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Synthetic Ionophores. Part 17. Synthesis of Ether-Amine-Amide Based *m*-Cyclophanes: A Search for Pb^{2+} Selective Ionophores ⋆

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Abstract. *m*-Cyclophanes **3**, **4**, and **5** possessing two ether oxygen, two amide, one NH and a π-system, an optimal combination of ligating sites for selective Pb^{2+} binding, have been synthesized by condensations of diethylenetriamine, 3,3′-diaminodipropylamine and 1,3-diaminopropane with 1,3-bis(ethoxycarbonylmethoxy) benzene (**6**) formed by the PTC reaction of resorcinol and ethyl chloroacetate. Ionophores **3-5** induced cation extraction/transport could not be studied due to their insolubility in $CHCl_3/CH_2Cl_2$ and solubility in water, but ^{13}CNMR titrations of **4** with metal ions point to its binding preferences for Ag^+ and Pb^{2+} over alkali/alkaline earth cations.

Key words: ionophores, diesters-diamides, *m*-cyclophanes, Pb^{2+} picrate.

1. Introduction and Design

The development of fast, sensitive and economical estimation and separation techniques for highly poisonous and environmentally hazardous Pb^{2+}, especially in relation to similarly binding and co-existing Ag^+, has attained paramount significance. Host–guest chemistry [2], responsible for providing metal ion selective ionophores for such uses, has immense potential for the design of Pb^{2+} selective ionophores[3]. In our earlier reported amine-ether-amide π-system based Pb^{2+} selective 15- and 17-membered ionophores (**1**, **2**) [4, 5], amide O binding sites adopted an exterior disposition which would inhibit cavity induced binding for Pb^{2+}. Consequently, we have designed 16- and 18-membered *m*-cyclophanes **3** and **4,** possessing the same optimal combination of binding sites and envisaged that even a marginal ring size increase [6, 7] could allow amide oxygen to acquire the appropriate geometry for selective complexation towards polarizable Pb^{2+}.

Since the two amide groups in these macrocycles, due to resonance of the nitrogen lone pair with the carbonyl group, can invoke cisoid–cisoid, cisoid–transoid and transoid-transoid configurations, in order to visualise the order of preference for the existence of either one or more of these configurations (Figure 1), we have

