

Di-2-(2-methoxyethoxy)ethyl phthalate as a bi-brachial podand: complex formation with mono- and divalent cations

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Abstract

Complexation of the title bi-brachial podand (3) with a range of cations has been examined by ¹H and ¹³C NMR and the solid-state structure of the complex (2) between (3) and barium perchlorate determined by X-ray crystallography. The pendent arms surround the barium cation in a spiral configuration to render the complex chiral.

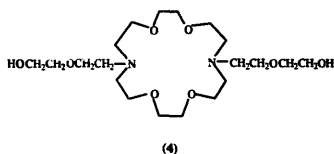
Keywords: Bi-brachial; Pendent; Ligands; NMR; X-ray diffraction; Chiral

1. Introduction

Compounds with long podand arms have attracted considerable attention recently as ligands for a variety of metal cations [1–3]. Although such compounds do not usually form complexes which are as stable as those produced by macrocycles or cryptands, they are extremely flexible host molecules in which the coordinating donor groups can envelop the guest cation. This produces stable complexes especially with donor 'end-groups' such as methoxy or 8-quinolinyl [1,2] and large cations such as Ba²⁺ or Pb²⁺. Thus the bi-brachial pendent ligand (4) derived from 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane forms complexes with K⁺ and Ba²⁺, both of which have been studied by X-ray crystallography [4]. The nine-coordinate K⁺ complex had a trans geometry for the podand ligands whereas the 11-coordinate Ba²⁺ complex had a cis conformation with a molecule of water occupying a coordination site from below the ring.

During a mechanistic study of the use of metal cations as catalysts for the formation (or hydrolysis) of esters we decided to investigate the formation of complexes (2) between polyethylene oxy esters of ortho-phthalic acid (1) and a variety of metal cations. This paper reports the results of a systematic investigation of such complex formation (Scheme 1) and, in particular,

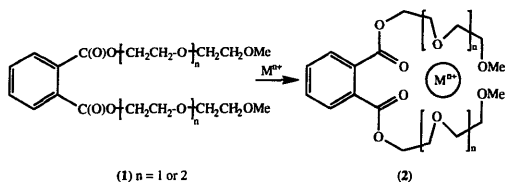
the structure of a crystalline complex (2, Mⁿ⁺ = Ba²⁺) isolated from the interaction of (1, n = 1) with barium perchlorate.



2. Experimental

NMR spectra were obtained at 360 MHz (¹H) and 90 MHz (¹³C) on a Bruker AM360 spectrometer against TMS as internal standard. The decoupled proton and heteronuclear ¹H/¹³C correlation spectra were obtained using standard Bruker pulse sequences. Mass spectra were obtained by the ULIRS Mass Spectrometry Services at King's College London and the School of Pharmacy, Brunswick Sq., London. The FAB mass spectrum of the Ba²⁺ complex of (3) was obtained from a thiglycerol matrix on a Kratos MS890MS spectrome-

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Scheme 1. Representation of the complex (2) formed between (1) and metal cations (M^{n+}).

ter and the high resolution EI mass spectrum of (3) on a Jeol JMS-AX505W instrument (KCL). The accurate mass data on the complex of (3) with $Ba^{2+}(ClO_4^-)_2$ (3-NBA matrix + NaI) was obtained on a V.G. Analytical ZAB-SE double focusing reverse geometry mass spectrometer at 10000 resolution using a standard VG FAB source and VG Opus software on a Deck α -station (School of Pharmacy).

2.1. Preparative details

2.1.1. Preparation of di-2-(2-methoxyethoxy)ethyl phthalate, (di-2-(2-ME)EP)

Phthalic anhydride (21.6 g, 0.146 mol) and 2-(2-methoxyethoxy)ethanol (18 ml, 0.151 mol) were placed in a 100 ml round-bottomed flask fitted with a reflux condenser. The mixture was heated at 100°C with stirring for 22 h. A further amount of 2-(2-methoxyethoxy)ethanol (18 ml, 0.151 mol) and a catalytic amount of concentrated H_2SO_4 were added and the mixture was heated at 100°C with stirring for 24 h. The reaction was allowed to cool and was extracted with CH_2Cl_2 (100 ml) and washed with 1M Na_2CO_3 to neutralise any remaining acid. Distilled water (25 ml) was added to aid separation of the layers. The organic layer was separated and the aqueous layer was washed further with CH_2Cl_2 (50 ml). The organic layers were combined, dried with anhydrous $MgSO_4$, filtered and the solvent evaporated to leave the crude product. The pure product was obtained by distillation under reduced pressure of 12.9 g of the crude product to give 10.7 g (90%) of a colourless liquid, b.p. 235–240°C (0.05 mm Hg).

