DALTON
FULL PAPER

# Lead complexation by novel phenanthroline-containing macrocycles †

**Carla Bazzicalupi,[a] Andrea Bencini,*[a] Vieri Fusi,[b] Claudia Giorgi,[a] Piero Paoletti *[a] and Barbara Valtancoli[a]**

[a] *Department of Chemistry, University of Florence, Via Maragliano 75/77, 50144 Florence, Italy. E-mail: benc@chim1.unifi.it*
[b] *Institute of Chemical Sciences, University of Urbino, Italy*

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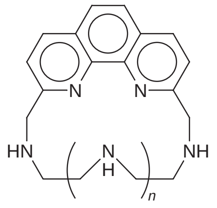
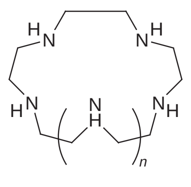
Two new polyamine macrocycles 2,5,8-triaza[9]-[9](2,9)[1,10]-phenanthrolinophane ($L^1$) and 2,5,8,11-tetraaza[12]-[12](2,9)[1,10]-phenanthrolinophane ($L^2$) have been synthesized and characterized. They contain a triamine ($L^1$) or a tetraamine ($L^2$) chain linking the 2,9 positions of a phenanthroline moiety. Like $L^3$, which contains a pentaamine chain connecting the 2,9-phenanthroline positions, they form stable 1 : 1 lead(II) complexes in aqueous solutions. These complexes can readily be extracted in non-aqueous solvents, such as $CHCl_3$ or $CH_2Cl_2$. The thermodynamic parameters for lead(II) complexation have been determined by means of potentiometric and microcalorimetric measurements in aqueous solutions. The stability of the complexes decreases from $L^1$ to $L^3$ mainly due to a marked decrease of the enthalpy changes related to the formation of the complexes, indicating that the overall metal–ligand interaction decreases from $L^1$ to $L^3$. Most likely, in the $[PbL^1]^{2+}$ complex all donors are strongly involved in metal co-ordination, while in $[PbL^2]^{2+}$ and $[PbL^3]^{2+}$ some of the amine groups are weakly bound, or not bound, to the metal. These considerations are supported by the crystal structures of $[(PbL^1Br)_2(\mu\text{-}Br)][PbL^1Br_2]Br\cdot 5H_2O$. In the latter complex the macrocycle wraps around the metal. On the other hand, three nitrogen donors interact at remarkably longer distance than the others. This observation may justify the lower stability of the $[PbL^3]^{2+}$ complex with respect to that of $[PbL^1]^{2+}$.

Macrocyclic ligands can be used as effective sequestering agents for toxic metals.[1] These ligands may contain central hydrophilic cavities ringed with electronegative binding atoms and exterior frameworks exhibiting hydrophobic behavior.[2] The hydrophobic exteriors may allow them to solubilize metal ions in non-aqueous solvent or in membrane media, resulting in their employment as models for carrier molecules in the study of active ion transport phenomena as well as in their potential use as sequestering agents for metals of environmental importance.[3] Among toxic metals, lead is one of the principal poisoning metals the environmental occurrence of which is mainly due to inorganic industrial derivatives and organic compounds from antiknock agents in petrol.

In this context, it is of interest to design and synthesize new macrocyclic ligands able to form stable complexes with this metal.[4–7] We have found that the saturated azamacrocycles of the series [3*k*]aneN$_k$[8] can form stable water-soluble lead(II) complexes.[9] With the purpose to get further insight into the co-ordination properties of Pb$^{II}$ and to design better ionophores for it, we have now introduced a phenanthroline moiety within a polyamine macrocyclic framework, having synthesized ligands $L^1$–$L^3$. The choice of phenanthroline is mainly due to two factors. This heteroaromatic moiety can provide a further binding site for metal cations. It is rigid, and provides two aromatic nitrogens whose unshared electron pairs are beautifully placed to act co-operatively in binding cations.[10] Therefore, polyamine macrocycles containing this moiety are expected to form more stable complexes than saturated polyamine ligands containing the same number of nitrogen donors. The insertion of phenanthroline within a macrocyclic framework may allow the resulting metal complexes to be solubilized in apolar solvents, due to the rather hydrophobic characteristics displayed by this aromatic unit.



