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N,N'-Bis(*ortho*-Acylaryl)Diaza-18-Crown-6 Ethers: Synthesis, Complexation in Solution, and Crystal Structure of the Complex with Lead Perchlorate

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Abstract—Two new lariat ethers were obtained from N,N'-diaryldiaza-18-crown-6 (Ar = 2-formyl-4-methylphenyl (**II**) and 2-benzoyl-4-methylphenyl (**III**)). In the ethers obtained, the carbonyl O atoms act as additional electron-donating sites. Complexation of lariat ethers **II** and **III** with metal cations in solution was studied by ^{1}H NMR spectroscopy (acetone-d_6, methanol-d_4). The stability constants of the resulting complexes were determined. For lariat ether **III** and its complexes, the magnetic anisotropy of the benzoyl groups substantially influences the chemical shifts of the protons of the macrocycle. The stability of the complexes increases from ether **II** to **III** and in the order $K^+ < Ba^{2+} < Pb^{2+}$. Complexes with La^{3+} were not obtained. The complex of lariat ether **II** (L) with $Pb(ClO_4)_2$, $[PbL(H_2O)](ClO_4)_2 \cdot H_2O$, was characterized by X-ray diffraction. The Pb^{2+} cation is in the cavity of the lariat ether and is coordinated by the formyl O atoms on one side of the macrocycle plane and by the water molecule on the other side (C.N. 9).

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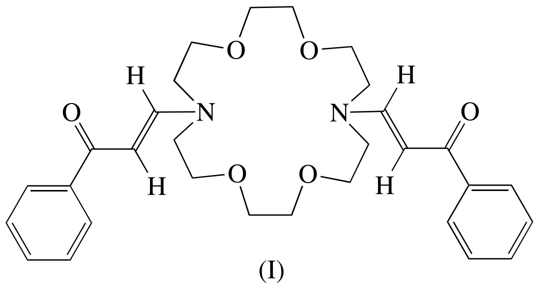
A convenient and widely used method of modifying macrocyclic ligands involves introduction of side chains bearing additional electron-donating sites [1, 2]. By varying such sites and bridges that link them with the macrocycle, one can substantially change the properties of the resulting lariat ether and perform its "fine tuning" for a particular metal cation (or a group of metal cations) [3–11]. In most cases, additional coordinating groups are attached to the N atoms of an azacrown ether through an aliphatic bridge consisting of one (or, less often, two or three) methylene unit (CH_2). At the same time, lariat ethers with aromatic and especially vinylic bridging groups remain less well studied [9–11].



(I)

In [12], we discovered that addition of *trans*-oxo vinylic groups to the N atoms of diaza-18-crown-6 ether makes the resulting ligand **I** selective for rare-earth cations, which is not characteristic of diaza-18-crown-6 itself [13]. According to the ^{1}H NMR, IR, and UV spectra of the complexes, the carbonyl O atoms coordinate the metal atom, despite obvious limitations due to the *trans*-geometry of the vinylic bridge. A similar system with the *cis*-configuration of the vinylic bridge would be much more suitable for coordination of a metal atom in the crown-ether cavity. Unfortunately, secondary acyclic *cis*-enaminones R_2N–CH=CH–C=O are unknown and probably cannot be obtained because of rapid isomerization into a more stable *trans*-form. Attempted introduction of a *cis*-oxo vinylic group into diaza-18-crown-6 by a reaction with *cis*-2-iodovinyl phenyl ketone gave only *trans*-isomer **I**. The problem was solved by employing aromatic bridging groups instead of vinylic ones. The carbonyl group and the N atom of azacrown ether in the *ortho*-position also make up an enaminone system in a fixed *cis*-configuration. In this study, we obtained N,N'-diaryl derivatives of diaza-18-crown-6 with formyl (**II**) and benzoyl (**III**) *ortho*-substituents and studied their complexation with K^+, Ba^{2+}, Pb^{2+}, and La^{3+}.

EXPERIMENTAL

^{1}H NMR spectra were recorded on a Bruker Avance spectrometer (400.13 MHz); the signals of the residual solvent protons served as standards. MALDI mass spectra were recorded on a Bruker Daltonics Autoflex II spectrometer (positive ion mode, N_2 laser (337 nm), accelerating voltage 19 kV, dithranol as a matrix). UV-Vis spectra were recorded on a Hewlett-Packard 8452 UV-Visible System spectrophotometer (quartz cell, l = 10 mm) with the HP UV-Visible ChemStations. The ligands obtained were isolated by column chromatography on Merck 60 silica gel.

***N,N'*-Bis(4-methylphenyl)diaza-18-crown-6** was synthesized from diaza-18-crown-6 (260 mg, 1 mmol), 4-bromotoluene (397 mg, 2.3 mmol), sodium *tert*-butoxide (276 mg, 2.9 mmol), $Pd_2dba_3 \cdot CHCl_3$ (15.4 mg, 0.015 mmol), and 2-dicyclohexylphosphino-2'-dimethylaminobiphenyl (14.6 mg, 0.037 mmol). The reaction mixture was stirred in toluene (4 ml) at 100°C for 18 h and chromatographed with CH_2Cl_2–CH_3OH (11 : 1) as an eluent. The yield was 370 mg (0.84 mmol, 84%).