1H NMR $\delta(CDCl_3)$, ppm): 3.28 (s, 6H, H16/H26), 3.46 (m, 4H, H14/H24), 3.58 (m, 4H, H13/H23), 3.72 (m, 4H, H11/H21), 4.37 (m, 4H, H10/H20), 7.63 (m, 2H, H3/H4), 7.73 (m, 2H, H2/H5).

^{13}C NMR $\delta(CDCl_3)$, ppm): 58.9 (C16/C26), 65.9 (C10/C20), 69.5 (C11/C21), 71.1 (C13/C23), 72.6 (C14/C24), 129.8 (C3/C4), 132.5 (C2/C5), 133.0 (C1/C6), 168.4 (C7/C17); see 3 for numbering scheme.

High resolution mass spectrum (EI): 370.1633; calc. $M^+ = 370.1628$.

2.1.2. Metal salts

Barium perchlorate (anhydrous) and lead(II) perchlorate trihydrate were obtained from Aldrich Chemical Co. Ltd. Calcium perchlorate $\cdot xH_2O$ was from Alfa Products and sodium perchlorate monohydrate from BDH Ltd. The water of crystallisation associated with $Ca(ClO_4)_2 \cdot xH_2O$ was determined by titration against 0.01 M EDTA solution [5] and found to be 4.

2.1.3. Preparation of $Zn(ClO_4)_2 \cdot 6H_2O$ and $Cu(ClO_4)_2 \cdot 6H_2O$

Zinc perchlorate hexahydrate was prepared by the neutralisation of zinc carbonate with excess 2M perchloric acid in water. The solution was then concentrated by evaporation of the solvent leading to crystallisation of the product. The water of crystallisation associated with the product was determined by titration against 0.01 M EDTA solution [5].

Copper(II) perchlorate hexahydrate was also prepared by the same method.

2.1.4. Preparation of KCF_3SO_3

Potassium triflate was prepared by the neutralisation of potassium carbonate with an equimolar quantity of triflic acid. The product was dissolved in CH_3CN and filtered to remove any impurities. The solvent was evaporated off and the pure product dried under vacuum.

2.1.5. Preparation of di-2-(2-ME)EP: $Ba(ClO_4)_2$ crystals

The di-ester (1, 60 mg, 1.62×10^{-4} mol) was dissolved in 0.5 ml CD_3CN and a solution of barium perchlorate (163 mg, 4.86×10^{-4} mol) in CH_3CN (0.5 ml) was added. Complexation was confirmed by ^{13}C NMR and the NMR sample tube was left for 1 week at room temperature after which crystals were observed in the NMR tube. These crystals turned out to be twinned. The procedure was repeated using CH_3CN alone and the solution was left in a sample vessel in a freezer set at $-30^\circ C$ for 1 month. The resulting crystals formed cleanly from the solution and were used for the X-ray crystallography.

Mass spectrum (FAB): $3 \cdot Ba^{2+}(ClO_4^-) = 607$; exact

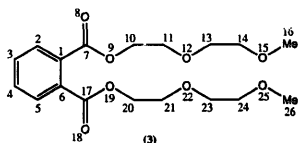


Fig. 1. Schematic representation of the structure of (3) showing the numbering scheme employed throughout.

mass (pNBA matrix) found: $3 \cdot \text{Ba}^{2+}(\text{ClO}_4)_2 \cdot \text{Na}^+ = 728.9530$; calculated: 728.9548. Elemental analysis. Found: C, 30.51; H, 3.60; Cl, 10.0. $\text{C}_{18}\text{H}_{26}\text{BaCl}_2\text{O}_{16}$. Calc.: C, 30.58; H, 3.68; Cl, 10.03%.