$n = 1$, $L^1$
$n = 2$, $L^2$
$n = 3$, $L^3$



[3*k*]aneN$_k$ series
$n = 1$ [15]aneN$_5$ $L^4$
$n = 2$ [18]aneN$_6$ $L^5$
$n = 3$ [21]aneN$_7$ $L^6$

In this paper we report on the synthesis and characterization of the new ligands $L^1$ and $L^2$. The synthesis of the lead(II) complexes with macrocycles $L^1$–$L^3$ is also reported. Aiming to elucidate the relationship between the structural features of these ligands and their co-ordination properties toward Pb$^{II}$, we have carried out a potentiometric and microcalorimetric study on the interaction with this metal in aqueous solution. The results are compared with those of saturated polyazacycloalkanes not containing the phenanthroline moiety.

## Results and discussion

### Synthesis

The synthetic pathway to obtain $L^1$ and $L^2$ is depicted in Scheme 1. Reaction of compound **1** with the tosylated polyamine **2** or **3** in $CH_3CN$ in the presence of $K_2CO_3$, a modification of the method of Richman and Atkins,[11] affords, after purification by chromatography, the tosylated macrocycles **4**

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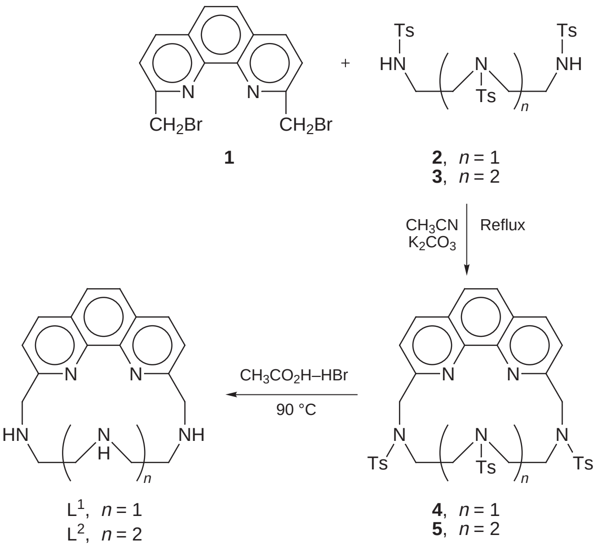
† *Supplementary data available*: protonation constants and thermodynamic parameters. For direct electronic access see http://www.rsc.org/suppdata/dt/1999/393/, otherwise available from BLDSC (No. SUP 57468, 2 pp.) or the RSC Library. See Instructions for Authors, 1999, Issue 1 (http://www.rsc.org/dalton).



**Scheme 1**

and **5**, respectively. Finally, the removal of the tosyl groups in HBr–$CH_3CO_2H$ gives the macrocycles $L^1$ and $L^2$ in good yields.

Ligands $L^1$–$L^3$ form stable lead(II) complexes in aqueous solution (see below). Therefore, synthesis of the complexes is carried out by reaction of $Pb(NO_3)_2$ with the ligands in 1:1 molar ratio in aqueous solution at neutral pH. The complexes can be isolated from the reaction mixture as nitrate salts by extraction with chloroform, followed by precipitation with hexane. It is to be noted that all the complexes can readily be extracted from aqueous solutions in $CHCl_3$ or $CH_2Cl_2$ and show a good solubility in these solvents (*ca.* 0.1 mol dm$^{-3}$).

### Crystal structure of [(PbL$^1$Br)$_2$(μ-Br)][PbL$^1$Br$_2$]Br·5H$_2$O

The [(PbL$^1$Br)$_2$(μ-Br)][PbL$^1$Br$_2$]Br·5H$_2$O complex crystallizes in the triclinic crystal system. The asymmetric unit contains two independent complexes, [(PbL$^1$Br)$_2$(μ-Br)]$^+$ (a) and [PbL$^1$Br$_2$] (b), a bromide as counter ion and five water solvent molecules. The ORTEP[13] drawings of the two independent molecules are shown in Figs. 1(a) and 1(b), respectively. Table 1 lists selected bond lengths and angles for the metal co-ordination environments.

The (a) complex consists of two PbL$^1$ units bridged by one bromide anion. The overall conformations of $L^1$ and the co-ordination geometry for the metal atoms are very similar in the two PbL$^1$ units. Atom Pb(1) is co-ordinated by the five nitrogens N(1), N(2), N(3), N(4) and N(5) [the Pb–N distances range from 2.44(1) Å for N(4) to 2.73(1) Å for N(3)] and two bromide anions, one of them weakly interacting [Br(1)] at 3.528(2) Å. The resulting arrangement for the seven donor atoms around the lead ion is rather asymmetric [Fig. 1(a)].

