Versatile Cation Complexation by a Calix[4]arene Tetraamide (L). Synthesis and Crystal Structure of $[ML][ClO_4]_2{\cdot}n\text{MeCN}$ ($M = Fe^{II}, Ni^{II}, Cu^{II}, Zn^{II}$ or Pb^{II})‡

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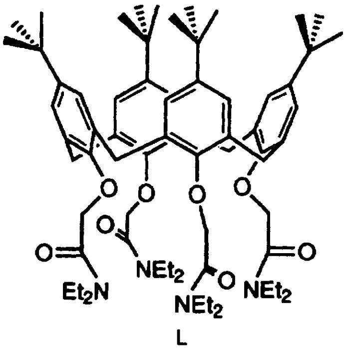
Transition-metal complexes of 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis(diethylcarbamoylmethoxy)calix[4]arene (L) in the cone conformation have been synthesised for the first time. Single-crystal structure determinations have been carried out on the complexes of Fe^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}, as well as of Pb^{2+}, the stoichiometry in each case being assigned as $[ML][ClO_4]_2{\cdot}n\text{MeCN}$ (n = 4–6). The structures of the complexes of Fe^{2+}, Zn^{2+} and Pb^{2+} are broadly similar with the metal atoms co-ordinated to all eight oxygen atoms of L. The copper complex is somewhat different with the four Cu–O (amide) distances being very much shorter than the four Cu–O (ether) distances. A completely different structure is observed in the nickel complex, where L has undergone significant rearrangement to accommodate the metal cation in a distorted-octahedral environment. Molecular-mechanics calculations have been carried out to investigate the remarkable versatility of L as a metal cation receptor.

Calixarenes are a family of synthetic macrocyclic receptors consisting of cyclic arrays of phenol moieties linked by methylene groups.[1] They can be modified at the lower rim to produce a wide variety of ionophores.[2] While reports of calixarenes functionalised with donor atoms appropriate for binding soft metal cations are increasing,[3–5] the most numerous examples of such systems involve the introduction of extra O donor atoms, producing ionophores known to bind alkali-metal, alkaline-earth metal and lanthanide cations.[6,7]

In particular, the tetrasubstituted calix[4]arenes have been found to form stable complexes with alkali-metal cations, where the observed selectivity depends on the conformation of the calixarene.[6,8,9] Despite this activity, there is a paucity of structural data for the complexes, and very little information in general on the binding of cations beyond Groups 1 and 2. Examining a variety of metal complexes of these calixarenes may help establish factors important to the selectivity of complexation. In addition, such ligands may provide unusual co-ordination environments for cations such as those of the transition metals, producing complexes which may have novel catalytic properties.[3,10] We report here the synthesis and structure of the first transition-metal complexes of the calix[4]arene tetraamide (L), as well as a molecular-mechanics investigation of the calixarene–cation interactions.

Experimental

Syntheses.—5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis(diethylcarbamoylmethoxy)calix[4]arene{4,11,18,25-tetra-*tert*-butyl-7,14,21,28-tetrakis(diethylcarbomoylmethoxy)[1.1.1.1]-metacyclophane} (L) was synthesised by the literature method.[11]


L

The metal complexes of L were prepared as follows. A slurry of L (0.011 g, 0.01 mmol) in methyl cyanide (1.5 cm^3) was treated with an excess of the appropriate metal(II) perchlorate hydrate (0.03–0.05 mmol). A clear solution formed which was filtered and left open to the atmosphere to evaporate, slowly depositing crystals (yield 50–80%). For X-ray diffraction studies, crystals were kept wet with supernatant solution. Crystals collected in the laboratory atmosphere, washed with methyl cyanide, and dried by vacuum desiccation rapidly effloresced and formed powders. Microanalyses were consistent with loss of solvent relative to the stoichiometries implied by the structure determinations: $[PbL][ClO_4]_2$ **1**, white solid (Found: C, 53.8; H, 6.70; N, 3.70. Calc. for $C_{68}H_{100}Cl_2N_4O_{16}Pb$: C, 54.2; H, 6.70; N, 3.70); $[FeL][ClO_4]_2$ **2**, white solid (Found: C, 60.0; H, 7.25; N, 4.25. Calc. for $C_{68}H_{100}Cl_2FeN_4O_{16}$: C, 60.2; H, 7.45; N, 4.15); $[ZnL][ClO_4]_2$ **3**, white solid (Found: C, 59.6; H, 7.50; N, 4.50. Calc. for $C_{68}H_{100}Cl_2N_4O_{16}Zn$: C, 59.8; H, 7.40; N, 4.10); $[CuL][ClO_4]_2{\cdot}H_2O{\cdot}MeCN$ **4**, pale green solid (Found: C, 58.9; H, 7.50; N, 4.75. Calc. for $C_{68}H_{100}Cl_2CuN_4O_{16}{\cdot}H_2O{\cdot}MeCN$: C, 59.1; H, 7.45; N, 4.90); $[NiL][ClO_4]_2$ **5**, pale yellow solid (Found: C, 60.3; H, 8.20; N, 4.05. Calc. for $C_{68}H_{100}Cl_2N_4NiO_{16}$: C, 60.1; H, 7.40; N, 4.10%).

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‡ *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Non-SI unit employed: cal = 4.184 J.

