocycle L in structure **2** may be described as $TGT_N\ TGT_O\ TGG_N\ TGT_N\ TGT_O\ TGG_N$.

In a crystal of **2**, the complex cation and perchlorate anions are linked by weak hydrogen bonds $(H_2O)O–H\cdots O(ClO_4)$ ($O\cdots O \geq 2.750$, $O\cdots H \geq 1.82$ Å, OHO angles of 139–163°) forming chains along the *a* axis. Stacking, *i.e.*, interaction between tetrafluoropyridyl rings N(4)F(5)–F(8)C(18)–C(22) of the adjacent cations bound with the inversion centre (distance 3.24 Å), arises in the direction of the *b* axis.

The distances Pb–N in **2** are larger than those in the known complexes of lead(II) with diaza-18-crown-6 ether and its derivatives[12] (Pb–N of 2.648–2.841 Å), the fact shows a weak participation of the nitrogen atoms in coordination of the metal and is in accord with a low stability of complexes formed by crown ether **1**. As demonstrated previously,[11] the LEP of nitrogen in macrocycle **1** is engaged in conjugation with the electron acceptor aromatic system and, hence, is weakly accessible for complex formation. The contacts (of the cation Pb^{2+}) with the F(4), F(5) atoms in the *ortho* positions of the perfluoropyridyl groups are apparently even more important for the complex stability than the interaction of the metal with the nitrogen atoms of the macrocycle. At least one of the distances Pb–F (2.890 Å) is shorter than Pb–N distances and not much longer than the shortest contacts $Pb\cdots F–C$ (2.76–2.78 Å) known at present.[2,12]

The formation of the Pb^{2+} complex with perfluoroarylated crown ether **1** is observable in solution by ^{1}H NMR spectroscopy if one uses less polar [^{2}H$_6$]acetone instead of methanol. With increasing concentration of $Pb(ClO_4)_2$, regular changes in chemical shifts of protons in the macrocycle are observed (Figure 2).[¶] In the spectrum, the presence of only three multiplets of chemi-

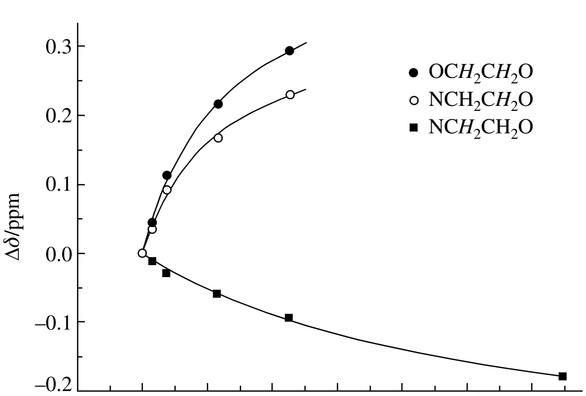

Figure 2 Dependence of the chemical shifts of protons of crown ether **1** on the concentration of $Pb(ClO_4)_2$, [^{2}H$_6$]acetone, 20 °C.

[†] Complex **2**. Found (%): C, 26.35; H, 2.77; N, 5.56. Calc. for $C_{22}H_{28}Cl_2F_8N_4O_{14}Pb$ (%): C, 26.36; H, 2.81; N, 5.59.

[‡] *Crystallographic data for* **2**: $C_{22}H_{28}Cl_2F_8N_4O_{14}Pb$, $M = 1002.6$, monoclinic, space group $P2_1/n$, $a = 9.260(2)$, $b = 16.986(2)$ and $c = 21.620(3)$ Å, $\beta = 96.01(2)°$, $V = 3381(9)$ Å^3, $Z = 4$, $d_{calc} = 1.969$ g cm^{-3}, λ(MoKα) = 0.7107 Å, μ(MoKα) = 5.260 mm^{-1}, $F(000) = 1952$, $T = 293(2)$ K. The experimental data were obtained with a Bruker P4 diffractometer ($\theta/2\theta$-scanning, $2\theta_{max} = 57.8°$). The structure was obtained by the direct method (SHELXS-97)[7] and refined by the least-square roots method (SHELXL-97)[8] in a full-matrix anisotropic approximation for all of the ordered non-hydrogen atoms. Occupancies of five (from eight) statistically disordered oxygen atoms of the ClO_4^- anions are as follows: 0.55 for O(7), O(8), O(11)–O(13) and 0.45 for O(7X), O(8X), O(11X)–O(13X). These O atoms were refined isotropically. The positions of the hydrogen atoms of the molecules of water were determined experimentally and refined in an isotropic approximation. The positions of the other H atoms were calculated from geometric reasons and refined by the riding method using isotropic temperature factors U_H in 1.2 times higher than the U_C factors of the atom to which the selected H atom is attached. The absorption was introduced by the method described in ref. 9. Final $R_1 = 0.0449$, $wR_2 = 0.1096$ and $S = 1.012$ for 5126 reflections with $I > 2\sigma(I)$.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference number 297782. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2006.

