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Synthesis and selective lead(II) binding of achiral and enantiomerically pure chiral acridono-18-crown-6 ether type ligands

Luca Szalay,[a] Viktor Farkas,[a] Elemér Vass,[a] Miklós Hollósi,[a,*] Ildikó Móczár,[b] Áron Pintér[b] and Péter Huszthy[b]

[a]*Department of Organic Chemistry, Eötvös Loránd University, H-1518 Budapest, 112 PO Box 32, Hungary*
[b]*Institute for Organic Chemistry, Budapest University of Technology and Economics and Research Group for Alkaloid Chemistry, Hungarian Academy of Sciences, H-1521 Budapest, PO Box 91, Hungary*

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Dedicated to Prof. Károly Lempert on the occasion of his 80th birthday

Abstract—Prompted by the increasing interest in cation complexes of supramolecular host molecules, herein we report the synthesis and CD studies on primary aralkylammonium and metal ion (Na^+, K^+, Mg^{2+}, Ca^{2+} and Ag^+, Zn^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}) complexes of acridono-18-crown-6 hosts **5**, a new family of macrocyclic ligands. CD studies in acetonitrile revealed the selective binding of Pb^{2+} ions by chiral acridono-18-crown-6 ligands. The CD and corresponding UV spectra show two isosbestic points. The isosbestic points are indicative of a rapid equilibrium of two tautomeric forms, the acridino and hydroxy-acridine, while the other species is the Pb^{2+} complex. This suggestion is also supported by the change in the FTIR spectra.

1. Introduction

The structures of supramolecular cation complexes have been studied extensively by X-ray crystallography, NMR, IR, UV and fluorescence spectroscopies as well as microcalorimetry.[1] The discriminating effectiveness of pyridino-**1**, pyridono- and thiopyridono-**2**, phenazino-**3** and acridino-**4** 18-crown-6 hosts as well as pyridino-**1** and phenazino-**3** 18-crown-6 hosts with allylic moieties attached either to the macrocyclic ring ($X = CH{-}CH_2{-}CH{=}CH_2$) or to the heterocyclic subunit ($Y = OCH_2CH{=}CH_2$, Scheme 1) has also been probed by circular dichroism (CD) spectroscopy using the enantiomers of aralkylamine hydrogenperchlorate salts [e.g., α-(1-naphthyl)ethylamine (1-NEA) hydrogenperchlorate].[2–8] Alkali and alkaline earth complexes of selected pyridino hosts have also been studied by CD spectroscopy.[9] The induced CD in the lowest energy $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of pyridine has been interpreted in terms of the one-electron theory of optical activity. Sector rules have been derived for each of these transitions and used to predict the conformation of the crown ethers and their complexes.[9]

In biological systems 'natural enantiomerically pure supramolecular hosts' such as cyclic and linear peptides and proteins, rather than achiral hosts, act as transporting, storage and functional molecules of cations having spherical charge density and a highly symmetrical ligand space. Increasing interest in cation complexes of supramolecular host molecules prompted us to study the chiroptical properties of chiral supramolecular complexes of hosts (Scheme 1) with selected cation guests (Na^+, K^+, Mg^{2+}, Ca^{2+} and Ag^+, Zn^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}). Herein we report the CD studies on primary aralkylammonium and metal cation complexes of acridono-18-crown-6 hosts **5** (Scheme 1), a new family of supramolecular ligands.

2. Results and discussion

Chiral crown ethers (*R*,*R*)-**5c** and (*R*,*R*)-**5d** are new compounds with their syntheses being shown in Scheme 2 and described in the Experimental section.

* Corresponding author. Tel.: +36-1-209-0596; fax: + 36-1-372-2620; e-mail: hollosi@ludens.elte.hu

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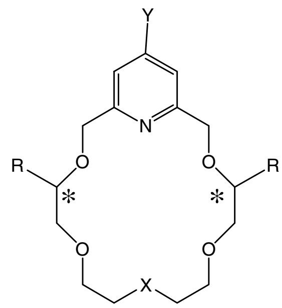
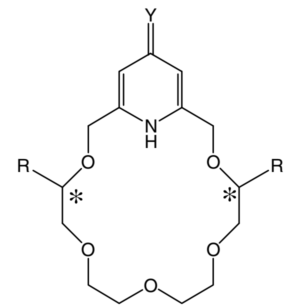
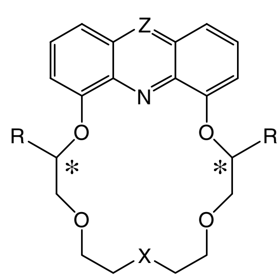