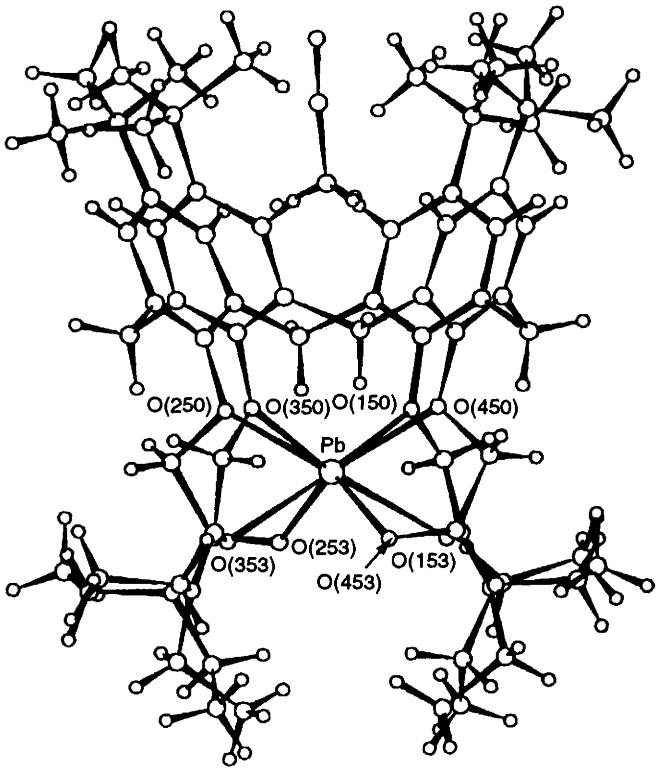

Fig. 1 Structure of $[PbL]^{2+}$ **1** together with the included MeCN

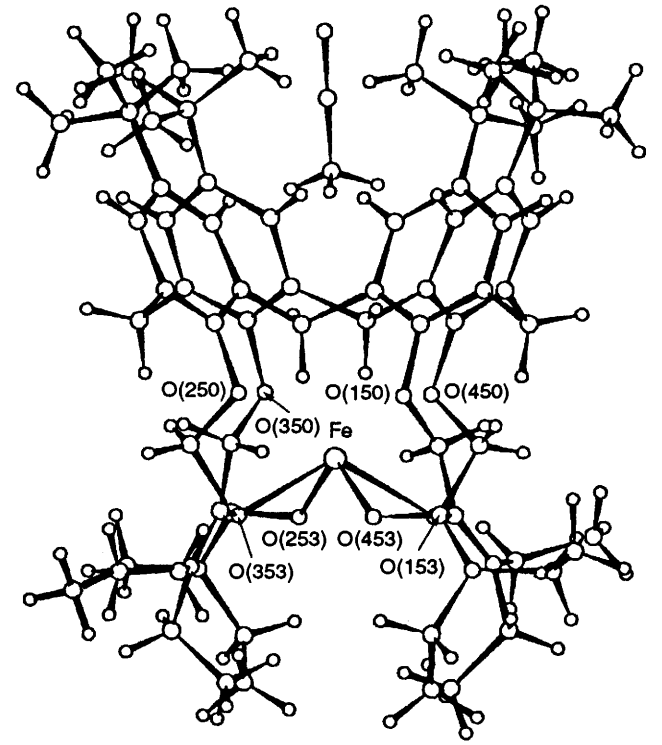

Fig. 2 Structure of $[FeL]^{2+}$ **2** together with the included MeCN

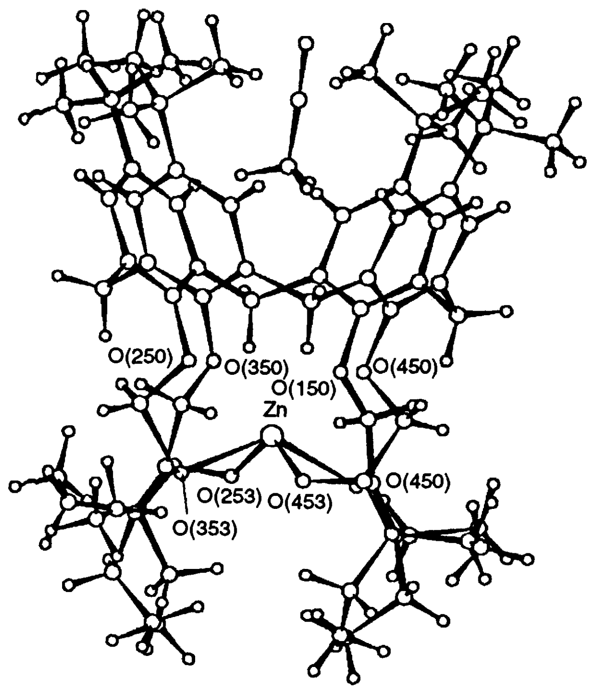

Fig. 3 Structure of $[ZnL]^{2+}$ **3** together with the included MeCN

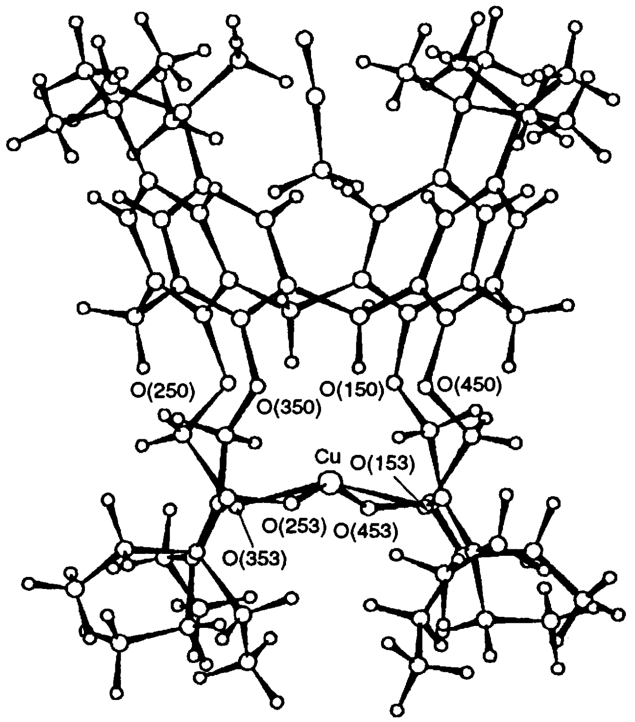

Fig. 4 Structure of $[CuL]^{2+}$ **4** together with the included MeCN

Structure Determinations.—Crystal data are given in Table 3, together with refinement details. Data for all five crystals were collected at 293(2) K with Mo-Kα radiation (λ = 0.710 70 Å) using the MARresearch image plate system. The crystals were positioned 75 mm from the plate and 95 frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program.[12] Four of the compounds (with Zn, Ni, Fe and Pb) were isomorphous but the copper complex was not. The two independent structures were solved using direct methods with the SHELXS 86 program.[13] For subsequent isomorphous structures, input coordinates were taken from the previously determined structure. All non-hydrogen atoms in the cations and anions were refined with anisotropic thermal parameters. The perchlorate anions had high thermal motion, as indeed did some of the Bu^t groups at the top of the calix[4]arene and the ethyl groups at the bottom, but disordered models did not give any significantly better fits. Solvent methyl cyanide molecules, of which there were many, were included with isotropic thermal parameters. Hydrogen atoms were included in geometric positions with thermal parameters equivalent to 1.2 times the atom to which they were bonded. The structures were then refined on F^2 using

Table 1 Bond lengths (Å) and angles (°) in the metal co-ordination spheres

	Pb	Fe	Zn	Cu	Ni
M–O(153)	2.461(8)	2.193(9)	2.087(8)	1.940(5)	1.992(7)
M–O(253)	2.394(9)	2.132(8)	2.036(9)	1.894(5)	2.003(8)
M–O(353)	2.493(8)	2.171(9)	2.085(8)	1.885(6)	1.997(8)
M–O(453)	2.533(11)	2.185(9)	2.110(8)	1.921(5)	—
M–O(150)	2.631(7)	2.451(8)	2.572(7)	[2.797(8)]	2.250(6)
M–O(250)	2.562(7)	2.446(8)	2.568(7)	[2.858(8)]	2.771(8)
M–O(350)	2.600(6)	2.476(8)	2.600(7)	[2.897(7)]	2.315(6)
M–O(450)	2.641(7)	2.435(8)	2.578(7)	[2.894(8)]	2.139(6)
O(253)–M–O(153)	75.6(3)	76.7(4)	79.9(3)	87.2(2)	84.9(4)
O(253)–M–O(353)	76.1(3)	75.5(4)	79.6(3)	87.3(2)	84.6(4)
O(153)–M–O(353)	120.5(3)	120.9(4)	129.5(3)	152.8(3)	90.5(3)
O(253)–M–O(453)	120.8(4)	121.3(4)	130.0(3)	153.7(3)	—
O(153)–M–O(453)	75.3(3)	76.3(4)	80.2(3)	86.0(2)	—
O(353)–M–O(453)	76.2(3)	75.5(4)	78.8(3)	87.1(2)	—
O(253)–M–O(250)	63.0(3)	67.1(3)	66.4(3)	—	61.2(6)
O(153)–M–O(250)	83.4(3)	80.8(3)	81.6(3)	—	129.5(6)
O(353)–M–O(250)	125.6(3)	130.7(3)	129.1(3)	—	119.4(6)
O(453)–M–O(250)	155.9(3)	152.3(3)	152.0(3)	—	—
O(253)–M–O(350)	84.3(3)	79.6(3)	80.7(3)	—	102.5(3)
O(153)–M–O(350)	158.2(3)	151.6(3)	151.7(3)	—	160.3(2)
O(353)–M–O(350)	60.9(2)	66.7(3)	66.0(3)	—	72.3(3)
O(453)–M–O(350)	123.4(3)	130.2(3)	128.1(3)	—	—
O(250)–M–O(350)	79.9(2)	75.7(3)	71.8(3)	—	69.1(3)
O(253)–M–O(150)	124.4(2)	131.0(3)	129.8(3)	—	92.6(4)
O(153)–M–O(150)	60.7(2)	65.9(3)	65.7(3)	—	74.8(3)
O(353)–M–O(150)	155.4(3)	151.4(3)	150.6(3)	—	165.2(3)
O(453)–M–O(150)	81.0(3)	80.0(3)	80.1(3)	—	—
O(250)–M–O(150)	78.7(2)	76.4(3)	73.1(2)	—	71.0(4)
O(350)–M–O(150)	128.3(2)	122.2(3)	113.6(2)	—	122.4(2)
O(253)–M–O(450)	155.8(2)	149.5(3)	150.0(3)	—	166.3(3)
O(153)–M–O(450)	123.9(3)	131.5(3)	130.1(3)	—	82.1(3)
O(353)–M–O(450)	81.0(3)	78.6(3)	79.2(3)	—	91.0(3)
O(453)–M–O(450)	59.6(3)	66.0(3)	65.3(3)	—	—
O(250)–M–O(450)	128.1(2)	121.9(3)	113.0(3)	—	131.6(3)
O(350)–M–O(450)	77.8(2)	75.6(3)	71.4(3)	—	88.5(2)
O(150)–M–O(450)	79.6(2)	78.1(3)	73.4(2)	—	88.3(2)