^{1}H NMR ($CDCl_3$), δ: 2.23 (s, 6H); 3.60 (t, 8H); 3.62 (s, 8H); 3.69 (t, 8H); 6.60 (d, 4H); 7.01 ppm (d, 4H).

MALDI MS, for $C_{26}H_{38}N_2O_4$ anal. calcd. M, 442.3; M – H + Na, 464.3.

Found: $[M]^+$, 442.6; $[M - H + Na]^+$, 464.6.

Attempted metalation of N,N'-bis(4-methylphenyl)diaza-18-crown-6 with BuLi. Butyllithium (0.36 mmol) as a 0.86 M solution in hexane (0.42 ml) was added under argon to a solution of N,N'-bis(4-methylphenyl)diaza-18-crown-6 (81 mg, 0.18 mmol) in anhydrous Et_2O (3 ml). The mixture was stirred for 17 h, whereupon DMF (74 mg, 1 mmol) was added. After 1 h, the mixture was hydrolyzed with aqueous NH_4Cl and organic material was extracted with $CHCl_3$ (3× 5 ml). 9-(4-Methylphenyl)-1-[(4-methylphenyl)amino]-3,6,12-trioxa-9-azatetradecan-14-ol was isolated by column chromatography with $CHCl_3$–CH_3OH (93 : 7) as an eluent. The yield was 56 mg (0.135 mmol, 75%).

^{1}H NMR ($CDCl_3$), δ: 2.24 (s, 6H); 3.27 (t, 2H); 3.52–3.58 (m, 6H); 3.62 (s, 4H); 3.64 (m, 4H); 3.68 (t, 4H); 6.57 (d, 2H); 6.66 (d, 2H); 6.99 (d, 2H); 7.03 ppm (d, 2H).

MALDI MS, for $C_{24}H_{36}N_2O_4$ anal. calcd. M, 416.3.

Found: $[M]^+$, 416.5.

N,N'-Bis(2-bromo-4-methylphenyl)diaza-18-crown-6. Sodium hydroxide (38 mg, 0.95 mmol) in water (0.2 ml) was added to a solution of N,N'-bis(4-methylphenyl)diaza-18-crown-6 (217 mg, 0.49 mmol) in dioxane (3 ml). Then bromine (0.05 ml, 0.98 mmol) in dioxane (1.54 ml) was added at 5°C for 10 min. The reaction mixture was treated with 40% NaOH (2 ml). The product was extracted with $CHCl_3$ (3 × 10 ml) and isolated by column chromatography with CH_2Cl_2–MeOH (50 : 1) as an eluent. The yield was 192 mg (0.32 mmol, 65%).

^{1}H NMR ($CDCl_3$), δ: 2.29 (s, 6H); 3.48 (m, 8H); 3.54 (m, 16H); 7.08 (d, 2H); 7.29 (m, 2H); 7.38 ppm (s, 2H).

MALDI MS, for $C_{26}H_{36}Br_2N_2O_4$ anal. calcd. M + H, 601.1.

Found: $[M + H]^+$, 600.7.

N,N'-Bis(2-formyl-4-methylphenyl)diaza-18-crown-6 (II). Butyllithium (0.33 mmol) as a 0.86 M solution in hexane (0.38 ml) was added under argon at –80°C to a stirred solution of N,N'-bis(2-bromo-4-methylphenyl)diaza-18-crown-6 (82.1 mg, 0.14 mmol) in anhydrous THF (2 ml). The mixture was allowed to warm to –20°C for 30 min, whereupon DMF (0.05 ml, 0.64 mmol) was added. The reaction mixture was hydrolyzed with aqueous NH_4Cl. The product was extracted with $CHCl_3$ (3 × 10 ml) and isolated by column chromatography with chloroform–light petroleum (9 : 1) as an eluent. The yield was 48 mg (0.096 mmol, 70%).

^{1}H NMR ($(CD_3)_2CO$), δ: 2.35 (s, 6H); 3.43 (t, 8H); 3.50 (s, 8H); 3.53 (t, 8H); 7.42 (d, 2H); 7.44 (d, 2H); 7.56 (s, 2H); 10.57 ppm (s, 2H).

MALDI MS, for $C_{28}H_{38}N_2O_6$ anal. calcd. M + H, 499.3.

Found: $[M + H]^+$, 498.8.

For $C_{28}H_{38}N_2O_6$			
anal. calcd, (%):	C, 67.45;	H, 7.68;	N, 5.62.
Found (%):	C, 67.67;	H, 7.59;	N, 5.45.