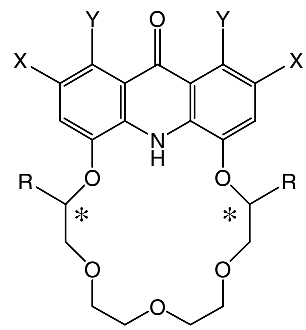
	X	R	Y
1	O	H	H
(S,S)-1a	O	Me	H
(S,S)-1b	$CHCH_2CH{=}CH_2$	Me	H
(S,S)-1c	$C(CH_2CH{=}CH_2)_2$	Me	H
(S,S)-1d	O	*i*Bu	H
(S,S)-1e	$CHCH_2CH{=}CH_2$	*i*Bu	H
(S,S)-1f	$C(CH_2CH{=}CH_2)_2$	*i*Bu	H
(S,S)-1g	O	*i*Bu	$OCH_2CH{=}CH_2$
(R,R)-1h	O	*t*Bu	H
(R,R)-1i	$CHCH_2CH{=}CH_2$	*t*Bu	H



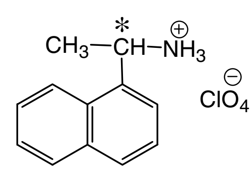
	Y	R
2	O	H
(S,S)-2a	O	*i*Bu
(R,R)-2b	O	*t*Bu
(S,S)-2c	S	Me



	X	R	Z
3	O	H	N
(R,R)-3a	O	Me	N
(R,R)-3b	$CHCH_2CH{=}CH_2$	Me	N
(R,R)-3c	$C(CH_2CH{=}CH_2)_2$	Me	N
(R,R)-3d	O	*i*Bu	N
(R,R)-3e	$CHCH_2CH{=}CH_2$	*i*Bu	N
(R,R)-3f	O	*s*Bu	N
4	O	H	CH
(R,R)-4a	O	Me	CH



	R	X	Y
5a	H	H	H
5b	H	Cl	NO_2
(R,R)-5c	Me	H	H
(R,R)-5d	*i*Bu	H	H

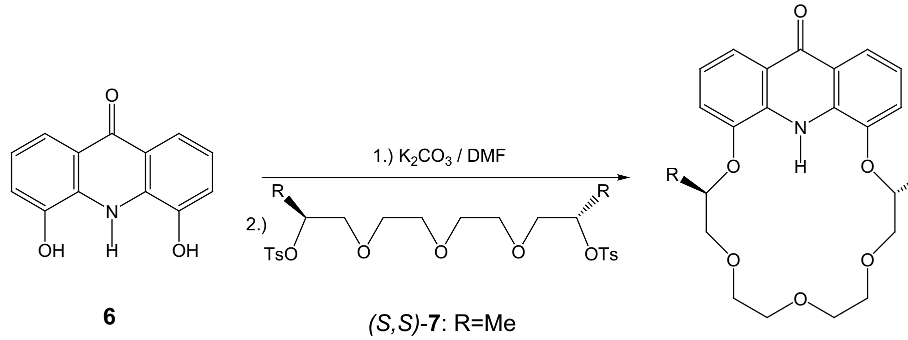


(*RS*)–1-NEA

Scheme 1. Structures of macrocycles containing heterocyclic subunits.

It is noteworthy that under the conditions applied, these reactions proceeded by an S_N2 mechanism with total inversion of configuration of tosylates (*S*,*S*)-**7** and (*S*,*S*)-**8** in accordance with similar reactions.[4] Acridono-18-crown-6 ligands **5a**, **5b**, (*R*,*R*)-**5c** and (*R*,*R*)-**5d** did not form complexes with either (*R*)- or (*S*)-1-NEA hydrogenperchlorate salts, which are well known to be the best-fitting guests of ligands **1**–**4**. This appears to be a consequence of the presence of the proton attached to the N-atom because the 1-NEA hydrogenperchlorate complexes of acridino ligand (*R*,*R*)-**4a** result in exciton CD (EC-CD) spectra indicating strong interaction.[7] The complexation preventing effect of the N–H proton is emphasized by the CD spectra of the 1-NEA complexes of achiral 17,23-dichloro-18,22-dinitro-acridono host **5b**[10] with increased N–H acidity (Fig. 1). As expected, the CD spectra of 1-NEA hydrogenperchlorate complexes of achiral did not differ significantly from the spectra of 1-NEA hydrogenperchlorate salt. However, the spectra of unprotonated 1-NEA complexes of **5b** showed marked changes.