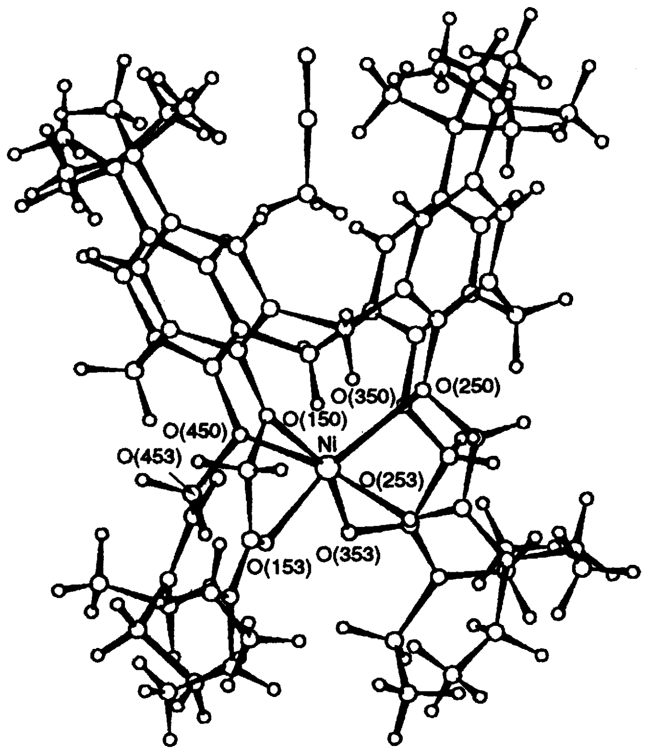

Fig. 5 Structure of [NiL]$^{2+}$ **5** together with the included MeCN

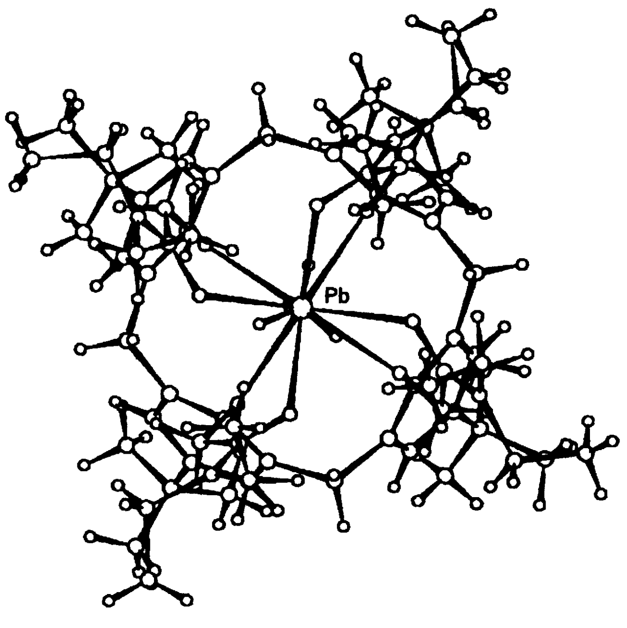

Fig. 6 Structure of [PbL]$^{2+}$ **1** viewed onto the plane of the four methylene groups and showing the geometry of the metal co-ordination sphere intermediate between a square antiprism and a cube. The included MeCN is also shown

Table 2 Least-squares planes calculations for structures **1**–**5**
Planes: 1, C(17), C(27), C(37), C(47); 2, O(150), O(250), O(350), O(450); 3, O(153), O(253), O(353), O(453)

	Pb	Fe	Zn	Cu	Ni
Distance (Å) of M from					
Plane 1	2.49	2.50	2.75	3.16	2.31
Plane 2	1.14	1.19	1.42	1.85	0.99
Plane 3	−1.22	−1.07	−0.88	−0.44	−1.09
Maximum deviation (Å) of a contributing atom from					
Plane 1	0.00	0.00	0.00	0.02	0.02
Plane 2	0.00	0.00	0.00	0.00	0.00
Plane 3	0.00	0.01	0.00	0.01	0.40
Angles (°) between planes					
1, 2	0.1	0.5	0.1	0.5	2.2
2, 3	0.8	0.5	0.5	0.4	18.2
1, 3	0.7	0.6	0.6	0.8	16.1

SHELXL 93.[14] Absorption corrections were not applied. All calculations were carried out on a Silicon Graphics R4000 Workstation at the University of Reading. The final coordinates for **1**–**5** are given in Tables 4–8 and important dimensions are compared in Table 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Transition-metal complexes of the calix[4]arene tetraamide (L) have been readily synthesised as methyl cyanide solvates, by combining L with the appropriate metal perchlorate hydrates in methyl cyanide solvent. The complexes are apparently stable in the normal laboratory atmosphere, unlike transition-metal complexes of the parent ligand, *p-tert*-butylcalix[4]arene,[15] and common amide ligands such as dimethylformamide,[16] which are generally hydrolysed upon exposure to atmospheric water. While the syntheses are straightforward, the processes taking place in solution are more complex, and are still under investigation. For example, the UV/VIS spectrum of the mixture containing L and Cu^{2+} changes over 24 h after the initial reaction, and the solution visibly changes from intense olive green to pale green. The decrease in the intensity of absorbance, predominantly of a peak at 430 nm, may indicate the initial formation of a species with a significant charge-transfer absorbance, which is not observed for the final product (consistent with structural studies described below). It is also noteworthy that the iron(II) complex can be synthesised using iron-(II) or -(III) perchlorate as starting material; presumably the iron(III) complex is reduced to Fe^{II} with concomitant oxidation of solvent or calixarene. The influence of various calixarene derivatives on the Fe^{III}–Fe^{II} redox couple will be the subject of a future publication.

The five structures are illustrated in Figs. 1–5 together with the common numbering system. They have many features in common, although there are significant differences. All consist of discrete [ML]$^{2+}$ complexes together with two independent perchlorate anions and several solvent molecules. The calix[4]arenes are in the cone conformation so that eight oxygen atoms in the lower rim [four from the ether oxygen atoms O(n50) and four from the carbonyl oxygens O(n53) (n = 1–4)] are available for bond formation to the metal atoms. The details of the metal co-ordination spheres are compared in Table 1.

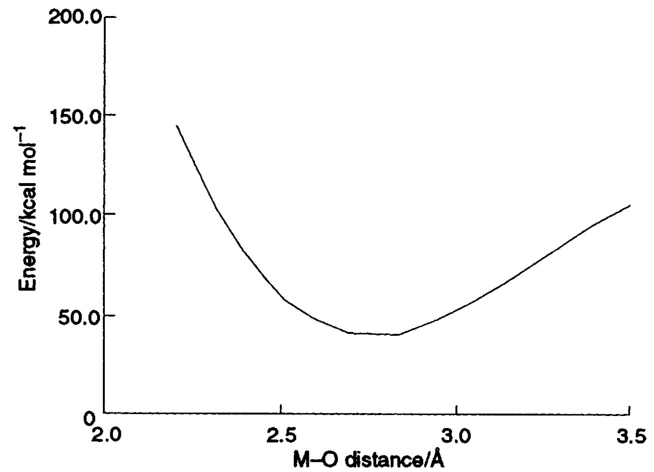

Fig. 7 Plot of energy against M–O distance for the eight-co-ordinate metal complexes ML

In previous work[17] we have described the crystal structures of the tetraamide in the 1,3-alternate conformation in which two potassium ions are encapsulated each within a co-ordination sphere of four oxygen atoms (two ether oxygen and two carbonyl oxygen atoms) and two phenyl rings. This contrasts with a previous structure determination of one potassium cation within the tetraamide in the cone conformation.[11] This structure is heavily disordered but the essential features are clear and very similar to that observed in the present lead structure **1** here, namely that the potassium ion is bonded to all eight oxygen atoms with K–O(n50) 2.74 and K–O(n53) 2.71 Å. In the lead structure (Table 1) the mean distances are 2.47 and 2.58 Å respectively. The two sets of four oxygen atoms each form a square-planar array within experimental error. The squares are parallel (angle of intersection 0.8°). The environment of the metal ion is intermediate between a cube and a square antiprism, but more like the latter as the angle of rotation from the eclipsed arrangement is 27.0° (45° for an ideal square antiprism). It is interesting that the plane of the four methylene groups in the calixarene is also parallel with these two planes of oxygen atoms. The projection of the lead structure onto the plane of the four methylene groups is shown in Fig. 6.

Clearly the spatial arrangement of the eight oxygen atoms fits the stereochemical requirements of the larger cations such as K$^+$ and Pb^{2+} so it is somewhat surprising that the four much smaller transition-metal ions have also formed complexes. With Zn, Fe and Cu the metal atom forms strong bonds to the four carbonyl oxygen atoms O(n53) and much weaker ones to the four ether oxygen atoms O(n50). This is shown clearly in the Figures. This distorted arrangement is due to the relative inflexibility of the ether oxygen atoms which cannot approach each other (and hence a metal atom) because of rigidity of the lower rim of the calix[4]arene. However, the positions of the carbonyl oxygen atoms are much more flexible and can approach to the required bonding distance from the transition metals.