[§] The O(3), O(4), O(5) atoms on short distances Pb–O 2.450–2.608 Å (average 2.539±0.089 Å) are located on one side of the metal atom, other three oxygen atoms (Pb–O 2.704–2.727 Å, average 2.717±0.013 Å), two nitrogen atoms (average Pb–N of 3.043±0.065 Å), and two fluorine atoms (average Pb–F of 3.007±0.117 Å) are located on the other side.

cally non-equivalent CH_2 groups, in contrast to total non-equivalence of all of the chains of the macrocycle in a crystal state, may be interpreted as evidence for the symmetrical coordination of the lead cation in a cavity of crown ether **1** or, more probably, as a fast exchange between several unsymmetrical complexes similar to that existing in a crystal state. The signals of protons of the chains $OCH_2\mathit{CH}_2O$ and $NCH_2\mathit{CH}_2O$ are shifted downfield. Their shifts achieve a maximum at a $Pb(ClO_4)_2$ concentration of ~0.2 mol dm^{-3} and remain practically constant. This concentration dependence of chemical shifts ($r^2 = 0.997$) is readily described by equation (1), which corresponds to the formation of the metal : ligand = 1 : 1 complex and makes it possible to calculate the formation constant of the complex by non-linear regression (Table 1).

$$\Delta\delta = \frac{\beta[M]_i\Delta\delta_\infty}{\beta[M]_i + 1}, \qquad (1)$$

where $\Delta\delta = \delta$(crown ether + metal salt) – δ(crown ether), β is the concentration stability constant of the complex and $\Delta\delta_\infty - \Delta\delta$ at the 100 % complex formation.

The signals of the protons of the NCH_2CO groups shift upfield upon the formation of the complex (Figure 2). Surprisingly, their shift continues at $Pb(ClO_4)_2$ concentrations higher than 0.2 mol dm^{-3}, when the chemical shifts of the other CH_2 groups of the macrocycle remain constant. Note that the upfield shift of the signals of this group of protons during the complex formation is a characteristic feature of *N*-arylazacrown ethers, and it is explained by the influence of the cone of magnetic deshielding of aromatic rings under their rotation and conformational changes of the macrocycle.[6,13] The chemical shifts of protons are quite sensitive to the effect of magnetic anisotropy. It is possible to suppose that minor conformational changes of the crown ether (bound in the complex with Pb^{2+}), *e.g.*, due to the formation of ion associates at high concentrations of $Pb(ClO_4)_2$, result in a significant shift of the NCH_2CO protons.

In the ^{19}F NMR spectrum, both signals of perfluoropyridyl groups of crown ether **1** shift downfield upon the formation of the complex. The signal of the fluorine atom in the *ortho* position to the nitrogen atom of the macrocycle shifts and broadens more strongly ($\Delta\delta = 6.2$ ppm, $\sigma_\omega \sim 300$ Hz) than the signal of the fluorine atom in the *meta* position ($\Delta\delta = 3$ ppm, $\sigma_\omega \sim 50$ Hz). Significant signal broadening suggests the coordination of the *ortho* fluorine atom with the Pb^{2+} cation similar to that observed in a crystal state.

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¶ The NMR spectra were recorded with a Bruker Avance 400 spectrometer (400.13 MHz for ^1H and 376.46 MHz for ^{19}F), the residual signals of solvents (^1H) and C_6F_6 (^{19}F, δ_F –162.9 Hz) were used as the internal standards. For crown ether **1**, ^1H NMR ([$^2H_6$]acetone) δ: 3.620 (s, 8H, OCH_2CH_2O), 3.791 (m, 16H, NCH_2CH_2O). ^{19}F NMR ([$^2H_6$]acetone) δ_F: –95.49 (m, 4F), –154.50 (m, 4F).