CD spectroscopy was used to probe the complexing of metal cations by acridono-18-crown-6 ligands (*R*,*R*)-**5c**



Scheme 2. Synthesis of new enantiopure chiral acridono-18-crown-6 type ligands.

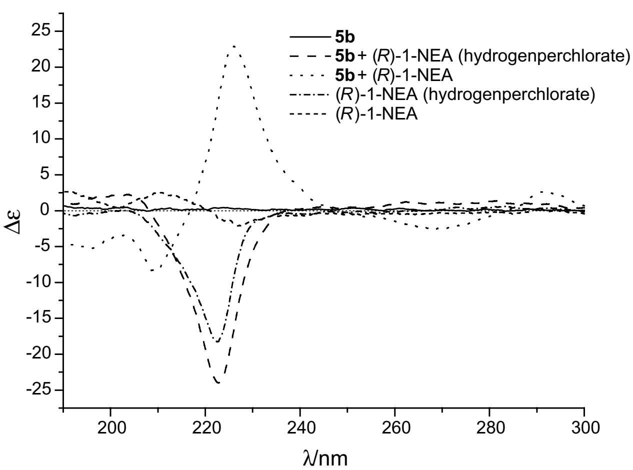


Figure 1. CD spectra of achiral 17,23-dichloro-18,22-dinitro-acridono-18-crown-6 ligand **5b** in the presence of equimolar (*R*)-1-NEA hydrogenperchlorate and (*R*)-1-NEA.

and (*R*,*R*)-**5d**. The coordination chemical parameters of the metal cations used and their biological ligands are listed in Table 1.

Figure 2 clearly shows that Na^+, K^+, Mg^{2+}, Ca^{2+}, Ag^+, Zn^{2+}, Ni^{2+} and Cd^{2+} do not influence the CD spectrum of the host (*R*,*R*)-**5d**. This indicates a lack of complexation or low stability of the complex(es). However Pb^{2+} gave rise to significant spectral changes. For comparison, CD spectra of the acridino host (*R*,*R*)-**4a** and pyridono host (*S*,*S*)-**2a** were also measured in the presence of the above cations at $r_{cat} = 2$ (r_{cat} = [cation]/[ligand]). Host (*R*,*R*)-**4a** has an unprotonated nitrogen comprised in a planar rigid heteroaromatic ring, while (*S*,*S*)-**2a** features a vinylogous amide system similar to that of acridono hosts **5a**-(*R*,*R*)-**5d**.

As shown in Figure 3a and b, all the cations under investigation gave rise to definite spectral changes with (*R*,*R*)-**4a**. The addition of cations to (*S*,*S*)-**2a** also caused changes in the CD spectrum of the host. Thus, the uniqueness of the spectral effect of Pb^{2+} for acridono hosts cannot be the consequence of either the size of the rigid heteroaromatic ring or the vinylogous amide electron system. On the other hand, tautomerization may play a role in Pb^{2+} binding. Upon addition of lead(II) perchlorate, the solution of the crown ethers turned to yellow; a sign of the transition of the conformational

Table 1. Coordination chemical parameters of the cations used and their biological ligands

Ion	Diameter[a] of ion $N = 6$[b] (pm)	Coordination number	Geometry	Biological ligands
Na^+	204	6	Octahedral	O, ether, hydroxyl, carboxylate
K^+	276	6–8	Flexible	O, ether, hydroxyl, carboxylate
Mg^{2+}	144	6	Octahedral	O, carboxylate, phosphate
Ca^{2+}	200	6–8	Flexible	O, carboxylate, carbonyl (phosphate)
Ni^{2+}	138	4	Square planar	S, thiolate N, imidazole N, polypyrrole
		6	Octahedral	Uncommon
Zn^{2+}	148	2–8	Various	O, carboxylate, carbonyl, S, thiolate N, imidazole N
Ag^+	230	2	Linear	—
		3	Trigonal planar	
		6	Octahedral	
Cd^{2+}	190	2	Various	—
		4–7		
Pb^{2+}	238	3–10	Flexible	—

[a] Inner diameters of 18-crown-6 ether type rings: 260–320 pm.[22]
[b] When coordination number is 6.