Table 3 Crystal data and structure refinement for complexes **1**–**5***

	1	**2**	**3**	**4**	**5**
	$[PbL][ClO_4]_2\cdot5MeCN$	$[FeL][ClO_4]_2\cdot4MeCN$	$[ZnL][ClO_4]_2\cdot5MeCN$	$[CuL][ClO_4]_2\cdot6MeCN$	$[NiL][ClO_4]_2\cdot5MeCN$
Empirical formula	$C_{78}H_{115}Cl_2N_9O_{16}Pb$	$C_{76}H_{112}Cl_2FeN_8O_{16}$	$C_{78}H_{115}Cl_2N_9O_{16}Zn$	$C_{80}H_{118}Cl_2CuN_{10}O_{16}$	$C_{78}H_{115}Cl_2N_9NiO_{16}$
M	1712.88	1520.52	1571.12	1610.24	1564.42
Space group	Cc	Cc	Cc	$P2_1/c$	Cc
a/Å	27.125(9)	26.942(9)	26.935(8)	14.397(8)	27.404(9)
b/Å	16.670(9)	16.405(8)	16.478(9)	23.930(8)	16.745(9)
c/Å	19.187(9)	19.316(9)	19.384(8)	25.364(8)	18.873(9)
β/°	102.39(10)	103.30(10)	103.050(10)	104.81(10)	104.49(10)
U/Å^3	8474(7)	8307(7)	8381(6)	8448(6)	8385(7)
D_c/Mg m^{-3}	1.343	1.216	1.245	1.266	1.239
μ/mm^{-1}	2.120	0.310	0.36	0.390	0.360
$F(000)$	3560	3248	3352	3436	3344
Crystal size/mm	0.25 × 0.25 × 0.20	0.3 × 0.3 × 0.2	0.3 × 0.3 × 0.25	0.2 × 0.25 × 0.3	0.3 × 0.3 × 0.25
θ range for data collection/°	2.97–26.12	1.93–24.91	1.71–25.03	1.69–25.32	2.88–25.90
hkl ranges	0–33, −20 to 20, −23 to 22	0–31, −19 to 19, −22 to 22	0–31, −19 to 19, −22 to 21	−17 to 0, −25 to 25, −29 to 29	0–33, −20 to 20, −23 to 22
Reflections collected	13 246	12 033	11 934	21 362	12 464
Independent reflections (R_{int})	7845 (0.0333)	6600 (0.0483)	6914 (0.041)	12 349 (0.0645)	7244 (0.0540)
Data, parameters	7845, 924	6600, 921	6914, 929	12 349, 946	7244, 919
Goodness-of-fit on F^2	0.821	0.834	0.931	1.080	1.047
Parameters a, b in weighting scheme	0.16, 13.60	0.23, 37.21	0.16, 37.60	0.75, 76.03	0.17, 2.23
Final R_1 and wR_2 indices $[I > 2\sigma(I)]$	0.0475, 0.1411	0.081, 0.179	0.0796, 0.2056	0.084, 0.177	0.0893, 0.2289
(all data)	0.0599, 0.1566	0.154, 0.320	0.1229, 0.2567	0.131, 0.258	0.1249, 0.2563
Largest difference peak and hole/e Å^{-3}	1.130, −1.393	0.976, −1.039	0.748, −0.747	0.544, −1.216	0.698, −0.356

* Details in common: monoclinic; $Z = 4$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [\mathrm{Max}(F_o^2) + 2F_c^2]/3$.

Table 4 Atomic coordinates (× 10^4) for complex **1**

Atom	*x*	*y*	*z*
Pb	860(1)	2551(1)	4431(1)
C(11)	203(4)	3801(6)	2396(5)
C(12)	−184(4)	4080(6)	1878(5)
C(13)	−579(4)	4525(5)	2016(6)
C(14)	−569(4)	4681(6)	2748(6)
C(15)	−181(4)	4422(6)	3283(6)
C(16)	215(4)	4030(5)	3093(5)
C(17)	−217(4)	4549(5)	4058(5)
C(21)	−579(4)	3918(5)	4243(5)
C(22)	−1093(4)	4018(6)	4025(5)
C(23)	−1437(4)	3454(6)	4136(6)
C(24)	−1242(4)	2735(7)	4424(6)
C(25)	−720(5)	2603(6)	4658(6)
C(26)	−412(4)	3221(6)	4588(5)
C(27)	−540(5)	1769(6)	4949(7)
C(31)	−555(4)	1200(5)	4332(5)
C(32)	−1022(4)	858(6)	3995(6)
C(33)	−1063(4)	371(6)	3416(5)
C(34)	−636(4)	259(6)	3147(7)
C(35)	−177(4)	569(6)	3448(6)
C(36)	−139(4)	1014(5)	4074(5)
C(37)	267(4)	470(7)	3092(6)
C(41)	212(4)	1084(6)	2487(5)
C(42)	−134(4)	947(6)	1861(6)
C(43)	−222(4)	1505(6)	1339(6)
C(44)	19(4)	2242(7)	1448(5)
C(45)	363(5)	2422(5)	2075(6)
C(46)	479(4)	1796(5)	2573(6)
C(47)	597(5)	3264(7)	2196(7)
C(100)	−1007(5)	4867(6)	1427(6)
C(101)	−1233(11)	4261(15)	891(20)
C(102)	−800(9)	5581(14)	1149(15)
C(103)	−1447(9)	5121(21)	1669(11)
C(200)	−2001(4)	3609(7)	3920(7)
C(201)	−2149(7)	4060(15)	3182(13)
C(202)	−2308(5)	2908(11)	3845(17)
C(203)	−2127(7)	4185(17)	4444(13)
C(300)	−1572(5)	−11(8)	3080(7)
C(301)	−2014(8)	412(30)	3225(23)
C(302)	−1590(14)	−781(18)	3357(27)
C(303)	−1662(9)	8(25)	2296(12)
C(400)	−584(5)	1320(7)	627(6)
C(401)	−912(22)	659(26)	602(27)
C(402)	−297(10)	1079(25)	102(14)
C(403)	−900(11)	2027(18)	383(14)
O(150)	632(2)	3831(4)	3625(4)
C(151)	1007(4)	4444(6)	3721(6)
C(152)	1360(4)	4333(5)	4425(6)
N(154)	1751(4)	4794(7)	4596(6)
O(153)	1250(3)	3846(5)	4851(4)
C(155)	2088(6)	4715(10)	5298(8)
C(156)	2466(8)	4024(16)	5338(13)
C(157)	1917(7)	5347(10)	4099(10)
C(158)	1774(9)	6176(12)	4163(14)
O(250)	110(2)	3110(5)	4892(4)
C(251)	248(4)	3484(6)	5575(5)
C(252)	732(5)	3095(7)	5961(6)
C(255)	760(6)	4074(9)	6914(8)
C(256)	474(8)	3853(13)	7467(11)
C(258)	1862(8)	3289(22)	6879(17)
C(257)	1392(7)	2956(15)	7003(9)
N(254)	951(4)	3369(9)	6596(6)
O(253)	923(4)	2527(4)	5695(5)
O(350)	334(3)	1248(4)	4437(4)
C(351)	539(5)	724(7)	5005(7)
C(352)	1120(5)	809(7)	5153(7)
N(354)	1374(5)	390(10)	5672(9)
O(353)	1308(3)	1268(5)	4818(5)
C(355)	1159(8)	−150(12)	6145(12)
C(356)	1094(17)	−1013(17)	5914(21)
C(357)	1937(7)	426(14)	5800(19)
C(358)	2107(13)	1059(29)	6260(19)
O(450)	861(2)	1935(4)	3163(4)
C(451)	1328(4)	1605(7)	3083(8)
C(452)	1751(4)	2078(6)	3564(6)
N(454)	2216(4)	1884(7)	3584(8)
O(453)	1645(4)	2625(6)	3918(6)
C(455)	2347(6)	1151(11)	3183(10)
C(456)	2438(9)	1368(16)	2458(13)
C(457)	2614(6)	2293(11)	4032(13)
C(458)	2755(8)	1945(14)	4740(12)
Cl(1)	538(2)	6218(2)	5066(2)
O(11)	781(9)	5574(11)	5420(14)
O(12)	56(8)	6260(18)	5156(12)
O(13)	786(7)	6927(9)	5333(10)
O(14)	533(6)	6129(10)	4347(8)
Cl(2)	4899(2)	3394(2)	1932(2)
O(21)	4963(19)	3403(17)	2625(11)
O(22)	4740(10)	2642(7)	1612(10)
O(23)	5229(11)	3716(21)	1633(18)
O(24)	4538(11)	3946(12)	1742(16)
C(602)	1878(16)	3362(25)	1418(24)
C(601)	1879(12)	3805(20)	2050(18)
N(600)	1816(18)	4249(30)	2467(23)
N(700)	1451(17)	−552(27)	3563(23)
C(701)	1236(15)	−1087(27)	3784(22)
C(702)	960(20)	−1752(31)	3918(25)
C(802)	−875(8)	2450(7)	2660(10)
C(801)	−1384(13)	2433(11)	2225(18)
N(800)	−1773(18)	2426(18)	1842(29)
N(900)	−1297(11)	6230(18)	3609(15)
C(901)	−994(9)	6571(14)	3470(12)
C(902)	−543(12)	7024(20)	3456(17)
N(903)	−1886(9)	1234(16)	5443(13)
C(904)	−1803(12)	1590(20)	5784(18)
C(905)	−1548(16)	2196(26)	6191(22)