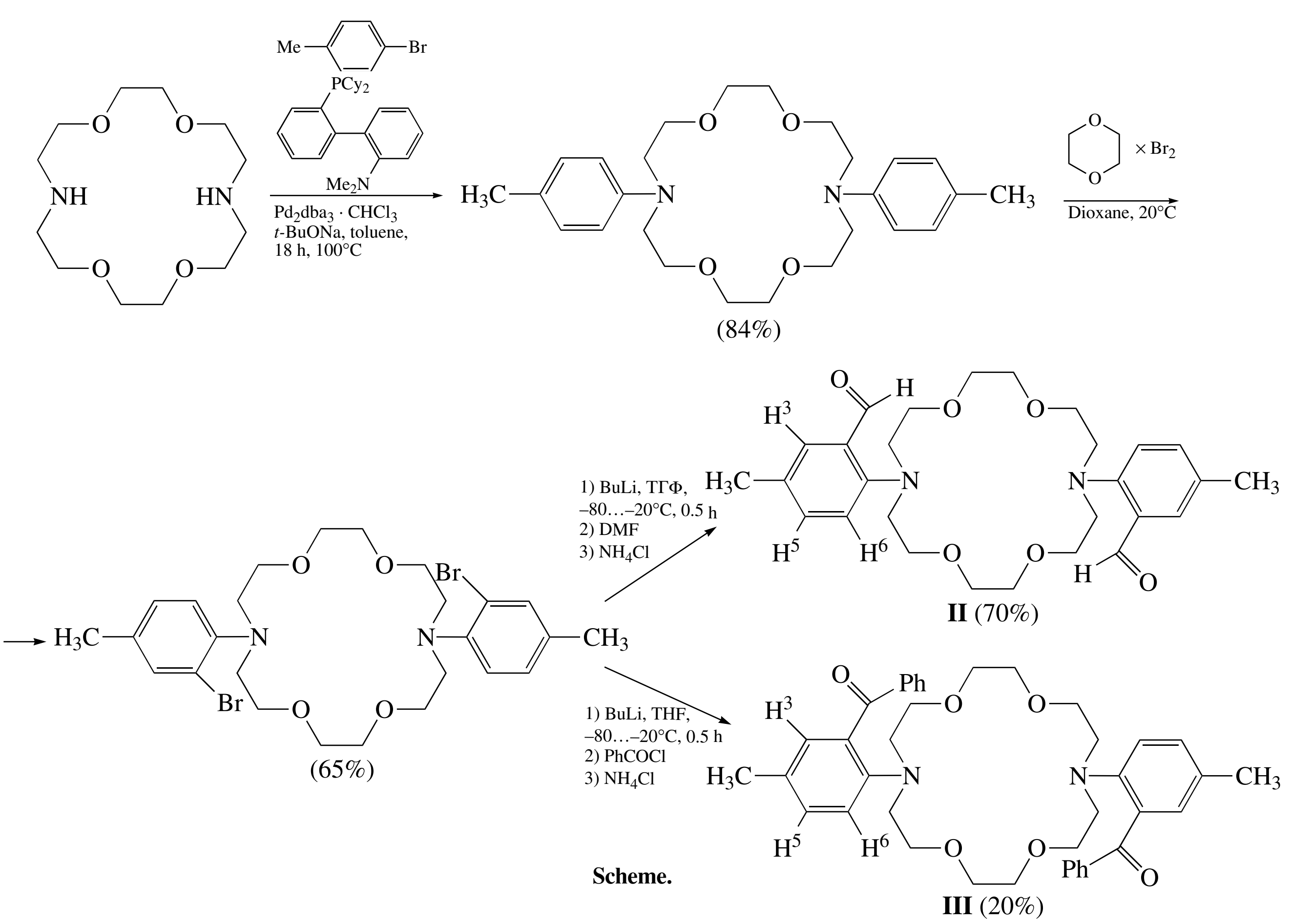
N,N'-Bis(2-benzoyl-4-methylphenyl)diaza-18-crown-6 (III). Butyllithium (0.34 mmol) as a 0.86 M solution in hexane (0.4 ml) was rapidly added under argon at –80°C to a stirred solution of N,N'-bis(2-bromo-4-methylphenyl)diaza-18-crown-6 (96 mg, 0.16 mmol) in anhydrous THF (3 ml). The mixture was slowly warmed to –20°C and kept at this temperature for 5 to 10 min. Benzoyl chloride (52 mg, 0.37 mmol) was added. Then the reaction mixture was warmed to 20°C, stirred for 12 h, concentrated *in vacuo*, and chromatographed first with CH_2Cl_2 and then with CH_2Cl_2–MeOH (from 50 : 1 to 10 : 1) as eluents. The fraction containing the product was additionally filtered through a short column with Al_2O_3. The yield was 21 mg (0.032 mmol, 20%).

^{1}H NMR ($CDCl_3$), δ: 2.33 (s, 6H); 3.21 (m, 16H); 3.35 (s, 8H); 7.12 (d, 1H, J = 1.8 Hz); 7.19 (d, 1H, J = 8.4 Hz); 7.23 (dd, 1H, J = 1.8 Hz, J = 8.4 Hz); 7.38 (t, 2H); 7.52 (t, 1H); 7.70 ppm (d, 2H).

MALDI MS, for $C_{40}H_{46}N_2O_6$ anal. calcd. M + H, 651.3; M + Na, 673.3.

Found: $[M + H]^+$, 651.3; $[M + Na]^+$, 673.3.

Crystals of the complex $[PbL(H_2O)](ClO_4)_2 \cdot H_2O$ (L stands for lariat ether II) were obtained by diffusion crystallization while carefully adding a solution of



Scheme.

$Pb(ClO_4)_2$ (11.8 mg, 0.026 mmol) in acetone (0.2 ml) to a tube (inner diameter 4.2 mm) with a solution of ligand **II** (13 mg, 0.026 mmol) in chloroform (0.2 ml).