2.2. Crystal data and structure analysis

X-ray intensity data were collected on an automated four-circle Picker diffractometer using Zr-filtered Mo K α radiation and pulse-height analysis. The crystal was a hexagonal prism, dimensions $0.4 \times 0.36 \times 0.3 \text{ mm}^3$. Crystal data: monoclinic, $P2_1/c$, $a = 14.45(2)$, $b = 9.711(6)$, $c = 18.87(2) \text{ \AA}$, $\beta = 91.69(9)^\circ$, $Z = 4$ molecules per cell. Crystal density (calc.) 1.77 Mg m^{-3} , (meas. KI soln.) 1.68 Mg m^{-3} . Data were collected in θ - 2θ scan mode to $2\theta(\text{max}) = 50^\circ$ at 2° min^{-1} . Data reduction was carried out using the

NRCVAX package [6]. Of 4669 reflections measured, 3521 had significant intensities ($I_{\text{net}} > 2.5\sigma(I_{\text{net}})$). Atomic parameters from the earlier structure solution were refined by full-matrix least squares. All non-hydrogen atoms had anisotropic thermal factors. Virtually all hydrogens were found on difference maps; those missing were the five out of six on the two methoxy groups. All were given theoretical positions (C–H, 1.08 Å). A Gaussian absorption correction was applied (max. and min. transmission 0.58 and 0.63). Residuals: $R_F = 0.048$, $R_w = 0.049$ (based on intensity statistics), goodness of fit = 2.95. On the last ΔF map, min. and max. densities were -1.97 and 1.45 e \AA^{-3} .

Atomic coordinates and thermal parameters are listed in Table 1 and the structure depicted in an ORTEP diagram (Fig. 4) [7]. Anisotropic thermal parameters and structure factors are available from the Cambridge Crystallographic Centre.

3. Results and discussion

The ester used in these studies was (3) and the numbering scheme adopted for both the multinuclear NMR and X-ray crystallography is shown in Fig. 1.

The bi-brachial ligand was characterised by ^1H and ^{13}C NMR and the assignment of the protons along the

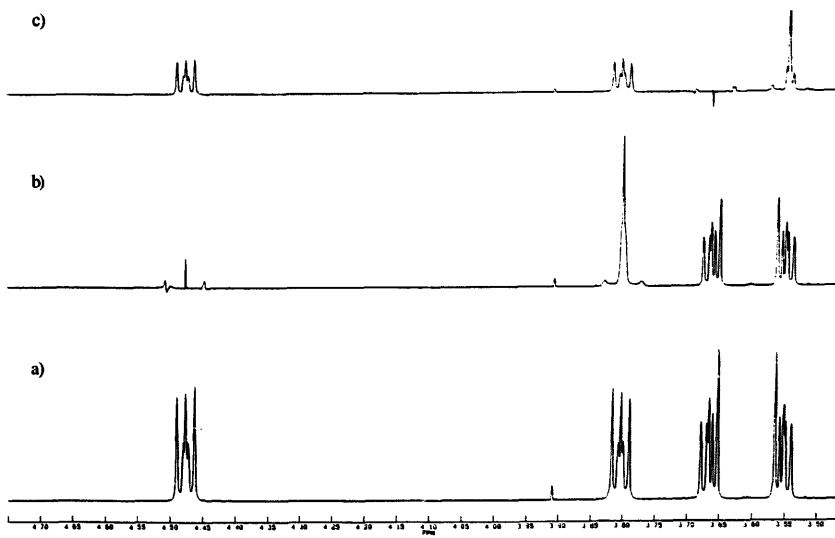


Fig. 2. $^1\text{H}/^1\text{H}$ decoupled NMR spectra for (3) in CDCl_3 : (a) no decoupling; (b) ^1H decoupled at 4.48 ppm; (c) ^1H decoupled at 3.67 ppm.

Table 1
Fractional atomic coordinates and equivalent isotropic temperature factors