Table 5 Atomic coordinates (× 10^4) for complex **2**

Atom	*x*	*y*	*z*
Fe	864(1)	2548(1)	4428(1)
C(11)	223(5)	3764(7)	2390(7)
C(12)	−170(5)	4086(9)	1848(7)
C(13)	−546(5)	4558(7)	1996(7)
C(14)	−536(5)	4712(8)	2661(8)
C(15)	−156(4)	4419(7)	3237(6)
C(16)	214(4)	3959(7)	3057(6)
C(17)	−195(5)	4581(7)	3976(8)
C(21)	−576(5)	3969(8)	4185(6)
C(22)	−1096(5)	4109(8)	3969(7)
C(23)	−1456(5)	3569(8)	4086(7)
C(24)	−1254(4)	2835(8)	4425(7)
C(25)	−745(6)	2661(8)	4636(7)
C(26)	−414(5)	3254(7)	4515(6)
C(27)	−576(5)	1825(8)	4933(7)
C(157)	1922(9)	5218(15)	4247(13)
C(158)	1750(15)	6053(17)	4219(21)
O(250)	117(3)	3112(5)	4777(4)
C(251)	268(5)	3429(9)	5479(6)
C(252)	725(6)	2975(9)	5849(6)
C(255)	809(13)	3965(30)	6898(13)
C(256)	612(26)	3853(45)	7352(38)
C(258)	1821(13)	2959(24)	6878(27)
C(257)	1345(13)	2667(21)	6898(13)
N(254)	940(5)	3179(10)	6506(6)
O(253)	901(4)	2423(5)	5537(4)
O(350)	294(3)	1361(5)	4416(5)
C(351)	528(5)	811(8)	4961(7)
C(352)	1086(6)	898(8)	5077(7)
N(354)	1392(6)	431(11)	5552(10)

Table 5 (*contd.*)

Atom	x	y	z
C(31)	−589(5)	1256(8)	4339(6)
C(32)	−1058(5)	889(8)	4014(7)
C(33)	−1107(6)	373(8)	3450(7)
C(34)	−682(5)	230(8)	3199(8)
C(35)	−221(4)	570(7)	3492(6)
C(36)	−185(4)	1070(7)	4078(6)
C(37)	224(5)	428(8)	3162(7)
C(41)	186(4)	1014(8)	2549(8)
C(42)	−148(5)	867(8)	1904(7)
C(43)	−224(5)	1413(8)	1328(7)
C(44)	42(6)	2136(8)	1449(6)
C(45)	366(5)	2328(8)	2083(7)
C(46)	438(4)	1767(7)	2633(7)
C(47)	604(4)	3171(8)	2204(6)
C(100)	−963(5)	4875(9)	1362(7)
C(101)	−1176(15)	4246(18)	875(19)
C(102)	−765(8)	5552(13)	1025(15)
C(103)	−1404(11)	5201(28)	1587(15)
C(200)	−2011(5)	3757(10)	3860(8)
C(201)	−2153(9)	4127(17)	3166(12)
C(202)	−2335(7)	3003(15)	3831(20)
C(203)	−2146(8)	4315(20)	4404(14)
C(300)	−1632(5)	−14(9)	3103(8)
C(301)	−2033(9)	443(28)	3198(27)
C(302)	−1702(20)	−704(30)	3513(31)
C(303)	−1692(11)	−179(29)	2367(17)
C(400)	−579(6)	1216(8)	659(7)
C(401)	−966(14)	543(24)	701(19)
C(402)	−279(12)	933(33)	199(14)
C(403)	−905(10)	1916(13)	360(14)
O(150)	622(3)	3711(5)	3624(4)
C(151)	1020(4)	4293(8)	3745(8)
C(152)	1332(5)	4213(8)	4477(7)
N(154)	1717(5)	4684(8)	4719(8)
O(153)	1187(3)	3714(6)	4871(5)
C(155)	1987(8)	4618(13)	5435(11)
C(156)	2420(11)	4020(22)	5586(17)
O(353)	1273(3)	1414(6)	4723(5)
C(355)	1204(8)	−143(20)	5961(17)
C(356)	1161(19)	8(35)	6591(32)
C(357)	1965(10)	455(16)	5605(17)
C(358)	2167(17)	1012(28)	6083(18)
O(450)	804(3)	1922(5)	3269(4)
C(451)	1284(5)	1635(8)	3207(8)
C(452)	1701(5)	2125(9)	3676(7)
N(454)	2152(4)	2003(7)	3624(7)
O(453)	1554(3)	2671(5)	4026(5)
C(455)	2306(7)	1381(14)	3220(12)
C(456)	2377(13)	1689(30)	2531(18)
C(457)	2550(6)	2501(11)	4075(13)
C(458)	2773(10)	2087(18)	4780(14)
Cl(1)	555(2)	6250(3)	5059(3)
O(11)	743(15)	5568(16)	5420(16)
O(12)	50(9)	6353(17)	5104(12)
O(13)	817(10)	6928(15)	5369(13)
O(14)	580(8)	6205(13)	4381(10)
Cl(2)	4872(2)	3333(3)	1930(3)
O(21)	5057(16)	3297(14)	2600(10)
O(22)	4711(8)	2556(8)	1637(9)
O(23)	5146(9)	3679(17)	1513(11)
O(24)	4454(10)	3808(13)	1920(19)
N(700)	1415(17)	−565(30)	3712(23)
C(701)	1233(12)	−1125(21)	3820(17)
C(702)	976(31)	−1910(50)	4041(41)
N(800)	−1828(15)	2502(18)	1829(20)
C(801)	−1399(12)	2475(14)	2202(15)
C(802)	−923(8)	2455(12)	2623(11)
N(900)	−1356(18)	6403(29)	3396(23)
C(901)	−986(10)	6712(16)	3495(13)
C(902)	−565(14)	6976(26)	3401(20)
N(903)	−1911(20)	1209(36)	5371(29)
C(904)	−1896(21)	1687(35)	5860(29)
C(905)	−1577(17)	2315(24)	6270(22)

Table 6 Atomic coordinates (× 10^4) for complex **3**

Atom	x	y	z
Zn	911(1)	2558(1)	4477(1)
C(11)	187(4)	3754(7)	2355(6)
C(12)	−196(4)	4073(7)	1818(6)
C(13)	−589(4)	4544(6)	1957(5)
C(14)	−574(4)	4688(6)	2654(6)
C(15)	−203(4)	4428(6)	3201(6)
C(16)	182(4)	3973(7)	3045(5)
C(17)	−233(4)	4557(7)	3974(6)
C(21)	−606(5)	3965(6)	4159(6)
C(22)	−1120(4)	4111(7)	3966(5)
C(23)	−1482(4)	3545(7)	4080(6)
C(24)	−1292(4)	2816(7)	4383(6)
C(25)	−779(4)	2646(7)	4617(5)
C(26)	−444(3)	3243(6)	4496(5)
C(27)	−619(4)	1849(7)	4900(6)
C(31)	−626(4)	1238(6)	4305(5)
C(32)	−1092(5)	870(7)	3980(6)
C(33)	−1139(4)	366(7)	3404(6)
C(34)	−706(4)	226(7)	3135(6)
C(35)	−244(4)	558(6)	3465(6)
C(36)	−209(3)	1055(6)	4052(5)
C(37)	197(4)	426(7)	3111(6)
C(41)	159(3)	1037(6)	2503(5)
C(42)	−166(4)	864(7)	1874(6)
C(43)	−237(4)	1412(7)	1302(5)
C(44)	11(4)	2142(7)	1426(5)
C(45)	338(4)	2332(7)	2063(6)
C(46)	409(4)	1774(6)	2605(6)
C(47)	563(4)	3175(7)	2172(6)
C(100)	−996(4)	4874(7)	1352(6)
C(101)	−1207(10)	4220(13)	829(11)
C(158)	1746(11)	6073(14)	4183(16)
O(250)	87(2)	3105(4)	4761(3)
C(251)	235(4)	3419(6)	5447(5)
C(252)	706(4)	2998(7)	5831(6)
C(255)	770(12)	3970(29)	6854(8)
C(256)	629(20)	3795(56)	7300(37)
C(258)	1806(12)	2935(31)	6843(24)
C(257)	1341(7)	2715(16)	6900(12)
N(254)	915(4)	3198(10)	6489(5)
O(253)	891(3)	2457(5)	5517(4)
O(350)	270(2)	1361(4)	4387(4)
C(351)	500(4)	814(7)	4926(6)
C(352)	1065(5)	907(8)	5067(6)
N(354)	1348(4)	442(9)	5535(8)
O(353)	1256(3)	1428(5)	4713(4)
C(355)	1161(8)	−128(15)	5934(18)
C(356)	1215(9)	−83(15)	6626(21)
C(357)	1920(6)	494(15)	5606(12)
C(358)	2155(9)	946(27)	6123(16)
O(450)	771(2)	1933(5)	3228(4)
C(451)	1257(4)	1615(7)	3179(6)
C(452)	1653(4)	2128(7)	3625(6)
N(454)	2133(3)	1979(7)	3605(6)
O(453)	1539(3)	2660(5)	4000(5)
C(455)	2282(5)	1319(11)	3187(9)
C(456)	2349(10)	1579(20)	2472(13)
C(457)	2540(6)	2468(10)	4041(10)
C(458)	2737(8)	2077(15)	4748(13)
Cl(1)	530(2)	6236(3)	5029(2)
O(11)	705(9)	5550(11)	5348(11)
O(12)	28(6)	6343(14)	5095(9)