X-ray diffraction analysis of the complex was carried out on a Bruker KAPPA APEX II automated four-circle diffractometer (MoK_α radiation, crystal fragment $0.30 \times 0.20 \times 0.10$ mm) fitted with an area detector at 100 K. Reflection intensities were measured in the reciprocal space hemisphere ($\theta_{max} = 30°$). All the reflections were used to refine the unit cell parameters. The experimental intensities were corrected for absorption (SADABS) [14]. The structure was solved by the direct method (SHELXS-97 [15]) and refined by the full-matrix least-squares method (SHELXS-97 [15]) on F^2 for all reflections in the anisotropic approximation for all non-hydrogen atoms. The H atoms of the organic ligand were located geometrically. The H atoms of coordinated and crystallization water were located from a difference electron-density map and refined with restrictions imposed on the O–H distance and the HOH angle.

Crystals are monoclinic; the empirical formula is $C_{28}H_{42}Cl_2N_2O_{16}Pb$ ($M = 940.734$), space group $C2/c$, $a = 17.1536(3)$, $b = 13.8619(3)$, $c = 14.4876(3)$ Å, $\beta = 96.9970(9)°$, $V = 3419.23(12)$ Å^3, $Z = 4$, $\rho(\text{calcd}) = 1.827$ g/cm^3, $F(000) = 1872$, $\mu(MoK_\alpha) = 5.166$ mm^{-1}. The number of measured reflections is 21 357, the number of independent reflections is 4958 ($R_{int} = 0.0210$), the number of reflections with $I > 2\sigma(I)$ is 4665; $-24 \le h \le 19$, $-19 \le k \le 17$, $-18 \le l \le 20$; $R_1 = 0.0173$ and $wR_2 = 0.0427$ for reflections with $I > 2\sigma(I)$; $R_1 = 0.0200$ and $wR_2 = 0.0439$ for all reflections; GOOF = 1.035; $\Delta\rho(\max)/\Delta\rho(\min) = 1.274/-0.896$ e Å^{-3}. Atomic coordinates, thermal parameters, bond lengths, and bond angles have been deposited with the Cambridge Crystallographic Data Collection (no. 718 724); deposit@ccdc.cam.ac.uk or http://www. ccdc. cam.ac.uk.

All calculations were based on the DFT approximation. The geometries of the ligands and the complexes were optimized with the PBE functional [16] and the full-electron three-exponent basis set TZ2P including the polarization functions. Chemical shifts were calculated by the GIAO method [17, 18] for the structures of the ligands and the complexes optimized at the same DFT level. All calculations were performed with the PRIRODA program [19, 20].

RESULTS AND DISCUSSION

ortho-Acylaryldiaza-18-crown-6 ethers **II** and **III** were obtained by sequential introduction of aryl and carbonyl functions into diaza-18-crown-6. First, Pd-

Table 1. Chemical shifts δ (ppm) of the signals for the protons in N,N'-bis(2-formyl-4-methylphenyl)diaza-18-crown-6 (**II**) and their changes $\Delta\delta^a$ (ppm) upon the complexation with K^+, Ba^{2+}, and $Pb^{2+\,b}$

M^+	NCH_2	$NCCH_2O$	$O(CH_2)_2O$	H^3	H^5	H^6	CH_3	CHO
	δ, ppm							
	3.53 (t)	3.43 (t)	3.50 (s)	7.56 (br.s)	7.45 (br.d)	7.42 (d)	2.35 (br.s)	10.57 (s)
	$\Delta\delta$, ppm[a]							
$K^{+\,c}$	–0.01	0.04	0.08	0.1	0.11	0.12	0.04	–0.07
$Ba^{2+\,d}$	–0.04	0.30	0.18	0.38	0.22	0.25	0.11	–0.58
$Pb^{2+\,e}$	–0.05	0.62	0.40	0.35	0.26	0.24	0.12	–0.96

[a] $\Delta\delta$ = δ(crown ether + metal salt) – δ(crown ether); [b] Acetone-d_6, 20°C, $c \approx 5 \times 10^{-3}$ mol l^{-1}; [c] KSCN (100 equiv.); [d] $Ba(ClO_4)_2$ (10 equiv.); [e] $Pb(ClO_4)_2$ (3 equiv.).

Table 2. DFT-calculated chemical shifts δ (ppm) of the signals for the protons in lariat ethers **II** and **III** and their change $\Delta\delta^a$ (ppm) upon complexation[b]

Entry	Lariat ether	M^+	NCH_2	$NCCH_2O$	$O(CH_2)_2O$	H^3	H^5	H^6	CHO
			δ, ppm						
1	**II**		3.89	3.73	3.65	7.36	7.26	7.16	10.18
2	**III**		3.30	3.18	3.65	7.37	7.22	6.96	
			$\Delta\delta$, ppm						
3[c]	**II**	Pb^{2+}	–0.53	0.32	0.36	0.23	0.72	0.27	–1.05
4[d]	**II**	Ba^{2+}	–0.22	–0.25	0.11	0.50	0.86	0.69	–0.24
5[e]	**III**	K^+	0.17	0.12	–0.38	–0.06	0.45	0.74	

[a] $\Delta\delta$ = δ(complex) – δ(crown ether); [b] The averaged chemical shifts of the signals for chemically equivalent protons are given; [c] The cation is coordinated by the carbonyl groups on the same side of the plane of the macrocycle (one-sided coordination); [d] The cation is coordinated by the carbonyl groups on the opposite sides of the plane of the macrocycle (symmetry C_i).