Atom	x	y	z	B_{eq} (\AA^2)
Ba	0.25093(3)	0.70806(5)	0.128668(25)	3.427(19)
Cl1	0.13787(16)	0.69328(24)	0.28823(11)	4.97(10)
Cl2	0.34958(17)	1.03398(23)	0.13752(13)	5.29(10)
O8	0.2245(4)	0.6432(6)	-0.0102(3)	4.29(24)
O9	0.3446(4)	0.6422(7)	-0.0816(3)	5.4(3)
O12	0.4214(4)	0.7007(7)	0.0530(3)	5.4(3)
O15	0.4062(4)	0.5939(7)	0.1915(4)	5.7(3)
O18	0.2759(4)	0.4423(5)	0.0837(3)	4.06(23)
O19	0.1525(4)	0.3059(6)	0.0733(3)	4.28(23)
O22	0.0754(3)	0.5593(6)	0.1066(3)	4.4(3)
O25	0.0935(4)	0.8447(6)	0.0835(4)	5.9(3)
O27	0.3109(8)	1.1532(8)	0.1638(6)	12.4(7)
O28	0.4375(6)	1.0585(11)	0.1149(5)	11.7(6)
O29	0.2935(6)	0.9772(7)	0.0810(4)	7.7(4)
O30	0.3543(5)	0.9312(7)	0.1913(4)	6.8(4)
O31	0.1568(6)	0.6974(11)	0.3601(4)	10.1(6)
O32	0.1653(6)	0.8149(7)	0.2541(4)	8.3(4)
O33	0.1860(5)	0.5817(7)	0.2555(3)	6.0(3)
O34	0.0417(5)	0.6750(9)	0.2766(4)	8.3(4)
C1	0.2600(5)	0.4410(9)	-0.0742(4)	4.0(4)
C2	0.2675(6)	0.4095(11)	-0.1459(5)	5.0(5)
C3	0.2531(7)	0.2748(14)	-0.1684(5)	6.3(5)
C4	0.2337(7)	0.1740(11)	-0.1209(6)	6.0(5)
C5	0.2253(6)	0.2040(10)	-0.0501(5)	4.9(4)
C6	0.2372(5)	0.3380(8)	-0.0268(4)	3.8(3)
C7	0.2725(5)	0.5858(9)	-0.0514(4)	4.2(4)
C10	0.3682(7)	0.7809(12)	-0.0600(5)	6.2(5)
C11	0.4463(7)	0.7750(11)	-0.0078(5)	6.2(5)
C13	0.4980(7)	0.6761(14)	0.1012(7)	8.0(7)
C14	0.4800(7)	0.5625(14)	0.1479(7)	7.8(7)
C16	0.4009(9)	0.4883(19)	0.2401(8)	11.1(9)
C17	0.2264(5)	0.3688(8)	0.0488(4)	3.8(3)
C20	0.1260(6)	0.3383(8)	0.1447(4)	4.5(4)
C21	0.0471(6)	0.4366(9)	0.1402(5)	4.6(4)
C23	-0.0012(6)	0.6429(11)	0.0862(6)	5.9(5)
C24	0.0312(6)	0.7597(10)	0.0440(5)	5.5(5)
C26	0.0536(9)	0.9524(12)	0.1200(7)	8.6(7)
H2	0.283	0.491	-0.184	6.0
H3	0.258	0.249	-0.225	7.0
H4	0.225	0.067	-0.140	6.8
H5	0.209	0.122	-0.012	5.8
H10A	0.387	0.844	-0.105	12.7
H10B	0.310	0.831	-0.034	12.7
H11A	0.472	0.878	0.010	7.1
H11B	0.508	0.724	-0.030	7.1
H13A	0.561	0.658	0.072	8.9
H13B	0.510	0.768	0.134	8.9
H14A	0.542	0.536	0.180	8.7
H14B	0.463	0.471	0.115	8.7
H16A	0.367	0.392	0.218	9.2
H16B	0.462	0.456	0.267	9.2
H16C	0.355	0.500	0.282	9.2
H20A	0.107	0.246	0.173	5.3
H20B	0.184	0.386	0.174	5.3
H21A	0.023	0.459	0.193	5.5
H21B	-0.010	0.390	0.110	5.5
H23A	-0.050	0.582	0.055	6.7
H23B	-0.034	0.682	0.132	6.7
H24A	-0.028	0.821	0.025	6.4
H24B	0.067	0.721	-0.003	6.4
H26A	0.016	0.910	0.165	9.2
H26B	0.004	1.005	0.086	9.2
H26C	0.094	1.023	0.141	9.2