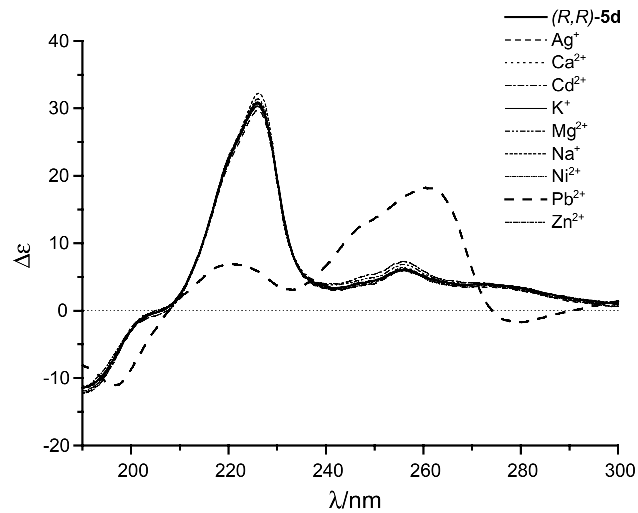


Figure 2. CD spectra of diisobutyl-substituted acridono-18-crown-6 ligand (*R*,*R*)-**5d** in the presence of 2 equiv of metal perchlorates.

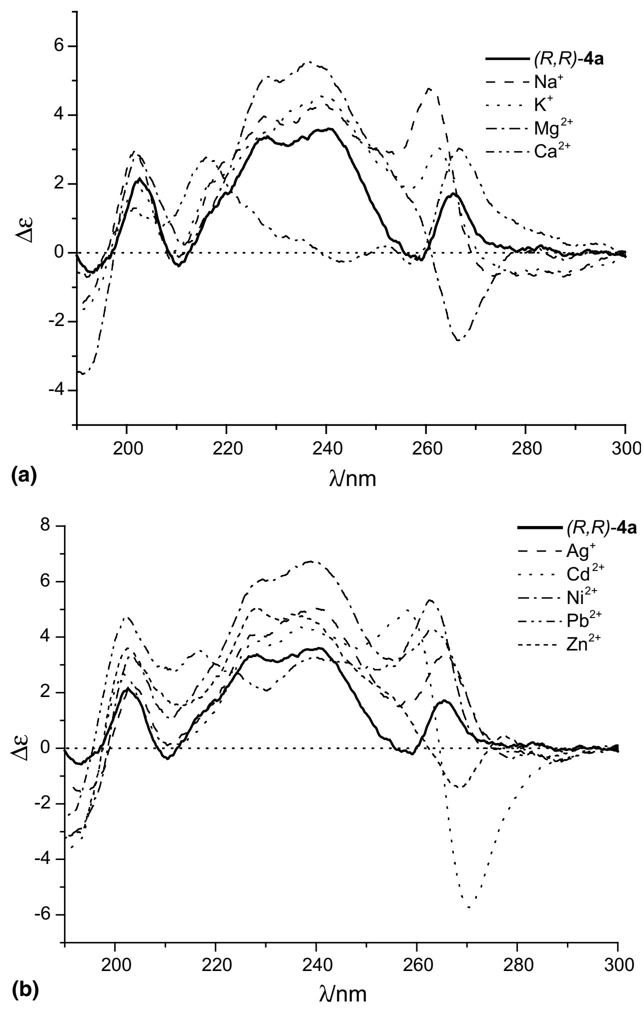


Figure 3. (a) CD spectra of dimethyl-substituted acridino-18-crown-6 ligand (*R*,*R*)-**4a** in the presence of 2 equiv of metal perchlorates (I). (b) CD spectra of dimethyl-substituted acridino-18-crown-6 ligand (*R*,*R*)-**4a** in the presence of 2 equiv of metal perchlorates (II).

equilibrium towards the tautomeric hydroxy-acridine form.

The FTIR spectra of (*R*,*R*)-**5d**, (*R*,*R*)-**5a** (very similar, not shown), as well as their Pb^{2+} complexes at $r_{Pb^{2+}} = 5$ were measured in acetonitrile. The spectra of the free ligands and those in the presence of K^+ ions at $r_{K^+} = 5$ are practically identical, indicating no complexation with K^+ (Fig. 4).