catalyzed arylation of diaza-18-crown-6 gave N,N'-bis(*p*-tolyl)diaza-18-crown-6 [21, 22]. However, during direct *ortho*-metalation of this ether with BuLi, its macrocycle underwent opening into 9-(4-methylphenyl)-1-[(4-methylphenyl)amino]-3,6,12-trioxa-9-azatetradecan-14-ol. The Vilsmeier *ortho*-formylation of N,N'-bis(*p*-tolyl)diaza-18-crown-6 also failed, which can be due to cyclization of an intermediate dimethyliminium cation [23]. For this reason, N,N'-bis(*p*-tolyl)diaza-18-crown-6 was brominated in the *ortho*-position and then lithiated in a metal–halogen exchange reaction (Scheme). Formyl and benzoyl functions were introduced by reactions with appropriate electrophiles (DMF (**II**) and benzoyl chloride (**III**)).

The ability of ligands **II** and **III** to form complexes with some cations in solution was studied by ^1H NMR spectroscopy (Tables 1, 3). In the presence of K^+, Ba^{2+}, and Pb^{2+}, the signals of the protons are shifted because of complexation. At the same time, addition of $La(NO_3)_3$ (2 equiv.) only produces slight broadening of the lines in the ^1H NMR spectra of both ligands ($\Delta\delta <$ 0.01 ppm). This indicates that *cis*-enaminone lariat ethers **II** and **III** fundamentally differ from *trans*-enaminone systems of the type **I**. Not only do the latter form complexes with lanthanide cations but also they are selective for this group of cations [12].

A complex of *ortho*-formylaryl derivative **II** (L) with lead perchlorate in the crystalline state was structurally characterized by X-ray diffraction. The crystals of the complex are built from separate $[PbL(H_2O)]^{2+} \cdot H_2O \cdot 2[ClO_4]^-$ molecules linked by Coulomb and van der Waals interactions. The Pb^{2+} cation is nearly in the center of the crown ether cavity (the deviation is less than 0.1 Å) and is coordinated by all six electron-donating sites of the macrocycle (two N atoms and four O atoms), the O atoms of both formyl groups on one side of the plane of the macrocycle, and a water molecule on the other side (C.N. 9; Fig. 1).

The complex has a twofold axis of symmetry passing through the Pb^{2+} cation and two water (coordinated and crystallization) molecules. Perchlorate anions and