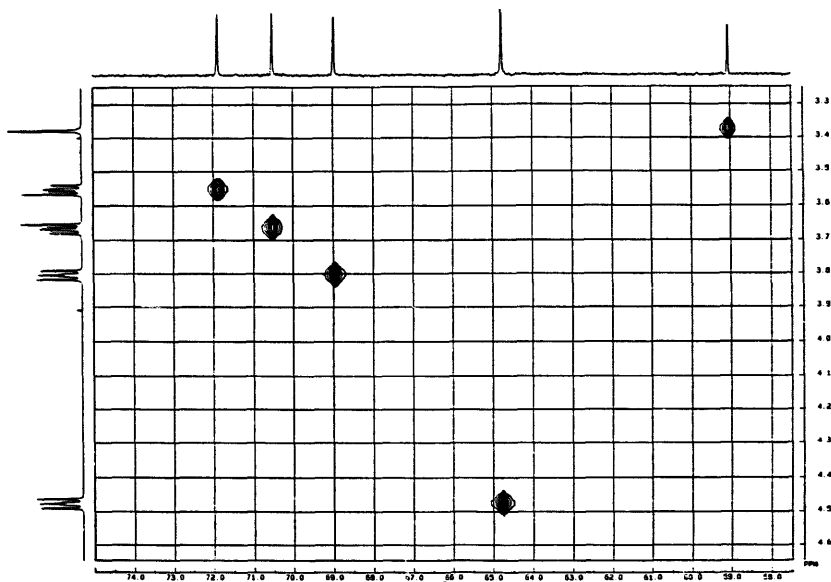
Fig. 3. $^1\text{H}/^{13}\text{C}$ correlation NMR spectrum of (3) in CDCl_3 .

Table 2

 ^1H chemical shift data (δ ppm against internal TMS) for complexed and uncomplexed (3) in CD_3CN ^a; ligand concentration 0.162 M

	H2, H5	H3, H4	H10, H20	H11, H21	H13, H23	H14, H24	H16, H26
(3)	7.73	7.64	4.37	3.72	3.58	3.46	3.28
(3): 3Ca^{2+}	+0.08	+0.06	+0.11	+0.11	+0.1	+0.1	+0.07
(3): 3Ba^{2+}	+0.17	+0.1	+0.3	+0.19	+0.17	+0.15	+0.16

^a Data for complexes are given as $\Delta\delta$ ppm with respect to the free ligand.

Table 3

 ^{13}C chemical shift data (δ ppm against internal TMS) for complexed and uncomplexed (3) in 1:1 $\text{CD}_3\text{CN}:\text{CH}_3\text{CN}$; ligand concentration 0.162 M

	C1, C6	C2, C5	C3, C4	C7, C17	C10, C20	C11, C21	C13, C23	C14, C24	C16, C26
(a) In 1:1 $\text{CD}_3\text{CN}:\text{CH}_3\text{CN}$ ^a									
(3)	133.0	132.5	129.8	168.4	65.9	69.5	71.1	72.6	58.9
(3): 3Pb^{2+}	-0.6	+0.6	+0.4	+1.1	-0.3	+0.8	-0.3	0	+0.9
(3): 3Ca^{2+}	-0.7	+0.3	+0.2	+0.7	0	+0.2	-0.5	-0.5	+0.3
(3): 3Ba^{2+}	-0.7	+0.5	+0.5	+1.1	-0.2	+0.7	-0.3	-0.3	+0.4
(3): 3Na^+	-0.3	+0.2	+0.1	+0.4	-0.1	+0.1	-0.4	-0.4	+0.1
(3): 3K^+	-0.2	+0.1	+0.1	+0.2	0	0	-0.2	-0.4	0
(b) In 1:1 $\text{CD}_3\text{OD}:\text{CH}_3\text{OH}$ ^a									
(3)	133.3	132.4	130.0	169.0	66.0	69.9	71.3	72.9	59.1
(3): 2Pb^{2+}	-0.2	+0.2	0	+0.2	0	-0.1	-0.1	-0.1	0
(3): 2Ba^{2+}	-0.2	+0.2	0	+0.2	+0.1	0	-0.1	-0.1	0

^a Data for complexes are given as $\Delta\delta$ ppm with respect to the free ligand.

Table 4

$^{13}\text{C}=\text{O}$ chemical shift data^a (δ ppm against internal TMS) for complexation of **3** with Na^+ and Pb^{2+} ; ligand concentration 0.162 M

Ratio $\text{Na}^+:\mathbf{3}$	$\delta^{13}\text{C}=\text{O}/\text{ppm}$	Ratio $\text{Pb}^{2+}:\mathbf{3}$	$\delta^{13}\text{C}=\text{O}/\text{ppm}$
0	168.37	0	168.37
1	168.54	2	169.44
3	168.78	4	169.51
5	168.92	6	169.52
7	169.03	8	169.57
9	169.09		