They show a sharp band at 3419 cm^{-1}, assigned to the NH stretching (ν_{NH}) vibration of the acridone moiety (found at 3414 cm^{-1} in KBr, see Experimental). The spectra have many bands in the 1700–1500 cm^{-1} region, showing carbonyl stretching ($\nu_{C=O}$) at 1632 cm^{-1} superimposed with the aromatic ring vibrations. The high intensity of the latter relative to the $\nu_{C=O}$ band is a result of strong coupling with the in-plane N–H bending (β_{NH}) modes in this highly conjugated system. Addition of Pb^{2+} gives rise to marked spectral changes resulting in a considerable decrease in the number and intensity of bands in the 1700–1500 cm^{-1} region, the disappearance of the ν_{NH} band at 3419 cm^{-1} and appearance of a broad ν_{OH} band at ~3260 cm^{-1}. These changes suggest a shift towards the hydroxyl-acridine tautomeric form associated with intermolecular interactions and the formation of strong H-bonds (note the broad and extremely low frequency ν_{OH} band) upon complexation with Pb^{2+}.

It is noteworthy that the parent pyridono-18-crown-6 ligand **2**, which exists in a pyridono tautomeric form in the solid state,[11] tautomerizes into its hydroxy-pyridine form upon complexation with potassium,[11] benzylammonium[12] and (*R*)-1-phenylethylammonium[12] cations according to X-ray analysis. It is also assumed that a lipophilic pyridono-18-crown-6 ligand tautomerizes into its hydroxy-pyridine form upon complexation with Ag^+ and Pb^{2+} cations in a bulk water/dichloromethane/water system.[13] The stoichiometry and stability of Pb^{2+} complexes of (*R*,*R*)-**5d** were monitored by CD and UV titration (Figs. 5 and 6).

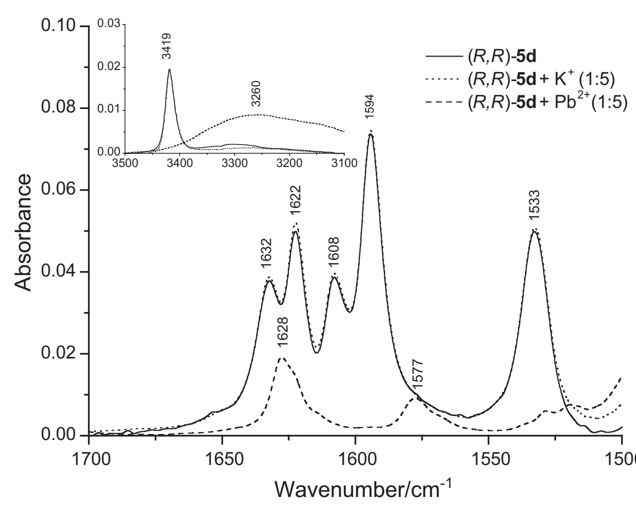


Figure 4. Effect of K^+ and Pb^{2+} ions on the FTIR spectrum of (*R*,*R*)-**5d** in acetonitrile.

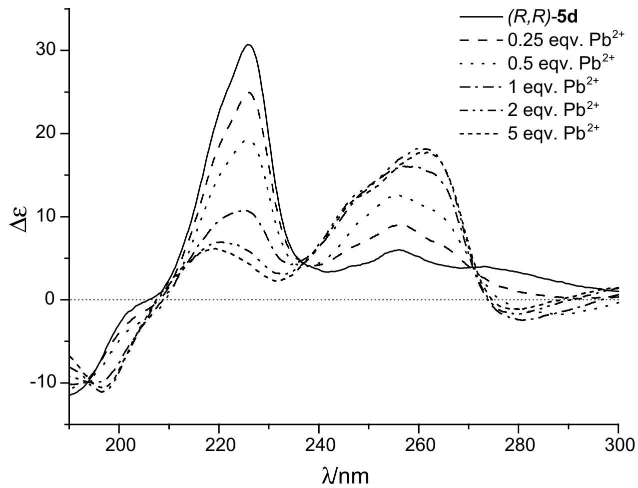


Figure 5. CD-monitored titration of diisobutyl-substituted acridono-18-crown-6 ligand (*R*,*R*)-**5d** with Pb^{2+}.