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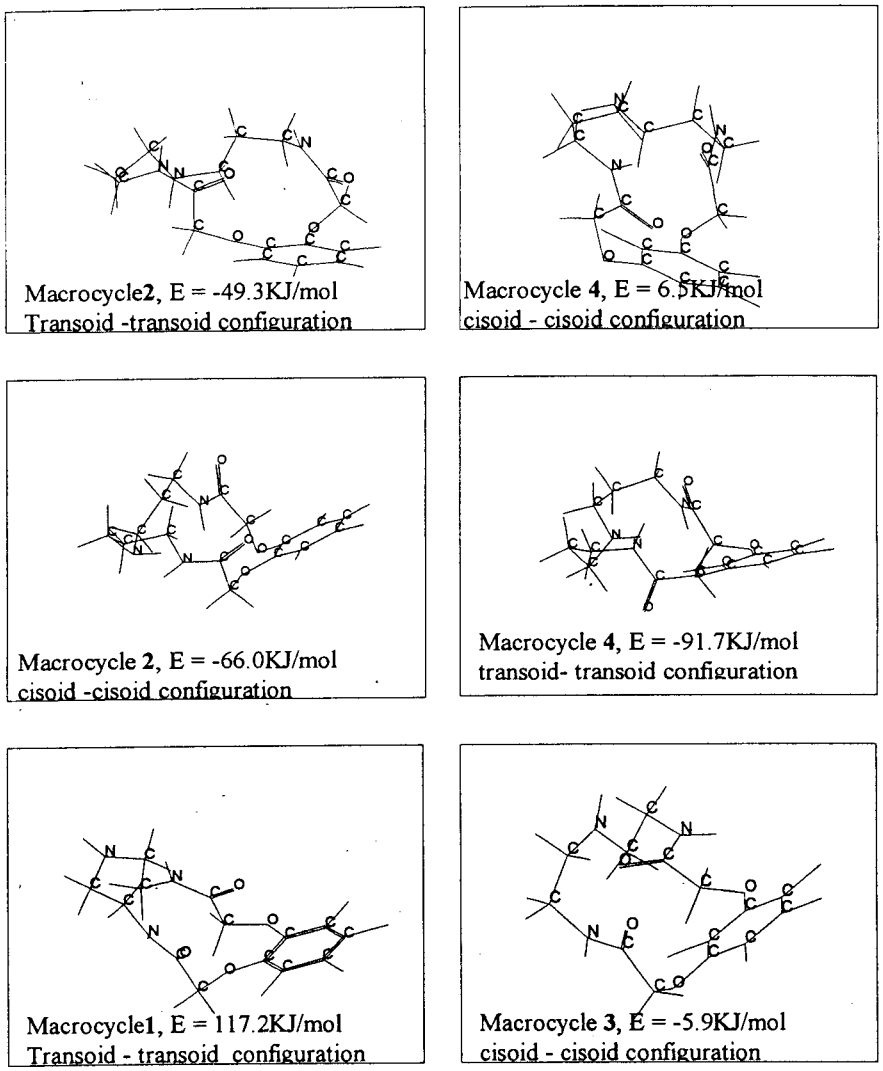
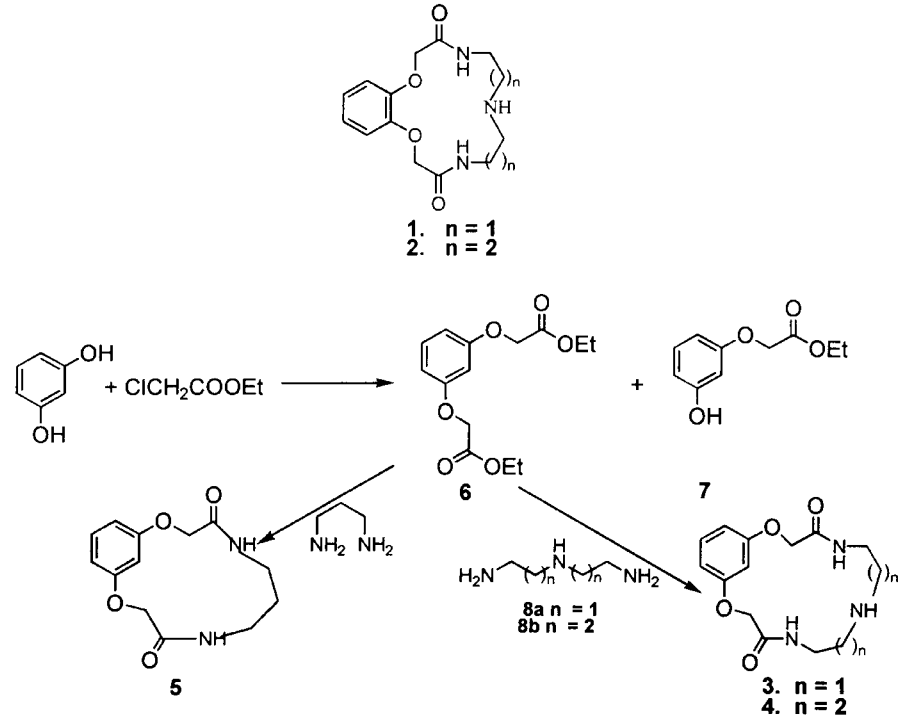


Figure 1. The energy minimized configurations of macrocycles **1**–**4**.

performed energy minimization studies using the DTMM 2.0-MM2 based energy minimization programme [8]. It has been revealed that the *o*-phenylene based 15 membered macrocycle **1** acquires a transoid–transoid configuration to which other possible configurations change on energy minimization. The *m*-phenylene based macrocycle **3** is stabilized in the cisoid–cisoid configuration. The 17 membered macrocyle **2** could achieve both transoid–transoid or cisoid–cisoid configurations, but the latter is more stable. Macrocycle **4** also could acquire both cisoid–cisoid and transoid–transoid configurations but the latter is more stable.