^a Data processed by fitting to $y = C_0 + C_1 \exp(-C_2 \times \text{ratio})$ in order to evaluate C_0 , the maximum value of y . This δ value was then used to calculate the concentration of 1:1 complex at any ratio of $(\mathbf{3}):\text{M}^{n+}$ and hence several values of the equilibrium constant K .

ethylene-oxy chains was achieved by two $^1\text{H}/^1\text{H}$ decoupling experiments (Fig. 2) together with a DEPT 135 spectrum. The heteronuclear $^1\text{H}/^{13}\text{C}$ correlation spectrum (Fig. 3) then allowed assignment of all the carbon atoms within the molecule. The $^1\text{H}/^{13}\text{C}$ correlation spectrum is unusual in that it indicates a reverse correlation of the methylene protons with respect to the carbons to which they are attached.

The ^1H spectra for **3** and the shifts associated with its complexes with excess Ca^{2+} and Ba^{2+} in CD_3CN are shown in Table 2. Significant downfield shifts are observed for all protons with those for the Ba^{2+} complex being more pronounced. The ^{13}C data for both these complexes plus those for Pb^{2+} , Na^+ and K^+ in $\text{CD}_3\text{CN}-\text{CH}_3\text{CN}$ are shown in Table 3(a). Significant upfield and downfield shifts are again observed for all the carbon atoms with downfield shifts on the carbonyl carbons being most pronounced and largest for Pb^{2+} and Ba^{2+} .

The shifts for Na^+ and K^+ , although observable are, as expected, less pronounced than those for the higher

Table 5

Selected bond lengths (\AA) with esds in parentheses

Ba–O8	2.710(6)	O12–C11	1.410(12)
Ba–O12	2.887(7)	O12–C13	1.428(13)
Ba–O15	2.747(7)	O15–C14	1.402(14)
Ba–O18	2.744(6)	O15–C16	1.429(16)
Ba–O22	2.936(6)	O18–C17	1.192(10)
Ba–O25	2.750(7)	O19–C17	1.324(10)
Ba–O29	2.839(7)	O19–C20	1.446(10)
Ba–O30	2.870(7)	O22–C21	1.419(10)
Ba–O32	2.895(8)	O22–C23	1.418(11)
Ba–O33	2.870(7)	O25–C24	1.432(12)
		O25–C26	1.418(13)
C11–O31	1.372(7)	C1–C2	1.387(12)
C11–O32	1.409(8)	C1–C6	1.391(12)
C11–O33	1.437(7)	C1–C7	1.480(13)
C11–O34	1.408(8)	C2–C3	1.390(13)
C12–O27	1.386(9)	C3–C4	1.361(18)
C12–O28	1.373(9)	C4–C5	1.373(14)
C12–O29	1.431(8)	C5–C6	1.383(13)
C12–O30	1.424(7)	C6–C17	1.475(12)
		C10–C11	1.472(16)
O8–C7	1.198(10)	C13–C14	1.447(18)
O9–C7	1.320(10)	C20–C21	1.484(13)
O9–C10	1.444(13)	C23–C24	1.484(15)

charge-density divalent cations. The data suggest that, at least for the divalent cations, all the ligand oxygen atoms except those of the alkoxy group in the ester function are involved in coordinating the guest cation. Shifts for the aromatic and carbonyl carbons are also observed in $\text{Cl}_3\text{OD}-\text{CH}_3\text{OH}$ as solvent on complexation with Pb^{2+} and Ba^{2+} (Table 3(b)) but clearly, solvation of the cation by methanol competes with the bi-brachial ligand.

An attempt was made to evaluate the equilibrium constants for complexation of **3** with Na^+ and Pb^{2+} in $\text{CD}_3\text{CN}-\text{CH}_3\text{CN}$ by fitting the data for shifts on the

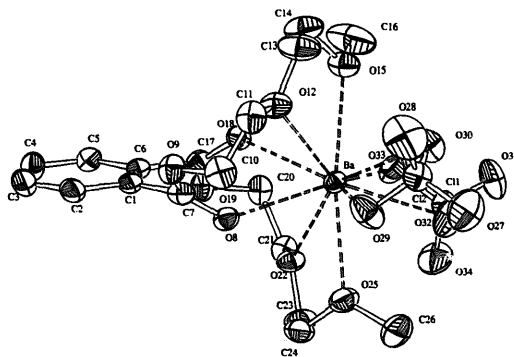


Fig. 4. ORTEP plot of $\mathbf{3} \cdot \text{Ba}(\text{ClO}_4)_2$. Thermal ellipsoids are shown at 50% probability level. Hydrogen atoms are omitted for clarity.