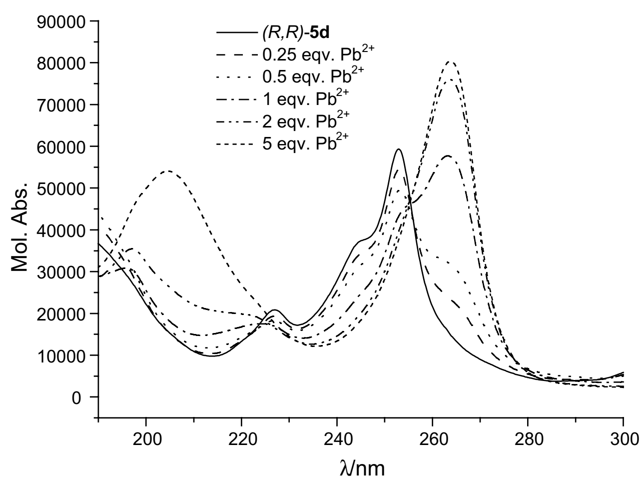


Figure 6. UV-monitored titration of diisobutyl-substituted acridono-18-crown-6 ligand (*R*,*R*)-**5d** with Pb^{2+}.

The CD and corresponding UV spectra show two isosbestic points (at 236.5 nm and 271.0 nm on the CD spectra) as a sign of the presence of two species: the free host and the complex. The UV and CD spectra change continuously until $r_{Pb} \approx 5$.

UV titration was performed in order to determine the stoichiometry and stability constant (K_s) of the Pb^{2+} complex. UV spectra were measured at 23 different Pb^{2+} to (*R*,*R*)-**5d** ratios. Surprisingly, calculations did not confirm the formation of either a 1:1 or 2:1 Pb^{2+}/(*R*,*R*)-**5d** complex. Accordingly, the isosbestic points of the spectra in Figures 5 and 6 are indicative of the rapid equilibrium of two tautomeric forms, the acridino and hydroxy-acridine, with the other species as the Pb^{2+} complex.

CD studies in acetonitrile (Fig. 2) revealed the selective binding of Pb^{2+} ions by chiral acridono-18-crown-6 ligands (*R*,*R*)-**5c** and (*R*,*R*)-**5d** [CD spectra are shown only for (*R*,*R*)-**5d**]. CD and UV measurements showed no Pb^{2+} complexing in methanol.

Concerning the CD spectra of cation complexes, the most interesting question is the position of the cation relative to the plane of the macroring. According to X-ray crystallography, the water complex of achiral acridone ligands **5a** and **5b** has a nonplanar geometry.[14] Chiral acridone ligands (*R*,*R*)-**5c** and (*R*,*R*)-**5d** are expected to have an even more distorted structure.

The chiroptical properties of supramolecular cation complexes are determined by the perturbing substituents on the macroring and by the location of the cation. In addition, the cation may also fix one of the rotamers of the hydroxy-acridine tautomer, the macroring atoms of which also contribute to the rotational strength. It is very likely that it is the hydroxy-acridine tautomer, which prevails in the complex.

Our knowledge regarding the structure of Pb^{2+} complexes of chiral supramolecular hosts is rather limited. Pb^{2+} exhibits a wide degree of flexibility in the geometry and coordination number of its complexes.[15] A wide variety of achiral N,O donor macrocycles have been reported as ligands of Pb^{2+}.[14] Pyridino-18-crown-6 ligands with pyridine, oxygen and –NH– binding sites are also known.[15,16] Substituents of the macroring such as alcoholic or phenolic groups may also be involved in Pb^{2+} binding. Many ligands form a 1:1 Pb^{2+} complex but binuclear and polymeric complexes have also been described.[15,16] In a possible distorted square pyramidal structure of a 1:1 chiral acridono-18-crown-6 Pb^{2+} complex,[15] the cation is not situated in the nodal or symmetry plane of the heterocyclic ring and thus has a strong perturbing effect. We did not succeed in determining the stoichiometry and stability constant of the Pb^{2+} complex(es) of (*R*,*R*)-**5d** because UV titration reflects both the equilibrium between the tautomeric forms and the formation of the Pb^{2+} complex. Currently we are not able to crystallize a lead complex of achiral or chiral acridono ligands. Further studies are needed to clarify the geometry of the Pb^{2+} complex.