The co-ordination geometry can be best decribed as a distorted capped trigonal prism, the two bases being defined by N(1), N(2) and Br(1) and by N(3), N(4) and Br(3), respectively. Atom N(5) caps the N(1)–N(4)–Br(1)–Br(3) face of the trigonal prism. The co-ordination environment of Pb(2) is very similar to that of Pb(1) and is determined by N(6), N(7), N(8), N(9) and N(10) [the bond distances range from 2.44(1) Å for N(9) to 2.74(1) Å for N(10)], Br(3) [Pb(2)–Br(3) 3.104(2) Å] and Br(2) [Pb(2)–Br(2) 3.333(2) Å]. These donors give rise to a distorted trigonal prismatic geometry around the metal. The bases of the trigonal prism are defined by N(6), N(7) and Br(2) and by N(9), N(10) and Br(3), respectively. Atom N(8) caps the N(7)–N(9)–Br(2)–Br(3) face of the prism.

As far as the [PbL$^1$Br$_2$] (b) is concerned [Fig. 1(b)], the co-ordination geometry of the metal and the conformation of the macrocycle are almost equal to that found in the (a) complex. Analogously to Pb(1) and Pb(2), all the nitrogen atoms of the ligand [N(11), N(12), N(13), N(14) and N(15)] are co-ordinated to the lead atom, and the metal to nitrogen bond distances fall in the range 2.46(1)–2.76(1) Å. Two bromide anions complete the co-ordination environment of the metal [Pb–Br(4) 3.215(2) and Pb–Br(5) 3.333(2) Å]. Once more, the resulting co-ordination environment is a distorted capped trigonal prism, with N(15) capping the Br(4)–Br(5)–N(11)–N(14) face of the prism.

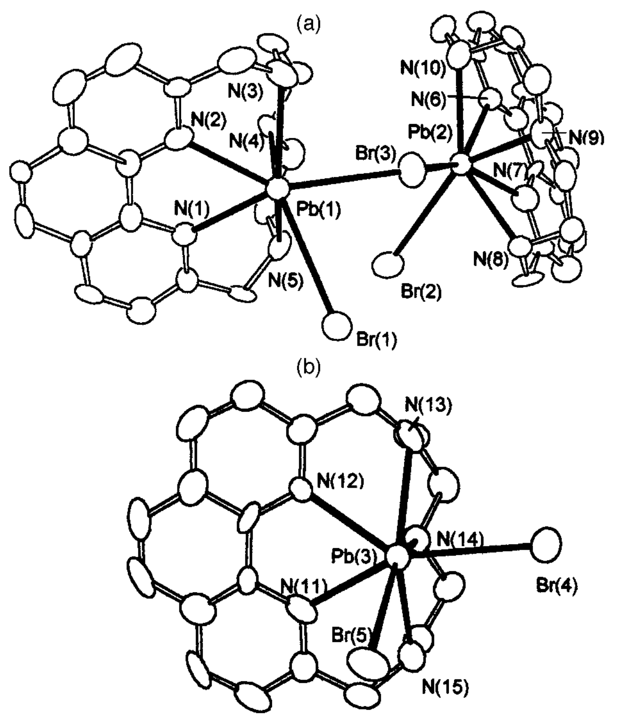


Fig. 1 The ORTEP drawings of the [(PbL$^1$Br)$_2$(μ-Br)]$^+$ complex (a) and of [PbL$^1$Br$_2$] (b). Labels of carbon atoms are omitted for clarity.

The interatomic metal–metal distance in the (a) binuclear cation is Pb(1) ··· Pb(2) 5.618(1) Å, while the shorter distances between symmetry related ($-x + 1$, $-y$, $-z + 1$) lead atoms are Pb(1) ··· Pb(3) 7.032(2) Å and Pb(2) ··· Pb(3) 7.903(2) Å.

In the three PbL$^1$ units, the $L^1$ ligand assumes very similar overall conformations: the planes containing the aromatic and the aliphatic moieties, defined by the the three secondary nitrogens of each macrocycle, form dihedral angles of 94.5(6), 91.2(5) and 94.5(6)° in the Pb(1)L$^1$, Pb(2)L$^1$ and Pb(3)L$^1$ moieties, respectively.

Considering the crystal packing, the aromatic moieties of ligands, symmetry related by inversion centers, are coupled by π-stacking interactions, as shown in Fig. 2. The aromatic moieties of symmetry related [(PbL$^1$Br)$_2$(μ-Br)]$^+$ complexes are parallel, *i.e.* they exhibit π–π attractive interactions with stacking distances of 3.98 Å [between the plane of the phenanthroline units co-ordinated to Pb(2)] and 3.66 Å [between the plane of the phenanthroline units co-ordinated to Pb(1)]. Therefore, these interactions give rise to polymeric linkages between the [(PbL$^1$Br)$_2$(μ-Br)]$^+$ complexes. Symmetry related pairs of [PbL$^1$Br$_2$] molecules, with a distance of 4.21 Å between the aromatic planes, are intercalated among the [(PbL$^1$Br)$_2$(μ-Br)]$^+$ chains.