Table 6

Selected bond angles (deg) with esds in parentheses			
C1–C2–C3	119.5(5)	O12–C13–C14	111.7(9)
C2–C3–C4	120.3(9)	C13–C14–O15	110.7(10)
C3–C4–C5	120.9(9)	C14–O15–C16	106.7(9)
C4–C5–C6	119.6(9)	C1–C6–C17	120.8(7)
C5–C6–C1	120.1(8)	C5–C6–C17	119.1(8)
C6–C1–C2	119.5(8)	C6–C17–O18	125.1(7)
		O18–C17–O19	124.3(7)
C2–C1–C7	118.8(8)	C6–C17–O19	110.6(7)
C6–C1–C7	121.6(7)	C17–O19–C20	117.3(6)
C1–C7–O8	124.4(8)	O19–C20–C21	108.3(7)
O8–C7–O9	124.5(8)	C20–C21–O22	109.5(7)
C1–C7–O9	111.1(7)	C21–O22–C23	112.0(7)
C7–O9–C10	116.6(7)	O22–C23–C24	109.8(7)
O9–C10–C11	108.9(9)	C23–C24–O25	109.8(8)
C10–C11–O12	110.6(8)	C24–O25–C26	116.5(8)
C11–O12–C13	112.9(7)		

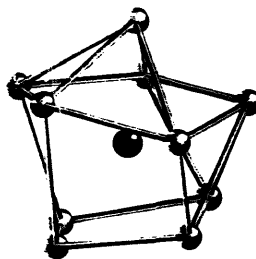


Fig. 5. Coordination sphere around a Ba^{2+} cation illustrating the unusual coordination geometry by ten oxygen atoms (cf. Fig. 4).

carbonyl group to an equilibrium of 1:1 stoichiometry (Table 4). The results give values of K in the region of 2.4 ± 0.4 (for Na^+) and 56 ± 3 (for Pb^{2+}) at 30°C .

The major achievement in this work, however, was the isolation of beautiful hexagonal prisms of the 1:1 Ba^{2+} complex which were suitable for X-ray crystallography. The barium atom is encapsulated by ten oxygen atoms (Fig. 4) including two carbonyl oxygens, four ethylene-oxy units and four oxygen atoms from two perchlorate ions. Selected bond lengths and angles are given in Tables 5 and 6.

The complex shows approximate C_2 symmetry about a line from the barium ion through the aromatic ring. Moreover, the molecule is chiral by virtue of the spiral nature of the binding provided by each arm of the bi-brachial ligand. The ten-coordinate nature of the complex is unusual (Ba^{2+} is normally six–eight coordinate) [8] and the arrangement of the coordinating oxygens around the barium cation can best be described as forming a bi-capped highly distorted cube (Fig. 5).

There are four molecules in the unit cell arranged as two pairs of enantiomers and despite several attempts to crystallise the system at various temperatures, spontaneous resolution has yet to be achieved. It is obvious, however, that if a suitable chiral anion was used as counterion to the barium, it should be possible to crystallise diastereomeric forms of the chiral bi-brachial

complex. Experiments are in hand to test this hypothesis.

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References

- [1] F. Vögtle, *Supramolecular Chemistry*, Wiley, Chichester, UK, 1993, p. 33.
- [2] G.W. Gokel, *Crown Ethers and Cryptands, Monographs in Supramolecular Chemistry*, Royal Society of Chemistry, Cambridge, UK, 1991, p. 49; 110.
- [3] J.-M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, 1995.
- [4] R. Bhavan, R.D. Hancock, P.W. Wade, J.C.A. Boeyens and S.M. Dobson, *Inorg. Chim. Acta*, 171 (1990) 235.
- [5] H.A. Flaschka, *EDTA Titrations*, Pergamon, Oxford, 2nd edn., 1964.
- [6] E.J. Gabe, Y. Le Page, J.P. Charland, F.L. Lee and P.S. White, *J. Appl. Crystallogr.*, 22 (1989) 384.
- [7] C.K. Johnson, ORTEP, Rep. ORNL-3794, 1965 (Oak Ridge National Laboratory, TN, USA).
- [8] N.N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon, Oxford, 1984.