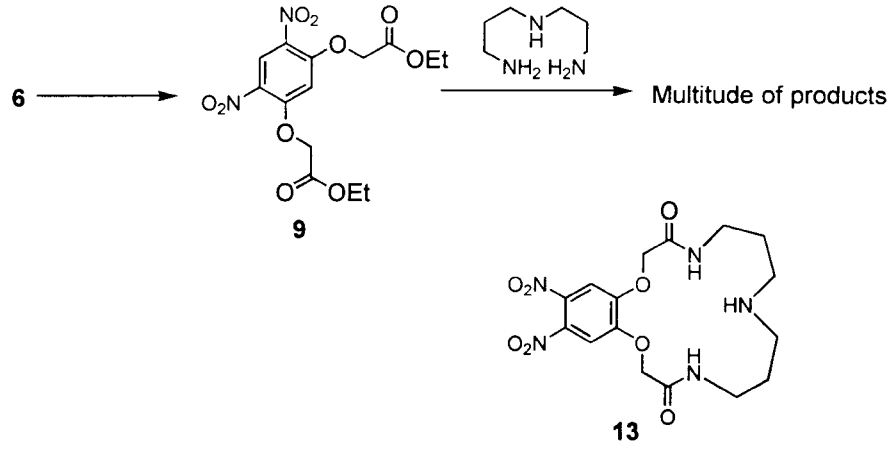
Scheme 1.

Therefore, DTMM 2.0 based energy minimization studies show that the replacement of the *o*-phenylene ring with a *m*-phenylene ring leads to stabilization of different configurational isomers and would result in different spatial topologies of the macrocycles. Further the π-rings in *m*-phenylene based macrocycles face the macrocyclic ring and could be more available for interactions with electron deficient or positively charged guest species.

In the present investigations, *m*-phenylene based macrocycles **3-5,** possessing ether-, amine- and amide ligating units, have been synthesized. The ionophore **4**, in ^{13}C NMR titration studies shows its binding preference with Pb^{2+} and Ag^{+} over alkali and alkaline earth cations, but its high solubility in water restricts its applications as an ionophore.

2. Experimental

For general experimental see Ref. 6b.



Scheme 2.

2.1. SYNTHESIS OF 1,3-BIS(ETHOXYCARBONYLMETHOXY) BENZENE (**6**) AND 3-(ETHOXYCARBONYLMETHOXY) PHENOL (**7**)

A solution of resorcinol (11.0 g, 0.1 mol) and ethyl chloroacetate (28.8 g, 0.23 mol) in acetonitrile (dry, 50 mL) containing anhydrous K_2CO_3 (27.8 g, 0.4 mol), tetrabutylammonium hydrogensulphate (TBA HSO_4, 40–50 mg) and 18-crown-6 (10–15 mg) was refluxed at 100 ± 5 °C in an oil bath. After completion of the reaction (TLC, 16 h), the solid was filtered off and the residue was washed with acetonitrile. The combined filtrates were distilled under vacuum and the residue was column chromatographed to isolate compounds **6** and **7**.