Table 6 (*contd.*)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
C(102)	−777(7)	5530(14)	1012(12)	O(13)	771(8)	6929(11)	5318(11)
C(103)	−1429(8)	5229(19)	1611(10)	O(14)	537(6)	6157(11)	4327(8)
C(200)	−2041(4)	3729(8)	3864(7)	Cl(2)	4854(2)	3329(2)	1902(2)
C(201)	−2179(7)	4131(17)	3126(11)	O(21)	5089(15)	3303(17)	2600(8)
C(202)	−2366(5)	3017(12)	3834(15)	O(22)	4685(7)	2566(7)	1617(8)
C(203)	−2168(6)	4330(17)	4377(12)	O(23)	5152(8)	3679(13)	1502(10)
C(300)	−1645(5)	−41(9)	3075(6)	O(24)	4435(8)	3822(11)	1831(15)
C(301)	−2090(7)	475(25)	3143(21)	C(602)	1808(32)	3270(54)	1293(44)
C(302)	−1722(13)	−687(24)	3476(23)	C(601)	1826(21)	3705(34)	1930(35)
C(303)	−1718(8)	−49(20)	2292(13)	N(600)	1891(21)	3899(34)	2538(32)
C(400)	−610(5)	1223(8)	602(6)	N(700)	1408(12)	−566(19)	3686(16)
C(401)	−967(13)	576(22)	644(14)	C(701)	1188(11)	−1095(19)	3899(15)
C(402)	−303(9)	1023(22)	98(11)	C(702)	920(17)	−1784(27)	3947(22)
C(403)	−920(9)	1948(14)	335(12)	C(801)	−1432(9)	2461(11)	2178(12)
O(150)	593(2)	3711(4)	3593(4)	N(800)	−1843(16)	2445(17)	1823(21)
C(151)	980(4)	4293(7)	3704(6)	C(802)	−939(7)	2451(9)	2585(10)
C(152)	1303(4)	4210(7)	4421(6)	N(900)	−1352(15)	6369(23)	3496(19)
N(154)	1694(4)	4689(7)	4649(6)	C(901)	−1028(10)	6719(15)	3457(12)
O(153)	1173(3)	3707(5)	4838(4)	C(902)	−561(11)	7050(17)	3413(14)
C(155)	1978(6)	4629(10)	5397(9)	N(903)	−1964(16)	1234(27)	5383(22)
C(156)	2393(8)	4074(18)	5473(13)	C(904)	−1858(14)	1757(23)	5821(19)
C(157)	1880(7)	5235(12)	4175(10)	C(905)	−1600(15)	2334(18)	6230(19)

Table 7 Atomic coordinates (× 10^4) for complex **4**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cu	−908(1)	2138(1)	2016(1)	C(251)	−334(7)	767(4)	2008(4)
C(11)	2330(6)	2670(4)	2932(3)	C(252)	−1325(7)	987(3)	1825(3)
C(12)	3282(8)	2665(5)	3091(4)	O(253)	−1469(4)	1471(2)	1677(2)
C(13)	3815(8)	2179(5)	3224(4)	N(254)	−2012(6)	644(3)	1817(3)
C(14)	3308(8)	1693(5)	3176(3)	C(255)	−2965(8)	856(5)	1612(5)
C(15)	2321(7)	1675(4)	3007(3)	C(256)	−3321(10)	1184(6)	2009(6)
C(16)	1861(6)	2179(4)	2901(3)	C(257)	−1905(10)	47(5)	1931(6)
C(17)	1813(7)	1132(4)	2908(3)	C(258)	−2272(18)	−97(7)	2370(8)
C(21)	1865(7)	910(3)	2360(3)	O(350)	−246(4)	2075(2)	1031(2)
C(22)	2671(7)	662(4)	2299(3)	C(351)	−1120(7)	2063(4)	664(3)
C(23)	2816(7)	490(4)	1811(4)	C(352)	−1847(7)	2315(4)	929(3)
C(24)	2101(7)	595(3)	1363(3)	O(353)	−1596(4)	2520(2)	1388(2)
C(25)	1259(7)	850(3)	1397(3)	N(354)	−2714(6)	2329(4)	662(3)
C(26)	1163(5)	988(3)	1909(3)	C(355)	−3067(9)	2140(6)	92(4)
C(27)	557(7)	995(3)	891(3)	C(356)	−3793(15)	1701(7)	7(7)
C(31)	823(7)	1524(3)	655(3)	C(357)	−3454(10)	2551(7)	922(6)
C(32)	1498(7)	1514(3)	352(3)	C(358)	−3774(18)	3068(10)	732(10)
C(33)	1824(7)	1982(4)	155(3)	O(450)	325(4)	3041(2)	1852(2)
C(34)	1479(6)	2483(4)	283(3)	C(451)	−317(7)	3489(3)	1883(4)
C(35)	817(6)	2525(3)	588(3)	C(452)	−955(7)	3295(4)	2216(4)
C(36)	467(6)	2041(3)	755(3)	O(453)	−921(5)	2824(2)	2407(2)
C(37)	516(6)	3082(3)	747(3)	N(454)	−1589(7)	3651(3)	2313(4)
C(41)	1275(6)	3294(3)	1234(3)	C(455)	−2189(12)	3470(6)	2681(7)
C(42)	2061(7)	3525(4)	1145(4)	C(456)	−2967(17)	3174(11)	2412(9)
C(43)	2794(8)	3687(4)	1567(4)	C(457)	−1637(11)	4238(5)	2157(6)
C(44)	2700(7)	3592(4)	2087(3)	C(458)	−2393(15)	4375(7)	1757(7)
C(45)	1882(7)	3353(3)	2185(3)	C1(7)	−1835(4)	3838(2)	61(1)
C(46)	1167(6)	3236(3)	1757(3)	O(72)	−1677(12)	3871(7)	605(5)
C(47)	1837(7)	3211(4)	2763(3)	O(71)	−2507(17)	4161(11)	−188(9)
C(100)	4883(9)	2172(6)	3418(5)	O(73)	−1047(14)	4053(7)	−98(5)
C(101)	5095(13)	1989(9)	4009(6)	O(74)	−1879(13)	3307(6)	−92(7)
C(102)	5290(11)	1726(12)	3129(10)	C1(8)	−2115(3)	313(2)	189(2)
C(103)	5318(14)	2730(9)	3408(13)	O(81)	−1733(15)	−68(6)	−54(5)
C(200)	3707(7)	200(4)	1738(4)	O(83)	−1691(13)	432(11)	673(6)
C(201)	4107(9)	489(5)	1310(5)	O(84)	−3028(9)	270(8)	136(9)
C(202)	4507(9)	213(9)	2248(5)	O(85)	−1916(16)	800(8)	−53(11)
C(203)	3469(12)	−375(6)	1555(8)	N(500)	4591(18)	2198(9)	1542(9)
C(300)	2561(7)	1934(5)	−192(4)	C(501)	3887(15)	2137(7)	1624(7)
C(301)	2812(13)	2505(6)	−378(7)	C(502)	2972(9)	2079(5)	1677(5)
C(302)	3418(8)	1644(8)	103(6)	N(503)	−45(15)	5055(9)	1654(9)
C(303)	2126(11)	1609(7)	−702(5)	C(504)	243(15)	4914(9)	1298(9)
C(400)	3669(9)	3982(5)	1468(5)	C(505)	542(14)	4794(8)	825(7)
C(401)	4553(11)	3838(8)	1890(8)	N(506)	62(14)	4054(8)	3318(8)
C(402)	3843(13)	3833(10)	931(7)	C(507)	−121(13)	4191(8)	3700(8)
C(403)	3524(14)	4584(7)	1510(11)	C(508)	−296(13)	4364(7)	4194(7)
O(150)	878(4)	2177(2)	2779(2)	N(509)	4039(11)	912(6)	−1467(7)