Several hydrogen-bonding contacts involve the secondary nitrogens of $L^1$, the bromide ions and the water solvent molecules.

### Crystal structure of [PbL$^3$][ClO$_4$][BPh$_4$]

The crystal structure consists of [PbL$^3$]$^{2+}$ complex cations, $BPh_4^-$ and $ClO_4^-$ anions. An ORTEP[13] drawing showing the complex is shown in Fig. 3 and Table 2 lists selected bond distances and angles for the metal co-ordination sphere.

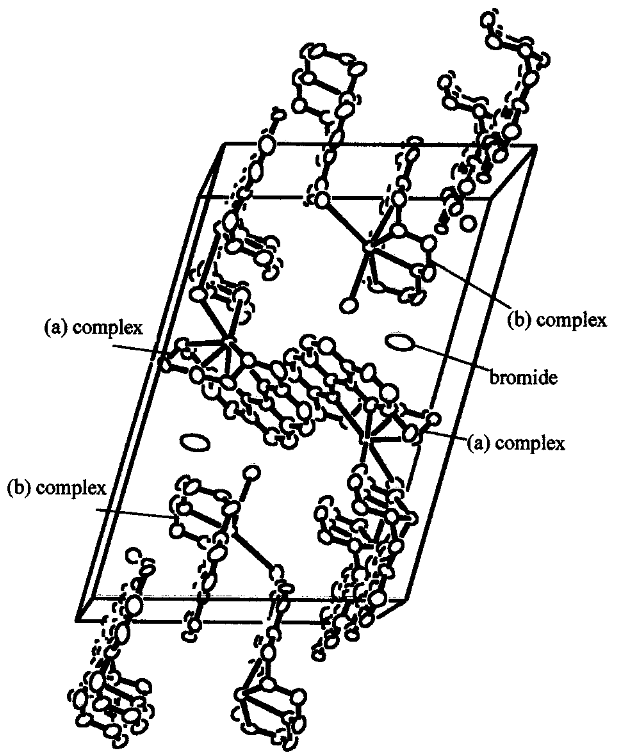


**Fig. 2** An ORTEP drawing of the crystal packing of the [(PbL$^1$Br)$_2$-(μ-Br)][PbL$^1$Br$_2$]Br·5H$_2$O complex [view normal to (001)]. The water molecules are omitted for clarity.

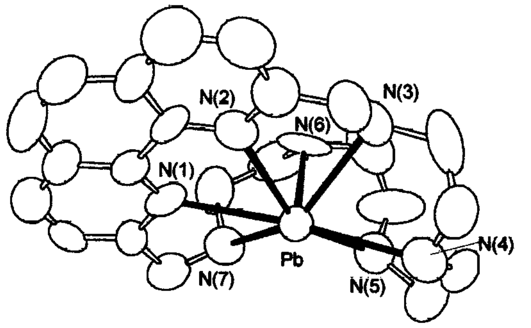


**Fig. 3** An ORTEP[13] drawing of the [PbL$^3$]$^{2+}$ complex. Labels of carbon atoms are omitted for clarity.

The metal atom is seven-co-ordinated by the nitrogen atoms of the macrocycle. The bond lengths range from 2.46(2) Å for Pb–N(6) to 2.88(2) Å for Pb–N(4) (see Table 2). In particular, the high values of the Pb–N(2), Pb–N(3) and Pb–N(4) bond distances [2.86(1), 2.87(2) and 2.88(1) Å] indicate a weak interaction of these three nitrogens with the metal. The resulting arrangement for the seven donor atoms around the lead ion is rather asymmetric, leaving a zone free from co-ordinated donor atoms, which is occupied by the lone pair of Pb$^{2+}$. Such a "gap" in the co-ordination geometry has been ascribed by several authors to the presence of a stereochemically active lone pair.[7,14,15] The Pb–N(6) bond is placed on the side opposite to the vacant zone and its length [2.46(2) Å] is in agreement with the values reported for complexes where the lone pair is active (2.37–2.56 Å).[7a]

It is noteworthy that the Pb$^{II}$ to nitrogen bond distances in the present complex are longer than in the L$^1$ complexes (see Tables 1 and 2). Furthermore, as shown by Fig. 3, the macrocyclic ligand assumes a folded conformation, which allows all seven nitrogens to interact with the Pb$^{2+}$ ion. Consequently, the aliphatic chain is strained; actually, several C–N–C and N–C–C bond angles show higher values than the sp$^3$ theoretical one. Only the zone occupied by the stereochemical active lone pair of the metal seems to be less crowded by the ligand.