*1,3-Bis(ethoxycarbonylmethoxy) benzene (**6**):* (65%); thick liquid,M^+ m/z 282; δ_H ($CDCl_3$): 1.27 (6H, t, J 6, 2 × CH_3), 4.20 (4H, q, J 6, 2 × CH_2), 4.67 (4H, s, 2 × OCH_2), 6.47-6.52 (3H, m, ArH), 7.17 (1H, t, J 8, ArH); δ_C ($CDCl_3$)(normal-DEPT-135): 13.68 (+ve , CH_3), 60.53 (−ve, CH_2), 64.44 (−ve, OCH_2), 101.69 (+ve, ArCH), 107.19 (+ve, ArCH), 129.57 (+ve, ArCH), 158.64 (absent, ArC), 168.10 (absent, CO); ν_{max} ($CHCl_3$): 1750 (CO) cm^{-1}.

*3-(Ethoxycarbonylmethoxy) phenol (**7**):* (15%), liquid, M^+ m/z 196; δ_H($CDCl_3$): 1.27 (3H, t, J 6, CH_3), 4.20 (2H, q, J 6, CH_2), 4.67 (2H, s, OCH_2), 6.34–6.47 (3H, m, ArH), 7.0 (1H, t, J 8, ArH), 7.27 (1H, brs, OH); δ_C ($CDCl_3$)(normal/DEPT-135): 13.98 (+ve, CH_3), 60.61 (−ve, CH_2), 64.73 (−ve, OCH_2), 102.00 (+ve,ArCH) , 105.9 (+ve , ArCH), 109.14 (+ve, ArCH), 130.00 (+ve, ArCH), 157.36 (absent, ArC), 158.77 (absent, ArC),169.45 (absent ,CO); ν_{max} ($CHCl_3$): 3400 (OH), 1750 (CO) cm^{-1}.

2.2. SYNTHESIS OF 5, 7-BENZO-4, 8-DIOXA-1, 11, 14-TRIAZACYCLOHEXADECANE 2, 10-DIONE (**3**)

The solution of diester **6** (2.8 g, 0.01 mol) and diethylene-triamine (1.09 g, 0.01 mol) in methanol (150 mL) was refluxed on a water bath. After completion of the reaction (24 h, TLC), the solvent was evaporated and the residue was chromatographed on a silica gel column using ethyl acetate–methanol mixtures as eluents and the solid isolated was recrystallised from methanol to give **3** (21%); m. p. 201 °C; M^+ m/z 293; δ_H ($CDCl_3$ + DMSO-d_6): 1.69 (1H, brs, NH), 2.65 (4H, t, J 6, 2 × CH_2), 3.39 (4H, q, J 6, 2 × CONH*CH*$_2$), 4.64 (4H, s, 2 × OCH_2), 6.64 (3H, m, ArH), 7.26 (1H, t, J 8, ArH); δ_C ($CDCl_3$ + DMSO-d_6) (normal/DEPT-135): 41.20 (−ve, $NHCH_2$), 46.58 (−ve, $NHCH_2$), 67.77 (−ve, OCH_2), 109.33 (+ve, ArCH), 112.19 (+ve, ArCH), 126.07 (+ve, ArCH), 158.96, (absent, ArC), 168.74 (absent, CO); ν_{max} ($CHCl_3$): 1665 (CO) cm^{-1} (Found: C, 57.30; H, 6.62; N, 13.9%; $C_{14}H_{19}N_3O_4$ requires C, 57.33; H, 6.48; N, 14.33%).