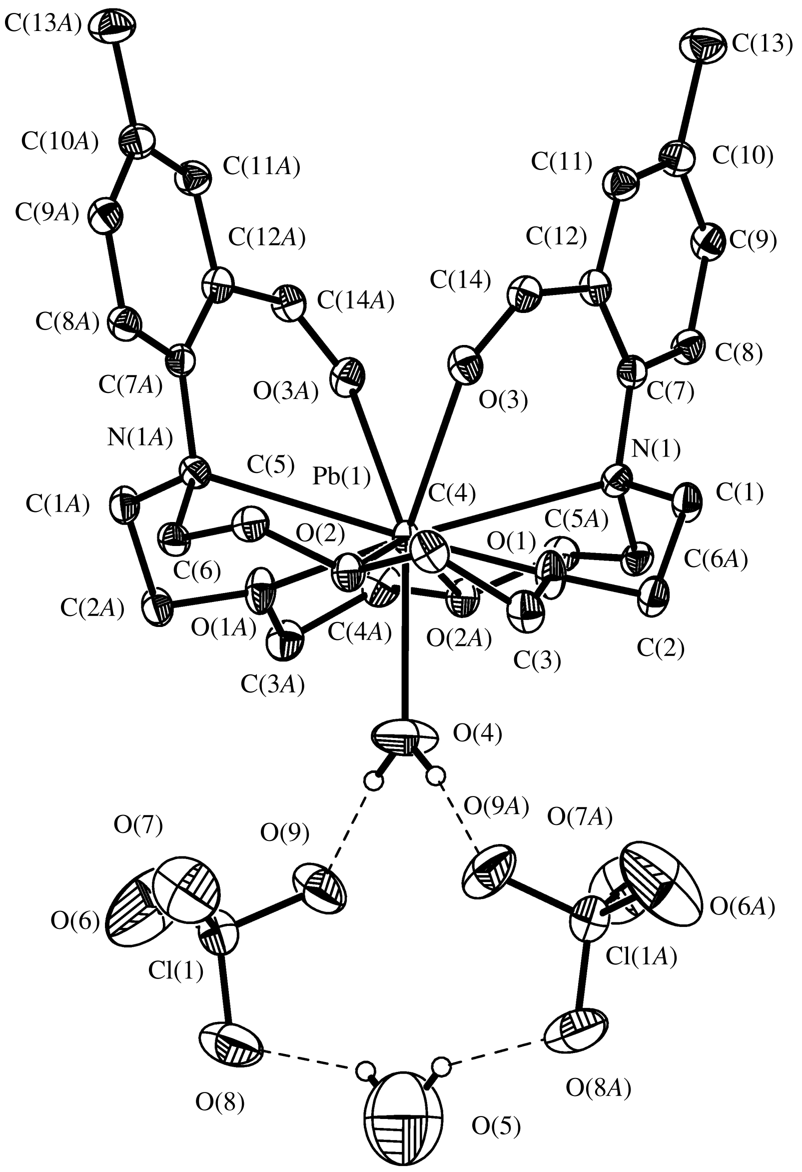


Fig. 1. Molecular structure of the complex $[PbL(H_2O)](ClO_4)_2 \cdot H_2O$ with atomic thermal displacement ellipsoids (50% probability). The H atoms of the organic ligand are omitted. The H atoms of the water molecules are depicted as spheres of arbitrary radii. Hydrogen bonds are indicated with dashed lines. The symmetry operation code for *A* is $1 - x, y, 0.5 - z$. Selected bond lengths are Pb(1)–O(1), 2.6042(14) Å; Pb(1)–O(2), 2.7050(14)Å; Pb(1)–O(3), 2.5788(14) Å; Pb(1)–O(4), 2.541(3) Å; Pb(1)–N(1), 2.8671(15) Å.

a $[PbL(H_2O)]^{2+}$ complex cation are united through hydrogen bonds (O···O 2.754(3) Å) formed by a coordinated water molecule. Another, crystallization water molecule is also hydrogen-bonded to ClO_4^- anions (Fig. 1).

The coordination geometry of the *p* elements in a low oxidation state largely depends on the localization degree of the lone electron pair [24, 25]. Its localization allows the Pb^{2+} cation to form shorter (and hence stronger) bonds to some electron-donating sites, though lengthening the distances from the other sites. The coordination of the lead atom in its complex with ligand L suggests a partial localization (stereochemical activity) of the lone electron pair of Pb^{2+}. The shortest coordination bond links the lead atom with the carbonyl O atom (Pb–O(3), 2.5791(14) Å). The O atoms of the macrocycle are somewhat more distant (Pb–O(1), 2.6041(14) Å; Pb–O(2), 2.7047(13) Å). The N atoms of the macrocycle are the most distant sites in the coordination sphere of lead (Pb–N(1), 2.8669(15) Å). The Pb–N distances are longer, while the Pb–O distances are shorter, than those in Pb^{2+} complexes with unsubstituted diaza-18-crown-6, in which the ligand retains the symmetry "pseudo-C_{3v}" and the lone electron pair of lead is delocalized [26]. As the result, the macrocycle of

Table 3. Chemical shifts δ (ppm) of the signals for the protons in N,N'-bis(2-benzoyl-4-methylphenyl)diaza-18-crown-6 (**III**) and their changes $\Delta\delta^{a}$ (ppm) upon the complexation with K^+, Ba^{2+}, and $Pb^{2+\ b}$

M^+	NCH_2	$NCCH_2O$	$O(CH_2)_2O$	H^3	H^5	H^6	CH_3	*o*-PhCO	*m*-PhCO	*p*-PhCO
	δ, ppm									
	3.17–3.21 (m)		3.31 (s)	7.09 (br.s)	7.29 (br.d)	7.26 (d)	2.34 (br.s)	7.68 (d)	7.47 (t)	7.60 (t)
	Δδ, ppm[a]									
$K^{+\ c}$	0.12		–0.19	0.08	0.26	0.19	0.02	0.20	0.10	0.09
$Ba^{2+\ d}$	~0.3 (br.)		~0.4 (br.)	0.27	0.28	0.36	0.03	0.32	0.18	0.21

[a] Δδ = δ(crown ether + metal salt) – δ(crown ether); [b] Acetone-d_6, 20°C, $c \approx 5 \times 10^{-3}$ mol l^{-1}; [c] KSCN (10 equiv.); [d] $Ba(ClO_4)_2$ (1.3 equiv.).

L in the complex is slightly compressed along the axis passing through both its N atoms. The coordination ability of the nitrogen atoms in N-arylated azacrown ethers is reduced by conjugation with the aromatic system [22, 27]. The aforementioned distortion of the macrocyclic geometry allows more efficient coordination of the Pb^{2+} cation by the crown-ether O atoms for the N atoms are made to leave the plane. One-sided coordination of Pb^{2+} to the carbonyl groups is also due to the compression of the macrocycle and the localization of the lone electron pair of lead. The Pb^{2+} cation deviates from the plane of the macrocycle (four O atoms) by 0.58 Å toward the carbonyl O atoms. In addition, the arrangement of both C=O groups on the one side of the macrocycle plane allows the Pb^{2+} cation to extend its coordination sphere by coordinating a water molecule on the opposite side of the plane (Pb(1)–O(4), 2.54 Å).