CD spectroscopy proved to be a simple and rapid method for providing qualitative information on cation selectivity. It can also be of great help in designing and testing new host molecules. An allylic group appended to the macroring of acridono-18-crown-6 ligands would allow the attachment of the supramolecular ligand to the solid matrix giving rise to a lead-specific chromatographic sorbent.

3. Experimental

3.1. General

Infrared spectra in KBr were recorded on a Zeiss Specord IR 75 spectrometer. FTIR spectra of (*R*,*R*)-**5d**, and (*R*,*R*)-**5c** in acetonitrile or in a solution of potassium perchlorate or lead(II) perchlorate in acetonitrile ($r_M = 5$) were measured on a Bruker Equinox55 spectrometer using 0.2 mm CaF_2 cells. Optical rotations were taken on a Perkin–Elmer 241 polarimeter that was calibrated by measuring the optical rotations of both enantiomers of menthol. ^1H (500 MHz) and ^{13}C (125 MHz) NMR spectra were taken on a Bruker DRX-500 Avance spectrometer. Molecular masses were determined by a VG-2AB-2 SEQ reverse geometry mass spectrometer. Elemental analyses were performed in the Microanalytical Laboratory of the Department of Organic Chemistry, L. Eötvös University, Budapest, Hungary. Melting points were taken on a Boetius micromelting point apparatus and are uncorrected. Starting materials were purchased from Aldrich Chemical Company unless otherwise noted. Silica gel 60 F_{254} (Merck) and aluminium oxide 60 F_{254} neutral type E (Merck) plates were used for TLC. Aluminium oxide (neutral, activated, Brockman I) and silica gel 60 (70–230 mesh, Merck) were used for column chromatography. Solvents were dried and purified according to the well-established methods.[17] Evaporations were carried out under reduced pressure.

3.2. 2,5,8,11,14-Pentaoxa-26-azatetracyclo-[13.9.3.0.^{19,27}.0^{21,25}]heptacosa-1(24),15,17,19(27),21(25),22-hexaene-20(26*H*)-one 5a and 17,23-dichloro-18,22-dinitro-2,5,8,11,14-pentaoxa-26-azatetracyclo-[13.9.3.0.^{19,27}.0^{21,25}]heptacosa-1(24),15,17,19(27),21(25),22-hexaene-20(26*H*)-one 5b

Compounds **5a** and **5b** were prepared as reported.[10] (*R*)- and (*S*)-1-(α-naphthyl)ethylamine (1-NEA) hydrogen-perchlorates were obtained according to the literature.[18]

3.3. (3*R*,13*R*)-3,13-Dimethyl-2,5,8,11,14-pentaoxa-26-azatetracyclo[13.9.3.0.^{19,27}.0^{21,25}]heptacosa-1(24),15,17,19(27),21(25),22-hexaene-20(26*H*)-one (*R*,*R*)-5c

A mixture of 4,5-dihydroxyacridine-9(10*H*)-one **6** monohydrate[19] (466 mg, 1.9 mmol), (2*S*,12*S*)-4,7,10-trioxadecane-2,12-diol-di-*p*-tosylate (*S*,*S*)-**7**[4] (1.06 g, 2.0 mmol), finely powdered anhydrous K_2CO_3 (2.76 g, 20.0 mol) and dry DMF (40 mL) was stirred vigorously under Ar at room temperature for 10 min then at 50 °C for 14 days. The solvent was removed at 35 °C under reduced pressure and the residue taken up in a mixture of ice-water (60 mL) and CH_2Cl_2 (60 mL). The aqueous phase was extracted with CH_2Cl_2 (3×30 mL). The combined organic phase was dried over $MgSO_4$, filtered and the solvent removed. The crude product was purified by column chromatography on alumina using 1% EtOH in toluene as eluent. The yellow solid was recrystallized from EtOH using charcoal to give (*R*,*R*)-**5c** monohydrate (205 mg, 25%). Mp: 203–205 °C; $R_f = 0.40$ (alumina TLC, 2.5% EtOH in toluene), $R_f = 0.22$ (silica gel TLC, 50% EtOAc in hexane); $[\alpha]_D^{25} = -14.1$ (*c* 1.60, CH_2Cl_2); IR (KBr) ν_{max} 3520, 3326, 3080, 2980, 2904, 2868, 1628, 1616, 1588, 1532, 1480, 1460, 1432, 1368, 1328, 1272, 1220, 1144, 1100, 1032, 1000, 928, 756 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.43 (d, $J = 6.3$ Hz, 6H), 2.70 (s, broad, complexed water, 2H), 3.67–3.75 (m, 4H), 3.86–3.94 (m, 8H), 4.71–4.77 (m, 2H), 7.12–717 (m, 4H), 8.06 (d, $J = 8.0$ Hz, 2H), 9.64 (s, broad, NH, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 15.48, 71.73, 72.03, 74.68, 75.04, 114.45, 118.82, 120.82, 122.38, 132.60, 145.71, 178.19; HRMS (FAB) calcd for $C_{23}H_{28}NO_6^+$ $(M+H)^+$: 414.1917. Found: 414.1908; Anal. Calcd for $C_{23}H_{27}NO_6 \cdot H_2O$: C, 64.02; H, 6.77; N, 3.24. Found: C, 63.90; H, 6.83; N, 3.22.