2.3. SYNTHESIS OF 5, 7-BENZO-4, 8-DIOXA-1, 11, 15-TRIAZACYCLOOCTADECANE 2, 10-DIONE (**4**)

The solution of diester **6** (2.8 g, 0.01 mol) and 3,3′-diamino-dipropylamine (1.4 g, 0.01 mol) in methanol on refluxing and workup as described above gave **4** (45%); thick liquid; M^+ m/z 321; δ_H ($CDCl_3$ + DMSO-d_6): 1.62 (4H, m, 2 × CH_2), 2.34 (4H, t, J 6, 2 × NH*CH*$_2$), 2.96 (1H, br, NH), 3.34 (4H, br, 2 × CONH*CH*$_2$), 4.52 (4H, s, 2 × OCH_2), 6.54 (3H, m, ArH), 7.22 (1H, t, J 8, ArH), 7.79 (2H, br, CONH); δ_C ($CDCl_3$ + DMSO-d_6) (normal/DEPT-135): 27.74 (−ve, CH_2), 36.90 (−ve, $NHCH_2$), 46.76 (−ve, CONH*CH*$_2$), 67.18 (−ve, O*CH*$_2$), 102.68 (+ve, ArCH), 106.88 (+ve, ArCH), 103.37 (+ve, ArCH), 158.54 (absent, ArC), 168.64 (absent, CO); ν_{max} ($CHCl_3$): 1665 (CO) cm^{-1}.

2.4. SYNTHESIS OF 5, 7-BENZO-4, 8-DIOXA-1, 11-DIAZACYCLOTETRADECANE 2, 10-DIONE (**5**)

A solution of **6** (2.0 g, 0.007 mol) and 1,3-diaminopropane (0.52 g, 0.007 mol) on refluxing in methanol and workup as described above gave macrocycle **5** (1%); m.p. 300 °C (decomp.); M^+ m/z 264; δ_H ($CDCl_3$ + DMSO-d_6): 1.67 (2H, quint, J = 6.0Hz, CH_2), 3.29 (4H, t, J = 6.0Hz, 2 × $NHCH_2$), 4.47 (4H, s, 2 × OCH_2), 6.55 (3H, m, ArH), 7.0 (1H, m, ArH), 7.74 (1H, brs, NH), 8.13 (1H, brs, NH); δ_C ($CDCl_3$ + DMSO-d_6) (normal/DEPT-135): 27.12 (−ve, CH_2), 52.54 (−ve, $NHCH_2$), 66.02 (−ve, OCH_2), 106.63 (+ve, ArCH), 112.30 (+ve, ArCH), 129.76 (+ve, ArCH), 141.20 (absent, ArC), 167.40 (absent, CO); ν_{max} ($CHCl_3$): 1665 (CO) cm^{-1}

2.5. SYNTHESIS OF 1, 3-BIS(ETHOXYCARBONYLMETHOXY)-4,6-DINITROBENZENE (**9**)

Nitric acid (conc.) (1.7 mL) was added to the solution of **6** (5.0 g, 0.018 mol) in acetic anhydride (9 mL, 0.08 mol) at 20–25 °C and stirring was continued for 5 hr. Water (200 mL) was added to the reaction mixture and it was extracted with ethyl acetate. The solvent was evaporated and the residue was recrystallized from methanol to give a light yellow solid (60%), m.p. 120 °C; M^+ m/z 372; δ_H ($CDCl_3$): 1.26 (6H, t, J 6, 2 × CH_3), 4.25 (4H, q, J 6, 2 × CH_2), 4.80 (4H, s, 2 × OCH_2), 6.52 (1H, s, ArH), 8.71 (1H, s, ArH); δ_C ($CDCl_3$) (normal/DEPT-135): 14.14 (+ve, CH_3), 62.19 (−ve, CH_2), 66.96 (−ve, OCH_2), 101.90 (+ve, ArCH), 125.57 (+ve, ArCH), 145.29 (absent, ArC), 156.11 (absent, ArC), 166.58 (absent, CO); ν_{max} ($CHCl_3$): 1750 (CO) cm^{-1}. (Found: C, 45.33; H, 4.11; N, 7.21. $C_{14}H_{16}N_2O_{10}$ requires C, 45.16; H, 4.30; N, 7.52%).