Table 7 (*contd.*)

Atom	x	y	z	Atom	x	y	z
C(151)	546(6)	2210(4)	3259(3)	C(510)	4284(11)	754(7)	−1058(7)
C(152)	−409(7)	1975(4)	3157(3)	C(511)	4586(12)	499(7)	−544(6)
O(153)	−809(4)	1768(2)	2709(2)	N(512)	−1375(25)	6224(15)	573(13)
N(154)	−863(6)	1968(3)	3554(3)	C(513)	−1717(22)	5871(14)	502(11)
C(155)	−445(8)	2177(4)	4095(3)	C(514)	−2194(21)	5368(12)	552(11)
C(156)	−756(10)	2752(5)	4174(4)	N(515)	−4236(22)	5312(12)	1143(13)
C(157)	−1820(9)	1745(5)	3462(4)	C(516)	−4701(34)	5432(17)	729(20)
C(158)	−1828(10)	1136(5)	3497(5)	C(517)	−5394(38)	5622(22)	217(21)
O(250)	293(4)	1201(2)	1959(2)				

Table 8 Atomic coordinates (× 10^4) for complex **5**

Atom	x	y	z	Atom	x	y	z
Ni	854(1)	2501(1)	4381(1)	C(158)	1915(11)	5514(19)	3774(20)
C(11)	225(3)	3795(5)	2489(5)	O(250)	28(2)	3044(4)	4839(3)
C(12)	−142(3)	4109(5)	1926(5)	C(251)	202(4)	3388(6)	5554(5)
C(13)	−551(4)	4552(5)	2028(5)	C(252)	734(3)	3344(8)	5767(5)
C(14)	−576(3)	4643(5)	2738(5)	O(253)	968(3)	3025(7)	5362(4)
C(15)	−219(3)	4347(5)	3351(5)	N(254)	981(4)	3683(9)	6380(6)
C(16)	182(3)	3934(5)	3191(4)	C(255)	738(7)	4152(12)	6847(8)
C(17)	−295(3)	4475(5)	4086(5)	C(256)	661(11)	3853(14)	7483(13)
C(21)	−663(3)	3883(5)	4238(5)	C(257)	1548(9)	3695(24)	6559(15)
C(22)	−1168(3)	3976(5)	4000(5)	C(258)	1756(18)	3043(32)	6942(29)
C(23)	−1501(3)	3405(6)	4073(5)	O(350)	320(2)	1456(3)	4473(3)
C(24)	−1313(4)	2684(6)	4386(5)	C(351)	554(4)	987(8)	5087(6)
C(25)	−806(3)	2549(5)	4633(5)	C(352)	1096(4)	1161(7)	5296(6)
C(26)	−486(3)	3145(5)	4563(4)	N(354)	1382(4)	742(8)	5836(8)
C(27)	−604(3)	1749(5)	4932(5)	O(353)	1275(3)	1620(5)	4931(4)
C(31)	−568(3)	1188(5)	4296(5)	C(355)	1160(7)	164(12)	6279(11)
C(32)	−989(4)	800(6)	3924(5)	C(356)	1304(13)	298(31)	7009(24)
C(33)	−999(4)	312(6)	3332(6)	C(357)	1937(7)	908(20)	6027(14)
C(34)	−548(4)	222(6)	3155(5)	C(358)	2172(17)	296(37)	5911(45)
C(35)	−114(3)	608(5)	3492(5)	O(450)	918(2)	2011(3)	3361(3)
C(36)	−127(3)	1110(5)	4088(5)	C(451)	1390(4)	1598(6)	3429(6)
C(37)	353(4)	545(5)	3202(6)	C(452)	1743(5)	1980(8)	3052(8)
C(41)	315(3)	1128(5)	2600(6)	O(453)	1599(4)	2471(7)	2584(7)
C(42)	−1(4)	955(6)	1917(5)	N(454)	2217(4)	1776(7)	3257(7)
C(43)	−104(4)	1533(6)	1350(6)	C(455)	2434(5)	1201(10)	3801(13)
C(44)	121(4)	2261(6)	1514(6)	C(456)	2645(8)	1595(17)	4537(15)
C(45)	442(3)	2446(5)	2178(5)	C(457)	2588(7)	2145(13)	2904(16)
C(46)	557(3)	1874(6)	2698(5)	C(458)	2613(12)	1659(24)	2256(21)
C(47)	634(3)	3292(5)	2336(5)	Cl(1)	618(2)	6096(2)	5115(2)
C(100)	−948(3)	4900(6)	1396(5)	O(11)	749(8)	5389(9)	5438(7)
C(101)	−990(13)	4469(21)	715(12)	O(12)	96(7)	6203(11)	5164(8)
C(102)	−848(9)	5704(13)	1289(17)	O(13)	888(10)	6728(12)	5485(11)
C(103)	−1454(6)	4879(31)	1509(14)	O(14)	626(5)	6031(7)	4397(6)
C(200)	−2072(3)	3574(6)	3860(6)	Cl(2)	4954(2)	3352(2)	1990(2)
C(201)	−2208(6)	4053(13)	3166(12)	O(21)	5098(8)	3422(9)	2733(7)
C(202)	−2369(5)	2815(13)	3691(17)	O(22)	4669(5)	2654(6)	1760(7)
C(203)	−2207(6)	4057(15)	4450(10)	O(23)	5377(10)	3239(15)	1705(11)
C(300)	−1464(4)	−136(8)	2932(7)	O(24)	4718(11)	3992(8)	1686(9)
C(301)	−1927(7)	186(24)	3115(21)	C(802)	−891(6)	2445(8)	2579(8)
C(302)	−1393(10)	−992(11)	3070(17)	C(801)	−1395(10)	2447(11)	2171(13)
C(303)	−1570(8)	−4(17)	2145(10)	N(800)	−1818(14)	2438(17)	1817(20)
C(400)	−451(5)	1355(7)	614(6)	N(900)	−1247(7)	6223(11)	3628(10)
C(401)	−744(11)	607(13)	620(11)	C(901)	−916(7)	6570(11)	3526(10)
C(402)	−98(10)	1249(16)	78(10)	C(902)	−481(8)	6931(13)	3427(12)
C(403)	−798(8)	2012(11)	338(11)	N(903)	−1903(12)	914(20)	5144(18)
O(150)	574(2)	3640(4)	3784(3)	C(904)	−1815(12)	1405(20)	5588(19)
C(151)	949(4)	4226(6)	4036(7)	C(905)	−1615(12)	2061(19)	6106(18)
C(152)	1442(4)	3836(6)	4281(5)	N(600)	1809(21)	4218(38)	2567(28)
N(154)	1857(4)	4281(6)	4455(6)	C(601)	1825(13)	4048(21)	1950(23)
O(153)	1472(2)	3086(4)	4306(4)	C(602)	2123(23)	3711(40)	1467(28)
C(155)	2345(6)	3878(11)	4603(13)	N(700)	1407(14)	−0501(19)	4158(20)
C(156)	2533(10)	3728(22)	5336(14)	C(701)	1231(12)	−1128(18)	4156(17)
C(157)	1849(6)	5128(9)	4436(12)	C(702)	1039(14)	−1926(19)	4081(15)

In all these three transition-metal structures the arrangement of the oxygen atoms is similar to that observed in the lead complex. The two sets of four oxygen atoms are each planar and parallel. The only difference is that the metal is far closer to the plane of the carbonyl oxygen atoms than to that of the ether oxygen atoms (see Table 2). In the iron and zinc structures the distances to the ether oxygen atoms (mean 2.45 and 2.58 Å respectively) probably indicate some residual bonding. A pertinent structure for comparison is the sandwich complex $[Fe(L'_2)]^{2+}$ (L′ = 12-crown-4 = 1,4,7,10-tetraoxacyclododecane) where the co-ordination sphere about the iron cation consists of eight ether oxygen atoms with a mean Fe–O distance of 2.40 Å.[18] The difference in the M–O distances is greatest in the copper structure, where the metal atom is only 0.44 Å from the plane of the carbonyl oxygen atoms, and the interaction with the ether oxygen atoms (mean 2.86 Å) is presumably weak or non-existent. This is also consistent with the lack of a strong charge-transfer absorbance in the UV spectrum of the copper complex as discussed above. A similar co-ordination environment is observed in a number of tetracarboxylates of Cu^{2+}; for example, the cation $[Cu(Me_3NCH_2CO_2)_4]^{2+}$ has four short (mean 1.97 Å) and four longer Cu–O distances (mean 2.77 Å).[19] In this case however the more distant oxygen atoms are disposed with two either side of the CuO_4 plane formed by the nearer O atoms.