3.4. (3*R*,13*R*)-3,13-Diisobutyl-2,5,8,11,14-pentaoxa-26-azatetracyclo[13.9.3.0.^{19,27}.0^{21,25}]heptacosa-1(24),15,17,19(27),21(25),22-hexaene-20(26*H*)-one (*R*,*R*)-5d

Crown ether (*R*,*R*)-**5d** was prepared as described above for its analogue (*R*,*R*)-**5c** using (4*S*,14*S*)-2,16-dimethyl-6,9,12-trioxaheptadecane-4,14-diol-di-*p*-tosylate (*S*,*S*)-**8**[4] (1.23 g, 2.0 mmol). This time the reaction was completed in 15 days. The crude product was purified by chromatography first on alumina using 0.8% EtOH in toluene as eluent then on silica gel using 30% EtOAc in hexane as eluent to give (*R*,*R*)-**5d** (199 mg, 21%) as a yellow solid. After recrystallization from ether, 161 mg (17%) of pale yellow crystals were obtained. Mp: 79–81 °C; $R_f = 0.45$ (alumina TLC, 2.5% EtOH in toluene), $R_f = 0.40$ (silica gel TLC, 50% EtOAc in hexane); $[\alpha]_D^{25} = +42.3$ (*c* 1.37, CH_2Cl_2); IR (KBr) ν_{max} 3414, 3080, 2952, 2872, 1624, 1616, 1592, 1532, 1480, 1368, 1272, 1220, 1108, 1072, 1056, 944, 752 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 0.96 (d, $J = 5.9$ Hz, 6H), 1.03 (d, $J = 5.9$ Hz, 6H), 1.73–1.81 (m, 6H), 3.64–3.71 (m, 4H), 3.85–3.93 (m, 8H), 4.65–4.66 (m, 2H), 7.11–718 (m, 4H), 8.06 (d, $J = 7.5$ Hz, 2H), 9.48 (s, broad, NH, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 22.43, 23.55, 25.10, 38.01, 71.40, 72.13, 72.16, 77.86, 114.36, 118.68, 120.58, 122.35, 132.46, 145.60, 178.20; HRMS (FAB) calcd for $C_{29}H_{40}NO_6^+$ $(M+H)^+$: 498.2856. Found: 498.2861; Anal. Calcd for $C_{29}H_{39}NO_6$: C, 70.00; H, 7.90; N, 2.81. Found: C, 69.87; H, 7.95; N, 2.78.

The synthesis of pyridino-18-crown-6 ligand **2a** and acridino-18-crown-6 ligand **4a** has been published.[20,21]

3.5. CD spectroscopy

CD spectra were recorded on a Jasco J-810 dichrograph (calibrated with ammonium *d*-10-camphor sulfonate) at room temperature using 0.02 cm cell for measurements between 190 and 300 nm and 0.1 cm above 300 nm. Acetonitrile (UVASOL), as well as methanol (UVASOL) were used as solvents with the concentration ranging from 0.5 to 1 mM dm^{-3}, depending on the absorption. The CD spectra of cation complexes of hosts (*R*,*R*)-**5c** and (*R*,*R*)-**5d** were measured at a cation to crown 2:1 molar ratio ($r_{cat} = 2$), unless otherwise stated. CD titration was performed at a constant concentration (0.5 mM) of the host.

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