2.6. SYNTHESIS OF 1, 2-BIS(ETHOXYCARBONYLMETHOXY) 4,5-DINITROBENZENE (**11**)

Nitric acid (conc.) (1 mL) was added to the solution of **10** (5.0 g, 0.018 mol) in acetic anhydride (9.0 g, 0.08 mol) at 20–25 °C and the reaction mixture was stirred at this temperature for 4 hr. Water (200 mL) was added to the reaction mixture and was extracted with ethyl acetate. The solvent was evaporated and the residue was recrystallised from methanol to give a light yellow product (80%), m.p. 85 °C; M^+ m/z 372; δ_H ($CDCl_3$): 1.30 (6H, t, J 6, 2 × CH_3), 4.30 (4H, q, J 6, 2 × CH_2), 4.83 (4H, s, 2 × OCH_2), 7.31 (2H, s, ArH); δ_C ($CDCl_3$) (normal/DEPT-135): 14.06 (+ve, CH_3), 62.06 (−ve, CH_2), 66.40 (−ve, OCH_2), 110.44 (+ve, ArCH), 118.26 (+ve, ArCH), 150.91 (absent, ArC), 164.56 (absent, CO); ν_{max} ($CHCl_3$): 1745 (CO) cm^{-1}.

2.7. SYNTHESIS OF 5,6-BENZO-4-OXA-4′,5′-DINITRO-1,7,11-TRIAZATETRADECANE 2-ONE (**12**)

The solution of diester **11** (1.6 g, 0.005 mol) and 3,3′-diaminodipropylamine (0.64 g, 0.004 mol) in methanol was refluxed on a water bath. After the completion of the reaction (24 h, TLC), the solvent was evaporated and the residue was chromatographed on a silica gel column using ethyl acetate-methanol mixtures as eluents to isolate **12** (1%); m.p. 220 °C (decomp.); M^+ m/z 353; δ_H ($CDCl_3$ + DMSO-d_6): 1.24 (1H, brs, NH), 1.66 (2H, t, J 6, CH_2), 2.02 (2H, t, J 6, CH_2), 2.90 (4H, t,J 6, 2 × $NHCH_2$), 3.36 (2H, q, J 6, $ArNHCH_2$), 3.49 (2H, q, J 6, $CONHCH_2$), 4.55 (2H, s, OCH_2), 8.26 (2H, s, ArH).

3. Results and Discussion

Resorcinol reacts with ethyl chloroacetate (2 equiv.) under phase transfer catalytic conditions in acetonitrile containing K_2CO_3 (anhyd.) and a mixture of catalysts [tetrabutylammonium hydrogensulphate ($TBAHSO_4$) and 18-crown-6] to give two products. The higher Rf component (65%), liquid, M^+ m/z 282, in its ^1H NMR spectrum shows a triplet [δ 1.27 ($2 \times CH_3$)], a quartet [δ 4.20 ($2 \times CH_2$)], and a singlet [δ 4.67 ($2 \times OCH_2$)] along with a ArH multiplet (4H). Its ^{13}C NMR (DEPT-135) spectrum shows one upfield +ve signal (13.68, CH_3), two -ve signals (60.53 and 64.44, CH_2) and three downfield +ve signals (101.69, 107.19, 129.57, ArCH) and two quaternary carbon signals, present in the normal ^{13}C NMR spectrum, are absent. These spectral data show this compound to have a symmetrical 1,3-disubstituted benzene structure **6**. The lower Rf component (15%), liquid, M^+ m/z 196 from its ^1H and ^{13}C NMR spectra could be assigned the structure **7**.

The condensation of **6** with diethylenetriamine (**8a**) in refluxing methanol gave a white crystalline product (21%), m.p. 201 °C, M^+ m/z 293. Its ^1H NMR spectrum lacks any signals due to the OCH_2CH_3 units of **6** and shows a new set of triplet [δ 2.65 ($2 \times NHCH_2$)] and quartet [δ 3.39 ($2 \times CONHCH_2CH_2$)] (CH_2 and NH coupling) signals alongwith a OCH_2 singlet (4.64) and a ArH multiplet. Its ^{13}C NMR (DEPT-135) spectrum shows three +ve aromatic CH signals (δ 109.33, 112.19, 126.07), three $-$ve CH_2 signals (δ 41.20, 46.58, 67.77) and two quaternary C signals, present in the normal ^{13}C NMR spectrum, are absent. These data assign the structure **3** for this compound. Similarly, the condensation of **6** with 3,3′-diaminodipropylamine and 1,3-diaminopropane in refluxing methanol gave macrocycles **4** (45%), M^+ m/z 321 and **5** (1%), m.p. 300 °C (decomp), M^+ m/z 264, respectively.