Table 4. Stability constants β of the complexes of N,N'-diaryldiaza-18-crown-6 ethers **II** and **III** with K^+, Ba^{2+}, and Pb^{2+} at 20°C. The literature data for N,N'-diphenyldiaza-18-crown-6 (**IV**) are given for comparison

Ligand	Aryl	Cation	Solvent	log β [l mol^{-1}]
II	*o*-C_6H_4CHO	K^+	Acetone-d_6	1.1 ± 0.1[a]
II	*o*-C_6H_4CHO	Ba^{2+}	Methanol-d_4	1.7 ± 0.1[a]
II	*o*-C_6H_4CHO	Pb^{2+}	Methanol	4.2 ± 0.2[b]
III	*o*-$C_6H_4C(O)Ph$	K^+	Methanol-d_4	2.4 ± 0.1[a]
III	*o*-$C_6H_4C(O)Ph$	Ba^{2+}	Methanol	2.7 ± 0.1[b]
IV	Ph	K^+	Methanol	1.1[c]
IV	Ph	Ba^{2+}	Methanol	<1[c] (0.4)[d]
IV	Ph	Pb^{2+}	Methanol	2.7[e]

[a] Determined by ^1H NMR spectroscopy; [b] Determined by UV spectroscopy; [c] Data from [9]; [d] The parenthetic estimate of log β for the Ba^{2+} cation was obtained from the relationship log β $[K^+]$ – log β $[Ba^{2+}]$ = 0.7 found earlier for *p*-substituted N,N'-diaryldiaza-18-crown-6 ethers [27]; [e] Data from [29].

Structural data for the complex of ligand **II** with $Pb(ClO_4)_2$ in the crystal are useful for interpretation of the ^1H NMR spectra of this complex in solution (Table 1). Upon complexation, the signals from the protons of ligand **II** generally experience changes observed earlier for other N-arylazacrown ethers [27–31]. Most of the signals are shifted downfield, which is probably due to a cation field effect. Another characteristic feature is the upfield shift of the signal for the NCH_2 protons of the macrocycle. Earlier, this shift was attributed to the shielding cone produced by rotation of the magnetically anisotropic aromatic rings in the complex [27, 29]. For ligand **II**, the upfield shift of the triplet at δ 3.53 ppm in the presence of metal cations allowed its assignment to the NCH_2 protons, which was confirmed by DFT calculations of the chemical shifts of the protons in ligand **II** (Table 2, entry 1). According to the calculated data, the NCH_2 protons are shielded more strongly than the OCH_2 protons. The calculations also correctly predict the upfield shift of the signal for the NCH_2 protons upon complexation, although with a substantial overestimation (Table 2, entries 3, 4).

It should be noted that the signals for the formyl protons are appreciably shifted upfield upon complexation, especially for the lead complex (Table 1). In the crystal structure of the complex of ligand **II** with $Pb(ClO_4)_2$, the formyl groups are above the planes of the aromatic rings. Thus, the observed shielding of the CHO protons can be explained by the cone effect of the magnetic anisotropy of the aromatic rings provided that the one-sided coordination of lead by the formyl groups is retained in solution. The Δδ value calculated for the complex with one-sided coordination (Table 2, entry 3) is virtually identical with the experimental shift. For the Ba^{2+} complex, two-sided coordination of the cation by

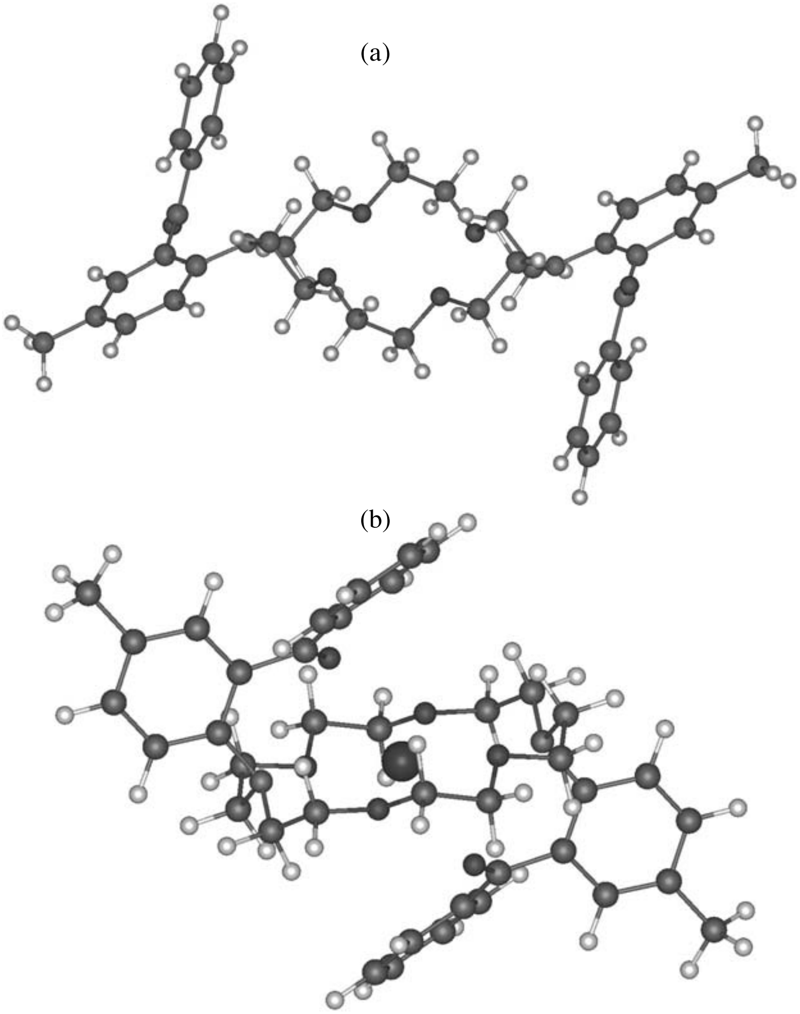


Fig. 2. DFT-calculated structures of (a) N,N'-bis(2-benzoyl-4-methylphenyl)diaza-18-crown-6 and (b) its complex with the K^+ cation.

the formyl groups seems to be more probable (symmetry C_i) [27]; however, a calculation also predicts an upfield shift of the CHO protons (Table 2, entry 4), though a much smaller one than for the Pb complex.