The nickel complex is the odd one out of the five structures. Given the well known propensity of this metal for orthogonal environments, clearly some substantial rearrangement is necessary to satisfy its stereochemical requirements. One of the carbonyl oxygen atoms O(453) is twisted away from the co-ordination sphere, well beyond a bonding distance [Ni • • • O(453) 4.37 Å]. In addition the nickel atom is placed significantly closer to three of the ether oxygen atoms than to the fourth, O(250), which is opposite to the unique carbonyl in the co-ordination sphere. This means that the nickel atom has six nearest neighbours in a distorted-octahedral environment with the M–O(*n*53) distances significantly less at 2.00 Å than the M–O(*n*50) distances at 2.23 Å. The UV/VIS spectrum of the complex in dichloromethane is also consistent with a pseudo-octahedral environment, exhibiting absorbances at 822 (6.4) and 428 nm (ε/dm^3 mol^{-1} cm^{-1} 26) typically associated with ν_2 $(^3A_{2g} \longrightarrow {}^3T_{1g})$ and ν_3 $[^3A_{2g} \longrightarrow {}^3T_{1g}(P)]$.[20] The unique ether oxygen atom O(250) may, however, be weakly attached to the metal at 2.771(8) Å and the geometry of the co-ordination sphere could alternatively be described as a capped-octahedral structure with O(250) as the capping atom, capping a face of O(253), O(150) and O(350). This flexibility is at first sight surprising, but on closer inspection is logical in that it is not due to any substantial rearrangement of the ether oxygen atoms, which are fixed by the calixarene (and indeed the atoms remain planar, see Table 2), but rather to significant rearrangement of the more mobile amide moieties. Despite these changes from the other structures, the nickel complex is isomorphous with the iron, zinc and lead compounds.

All five structures have substantial amounts of solvent in the unit cells, with four to six molecules of methyl cyanide in the asymmetric units. In all the structures one methyl cyanide is found within the cone with the methyl group furthest in. This

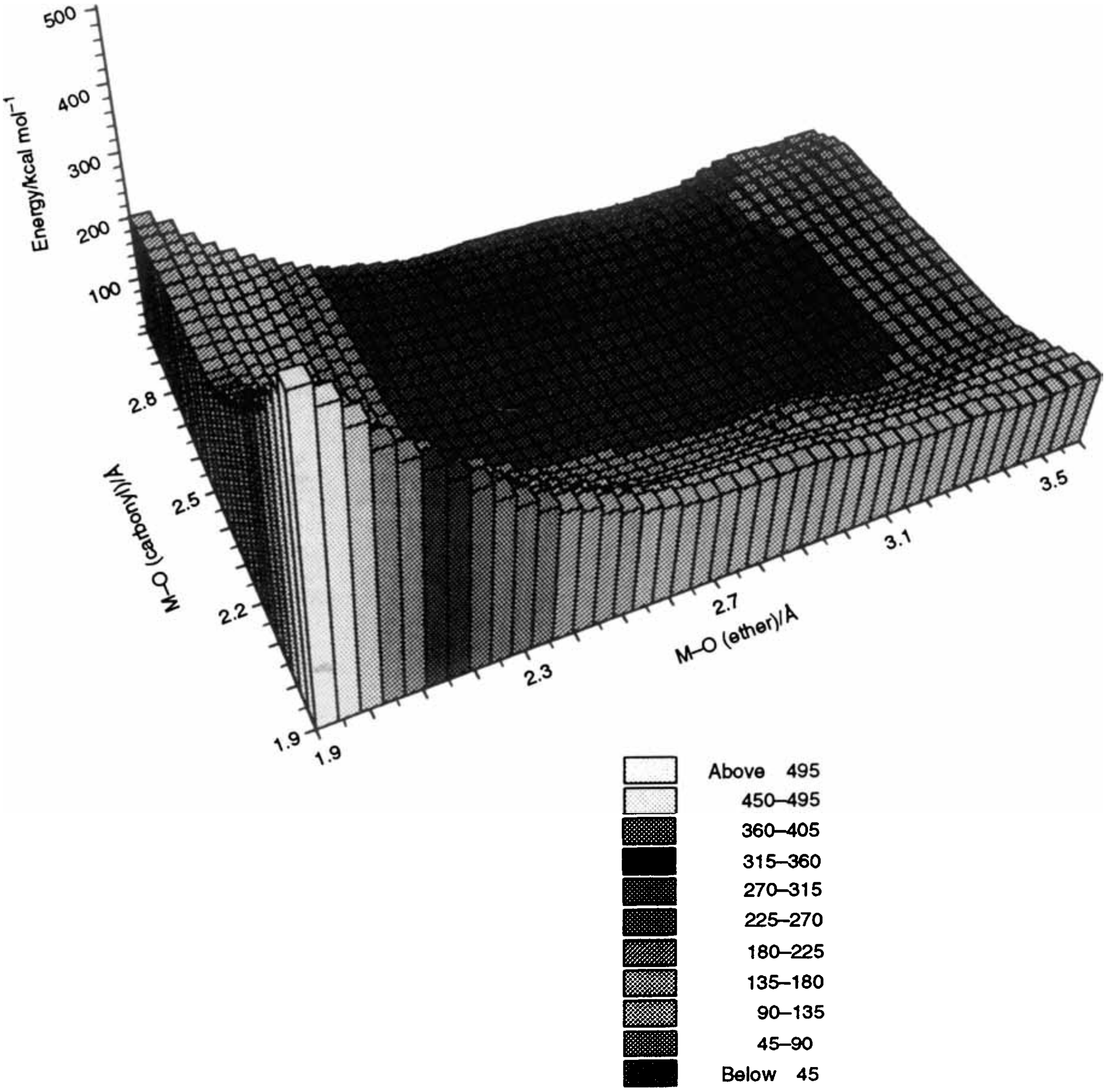

Fig. 8 Three-dimensional plot of energy against M–O (ether and carbonyl) distances for the ML metal complexes

arrangement is found in several calix[4]arene structures[21] and is presumably due to favourable electrostatic interactions between the hydrogen atoms of the methyl group and the phenyl rings. The remaining solvent molecules and the perchlorate ions fill the gaps between the cations. The solvent molecules within the cavity are shown in all the Figures but the others are excluded.

Molecular-mechanics Calculations.—We have carried out molecular-mechanics calculations to investigate the types of metal ions that could be encapsulated within this tetraamide in the cone conformation. The Dreiding II force field within the CERIUS package[22] was employed. We used the method previously developed[23] of fixing metal-to-ligand bond lengths at specific values (by including a large force constant for the M–L bond-stretch term) and allowing the rest of the molecule to relax. The resulting energy indicates how well the ligand can adapt to the specific M–L bond lengths. This method is often used for the calculation of macrocycle hole sizes. In this case we introduced a slight variant. Owing to the irregularities of the co-ordination sphere geometry, we did not include any angle-bending terms around the metal atom, although we did include non-bonded interactions between donor oxygen atoms in the co-ordination sphere. All eight M–O distances were fixed at specific values from 2.0 to 3.5 Å in steps of 0.05 Å. At each step the structure was minimised and the energy calculated. Results shown in Fig. 7 indicate that the ligand most readily accommodates metals of a size such that the M–O bond lengths are around 2.75 Å, the value found in the potassium structure. This plot clearly demonstrates the impossibility of the cavity adjusting its size so as to allow the much smaller transition-metal ions to fit in with eight equivalent bond lengths. There is a massive 50 kcal mol^{-1} difference between the energy of the molecule encapsulating the ion with M–O distances of 2.25 and 2.75 Å.

However, in the crystal structures of these transition-metal complexes, we observed two distinct M–O distances (to the carbonyl and ether oxygen atoms). We therefore carried out a further calculation allowing separate variations of the M–O(*n*50) and M–O(*n*53) type bonds through distances of 2.00 to 3.00, 3.60 Å respectively in steps of 0.1 Å. The results (Fig. 8) show that there is a very broad minimum centred at *ca*. 2.85 Å in the M–O (ether) distance and at 2.55 Å in the M–O (carbonyl) distance. This minimum encompasses the values found in the present crystal structures, and the plot is consistent with the fact that the metal cation in the transition-metal complexes is closer to the carbonyl than to the ether oxygen atoms, and with the observation that the calix[4]arene tetraamide is capable of encapsulating metals of a wide range of sizes. However, a regular structure with eight equivalent M–O distances is only suitable for large cations such as K^+ and Pb^{2+}. For smaller transition-metal cations the tetraamide provides a co-ordination geometry far removed from those usually found in transition-metal complexes, although this can be severely adjusted as in the nickel complex presented here. The structures of the iron, zinc and copper complexes are unusual and unexpected and present a significant reminder of the way in which steric effects can overrule electronic preferences for these transition metals.

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