The macrocycles **3** and **4** have very poor solubility in chloroform and acetonitrile but are freely soluble in water and studies on their ionophore character viz. extraction of cations, could not be performed. However, in an attempt to determine their complexation behaviour, ^{13}C NMR titration studies of macrocycle **4** with alkali (Li^+, Na^+, K^+), alkaline earth (Ca^{2+}, Sr^{2+}, Ba^{2+}), Tl^+, Pb^{2+} and Ag^+ picrates have been performed. For this purpose, ^{13}C NMR spectra of macrocycle **4** and its complexes (1 : 1) with metal pictrates in DMF-$CDCl_3$ (3 : 1) solutions have been recorded and co-ordination shifts ($\Delta\delta_C$) (Table I) are reported.

The addition of metal picrates (1 equiv) to the solution of macrocycle **4** causes co-ordination shifts with all the metal picrates but these shifts are much more prominent in the case of Ag^+ and Pb^{2+} picrates, indicating their higher degree of complexation than other cations. The carbon signals due to —CH_2—, $N_{amine}CH_2$, $N_{amide}CH_2$ and OCH_2 are invariably shifted upfield except in the case of addition of Ag^+ picrate where —CH_2— and $N_{amide}CH_2$ signals are shifted downfield. The carbon signals of the aromatic ring and carbonyl group are invariably shifted downfield (Table 1). The nature of the induced co-ordination shifts is quite similar to that observed [3b] on addition of metal picrates to macrocycle **2** but the magnitude

Table I. The co-ordination shifts ($\Delta\delta_C$)[#] of carbon signals (^{13}C NMR) of macrocycle **4** on addition of metal picrates (1 : 1).

Entry	Signal	CH_2	NCH_2	NCH_2	OCH_2	2Ar	4/6Ar	5Ar	3Ar—O	C=O
1	Li^+	−0.25		−0.23	−0.06	+0.14	+0.49	+0.22	−0.01	+0.98
2	Na^+	−0.17		−0.15	−0.01	+0.11	+0.34	+0.16	−0.00	+0.67
3	K^+	−0.03		−0.00	−0.05	+0.01	+0.39	+0.18	+0.02	+0.68
4	Ca^{2+}	−0.33		−0.33	−0.08	+0.04	+0.61	+0.23	−0.01	+0.98
5	Sr^{2+}	−0.21		−0.21	−0.01	+0.14	+0.58	+0.28	+0.01	+1.04
6	Ba^{2+}	−0.18		−0.18	−0.10	+0.07	+0.58	+0.24	+0.02	+0.93
7	Tl^+	−0.09		−0.17	−0.03	−0.11	+0.81	+0.26	+0.06	+0.98
8	Ag^+	+0.17	−1.15	+0.18	−0.00	+0.34	+0.80	+0.19	+0.08	+1.01
9	Pb^{2+}	−0.98	−1.24	−0.91	−0.04	+0.51	+0.86	+0.26	+0.08	+1.34
10	PicH	−0.51	−1.20	−0.91	−0.09	+0.52	+0.89	+0.27	+0.07	+1.37

[#] The chemical shifts were recorded with respect to $CDCl_3$ (middle peak δ_C 77.000 ppm) and the values were corrected to account for small discrepancies in the δ_C value of the middle peak at 77.000 ppm. The (+) and (−) signs of the $\Delta\delta_C$ values refer to downfield and upfield chemical shifts on addition of metal picrates as compared to the chemical shift in the macrocycle.

of the co-ordination shifts in the case of macrocycle **4** is significantly larger. In the case of macrocycle **2,** the aromatic carbon signals are affected to a very small extent. These enhanced co-ordination shifts of aromatic carbons, in the case of macrocycle **4** could be attributed to more effective participation of the *m*-phenylene ring in complexation.