The ^{1}H NMR spectra of *ortho*-benzoyl derivative **III** and its complexes are also influenced, with some specific features, by magnetic anisotropy (Table 3). Even for the ligand itself, the signals from the CH_2 protons are shifted upfield compared to δ values characteristic of crown ethers. Upon complexation with a K^+ cation, the signal for the OCH_2CH_2O fragments is shifted upfield, while the signals for the NCH_2CH_2O fragments are shifted downfield (Table 2). Both effects can be attributed to the ring current of the second benzene ring (in the benzoyl substituent). According to our calculations, the benzoyl groups in one of the most stable conformers of ligand **III** partially shield the protons of all three chemically nonequivalent fragments of the macrocycle (Fig. 2a). In the complex, the benzoyl groups are coordinated by the K^+ cation and their aromatic rings "overhang" the central OCH_2CH_2O fragments of the macrocycle (Fig. 2b), which should result in their additional shielding. These assumptions were confirmed by calculations showing that the CH_2 protons in crown ether **III** are shielded more strongly than those in crown ether **II** (cf. Table 2, entries 1, 2) and that the complexation with the K^+ cation results in additional shielding of the OCH_2CH_2O protons and in deshielding of the OCH_2CH_2N protons (Table 2, entry 5).

We determined the constants **β** of formation of the K^+, Ba^{2+}, and Pb^{2+} complexes with lariat ethers **II** and **III**. Using ^{1}H NMR and (for the more stable complexes) UV spectra (Table 4), we calculated the constants β by nonlinear regression from the chemical shifts (^{1}H NMR, equation 1) or the optical density (UV, equation 2)—these properties are linearly related to the concentration of the complex—as a function of the concentration of the metal salt. In all cases, the experimental data are in satisfactory agreement with the theoretical calculation ($r^2 > 0.98$), which confirms the formation of 1 : 1 complexes.[1]

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

$$A_i - A_\mathrm{L} = \frac{\beta[\mathrm{M}]_i A_\infty}{\beta[\mathrm{M}]_i + 1}. \qquad (2)$$

The stability of the complexes of formyl-containing lariat ether **II** increases in the order $\mathrm{K}^+ < \mathrm{Ba}^{2+} < \mathrm{Pb}^{2+}$, which is quite typical of lariat ethers based on diaza-18-crown-6 [13, 29]. A comparison with data for unsubstituted N,N'-diphenyldiaza-18-crown-6 (**IV**) [9] shows that introduction of *ortho*-formyl substituents increases the stability of the Ba^{2+} and Pb^{2+} complexes by over an order of magnitude (Table 4). This confirms the coordination of the carbonyl groups to the metal atom. On the other hand, the K^+ complex with lariat ether **II** is even less stable than an analogous complex with lariat ether **IV**.[2] Therefore, formyl groups do not play a serious role in the coordination of a singly charged cation (K^+). This is confirmed by an insignificant change in the chemical shift of the signal for the formyl proton in the presence of KSCN (Table 1).

The complexes of *ortho*-benzoyl derivative **III** are more stable than those of lariat ether **II**, especially with K^+ (Table 4). Unlike formyl groups, the more basic benzoyl groups seem to coordinate to the K^+ cation, which is evident from the noticeably changed chemical shifts of the signals for the PhCO protons in the K^+ complex (Table 3).

In conclusion, let us compare the selectivity of N,N'-bis(*ortho*-acylaryl)diaza-18-crown-6 ethers **II** and **III** with the known *trans*-oxo vinylic derivatives of the type **I**. In ligands **I**–**III**, the carbonyl group and the N atom of the azacrown ether form a conjugated enaminone system; however, in ligands **II** and **III**, this system has the *cis*-configuration. A comparison of ligands **I** and **III** is more correct since both contain benzoyl groups as additional electron-donating sites. Lariat ether **III** forms complexes with alkali (K^+) and alkaline-earth metals (Ba^{2+}), but has no affinity for La^{3+}. In contrast, lariat ethers of the type **I** are selective for rare-earth cations, being virtually inert to K^+ and Ba^{2+} [12]. Thus, although the nature of the specific selectivity of *trans*-oxo vinylic derivatives of diaza-18-crown-6 still remains unclear, it cannot obviously be associated only with the high affinity of the carbonyl O atom for hard rare-earth cations.

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[1] A_L is the optical density of the initial solution of the ligand, A_i and $\Delta\delta_i$ are the optical density and the relative chemical shift, respectively, for a solution with the concentration $[\mathrm{M}]_i$ of the free metal, A_∞ and $\Delta\delta_\infty$ are the limiting changes in the optical density and the chemical shift, respectively, for 100% complexation.

[2] Despite the equal $\log\beta$ values (Table 4), the K^+ complex with crown ether **IV** is more stable than that with lariat ether **II** since the data for the former are cited for a more polar solvent (methanol). When passing from methanol to acetone, the stability of complexes of metal cations with crown ethers increases by no less than one order of magnitude [13].

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