It could also be visualised that the electron rich dialkoxy *m*-phenylene ring forms a π-complex with the electron deficient picrate ring and the macrocyclic ring participates in complexation with metal ions. It was envisaged that if picric acid, which can provide H^+ and picrate anion, is added to the macrocycle, it could interact both with the amine and *m*-phenylene units of **4** in the same manner as Pb-picrate and would consequently induce similar changes in chemical shifts. It was found that on addition of picric acid, the ^{13}C NMR of **4** undergoes similar co-ordination shifts (compare entries 9 and 10, Table 1). Therefore, though macrocycle **4** shows a higher order of complexation with Ag^+ and Pb^{2+} than with the other metal ions, but due to the considerable degree of participation of the counter picrate anion in complexation, the effect of the π-system on selective complexation towards Ag^+ or Pb^{2+} could not be determined.

For incorporating a chromogenic group on the aryl rings of macrocycles **2** and **4**, diester **6** was nitrated with nitric acid (5.0 equiv.) in acetic anhydride at 0–10 °C to give a yellow solid (60%), m.p. 120 °C. Its ^{1}H NMR spectrum shows a triplet [δ 1.26 (6H, 2 × CH_3)], a quartet [δ 4.25 (4H, 2 × CH_2)], a singlet [δ 4.80 (4H, 2 × OCH_2)] and two 1H ArH signals. Its ^{13}C NMR (DEPT-135 spectrum) shows one upfield +ve signal (δ 14.14) and two -ve signals (δ 62.19 and 66.96), two downfield

+ve ArCH signals (δ 101.90, 125.57) and three quaternary carbon signals, present in the normal ^{13}C NMR spectrum, are absent. These data corroborate structure **9** for this compound. However, on refluxing **9** with 3,3′-diaminodipropylamine in methanol gives a multitude of products which could not be separated.

The nitration of 1,2-bis(ethoxycarbonyl methoxy) benzene (**10**) provides a light yellow solid (80%), m.p. 85 °C, M^+ m/z 372, which could be assigned the structure **11**. Its reaction with 3,3′-diaminodipropylamine gave a mixture of products, which on column chromatography provided a pure orange coloured compound (1%), m.p. 222 °C (decomp.), M^+ m/z 353. Its ^1H NMR spectrum shows only one OCH_2 singlet (2H) and different signals for each CH_2 in the —$NHCH_2CH_2NHCH_2CH_2$— unit and point to the unsymmetrical nature of the molecule. Its λ_{max} (410 nm) shows that it is a nitroaniline derivative. Based on these spectral data, the structure **12**, could be assigned to this compound. Thus, the presence of the NO_2 group in the diesters promotes the nucleophilic substitution at the position para to the NO_2 group and the symmetrical macrocycle **13** could not be obtained.

In conclusion, 1,3-bis(ethoxycarbonyl methoxy) benzene (**6**) with diethylene triamine, 3,3′-diaminobispropylamine and 1,3-diaminopropane provides the respective macrocycles **3–5**. These macrocycles, due to their poor solubility in water immiscible organic solvents, could not be used for performing extraction studies. However, ^{13}C NMR titration studies on macrocycle **4** show that it preferably binds with Ag^+ and Pb^{2+} over alkali (Li^+, Na^+, K^+), alkaline earth (Ca^{2+}, Ba^{2+}, Sr^{2+}) and Tl^+ picrates. But due to possible participation of the picrate ion in forming a π complex with the *m*-phenylene ring, the role of the π-system in metal complexation could not be evaluated. Attempts to synthesize analogous nitro substituted chromogenic ionophores lead to side reactions.

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