**Table 1** Selected bond lengths (Å) and angles (°) for [(PbL$^1$Br)$_2$-(μ-Br)][PbL$^1$Br$_2$]Br·5H$_2$O

| | | | |
|---|---|---|---|
| [(PbL$^1$Br)$_2$(μ-Br)]$^+$, complex (a) | | | |
| Pb(1)–N(4) | 2.440(12) | Pb(2)–N(9) | 2.441(13) |
| Pb(1)–N(1) | 2.567(12) | Pb(2)–N(7) | 2.554(14) |
| Pb(1)–N(5) | 2.627(13) | Pb(2)–N(8) | 2.598(13) |
| Pb(1)–N(2) | 2.632(12) | Pb(2)–N(6) | 2.620(13) |
| Pb(1)–N(3) | 2.730(14) | Pb(2)–N(10) | 2.744(14) |
| Pb(1)–Br(3) | 3.219(2) | Pb(2)–Br(3) | 3.104(2) |
| Pb(1)–Br(1) | 3.528(2) | Pb(2)–Br(2) | 3.333(2) |
| Br(1)–Pb(1)–Br(3) | 77.34(5) | Br(2)–Pb(2)–Br(3) | 91.42(5) |
| N(5)–Pb(1)–Br(1) | 73.6(3) | N(10)–Pb(2)–Br(2) | 144.0(3) |
| N(4)–Pb(1)–Br(1) | 139.6(3) | N(9)–Pb(2)–Br(2) | 147.0(3) |
| N(3)–Pb(1)–Br(1) | 141.8(3) | N(8)–Pb(2)–Br(2) | 77.2(3) |
| N(2)–Pb(1)–Br(1) | 130.7(3) | N(7)–Pb(2)–Br(2) | 83.9(3) |
| N(1)–Pb(1)–Br(1) | 91.1(3) | N(6)–Pb(2)–Br(2) | 117.1(3) |
| N(4)–Pb(1)–N(1) | 87.4(4) | N(9)–Pb(2)–N(7) | 85.5(4) |
| N(4)–Pb(1)–N(5) | 70.1(4) | N(9)–Pb(2)–N(8) | 70.1(4) |
| N(1)–Pb(1)–N(5) | 62.2(4) | N(7)–Pb(2)–N(8) | 62.8(4) |
| N(4)–Pb(1)–N(2) | 83.5(4) | N(9)–Pb(2)–N(6) | 85.3(4) |
| N(1)–Pb(1)–N(2) | 62.6(4) | N(7)–Pb(2)–N(6) | 63.7(4) |
| N(5)–Pb(1)–N(2) | 118.9(4) | N(8)–Pb(2)–N(6) | 122.1(4) |
| N(4)–Pb(1)–N(3) | 67.9(4) | N(9)–Pb(2)–N(10) | 67.3(4) |
| N(1)–Pb(1)–N(3) | 121.0(4) | N(7)–Pb(2)–N(10) | 118.7(4) |
| N(5)–Pb(1)–N(3) | 137.5(4) | N(8)–Pb(2)–N(10) | 136.9(4) |
| N(2)–Pb(1)–N(3) | 62.0(4) | N(6)–Pb(2)–N(10) | 60.3(4) |
| N(4)–Pb(1)–Br(3) | 83.2(3) | N(9)–Pb(2)–Br(3) | 81.5(3) |
| N(1)–Pb(1)–Br(3) | 148.6(3) | N(7)–Pb(2)–Br(3) | 148.2(3) |
| N(5)–Pb(1)–Br(3) | 86.4(3) | N(8)–Pb(2)–Br(3) | 85.5(3) |
| N(2)–Pb(1)–Br(3) | 144.8(3) | N(6)–Pb(2)–Br(3) | 142.8(3) |
| N(3)–Pb(1)–Br(3) | 82.8(3) | N(10)–Pb(2)–Br(3) | 82.5(3) |
| [PbL$^1$Br$_2$], complex (b) | | | |
| Pb(3)–N(14) | 2.458(13) | Pb(3)–N(13) | 2.761(14) |
| Pb(3)–N(11) | 2.582(13) | Pb(3)–Br(4) | 3.215(2) |
| Pb(3)–N(12) | 2.618(12) | Pb(3)–Br(5) | 3.333(2) |
| Pb(3)–N(15) | 2.618(14) | | |
| Br(2)–Pb(2)–Br(3) | 91.42(5) | N(8)–Pb(2)–N(6) | 122.1(4) |
| N(10)–Pb(2)–Br(2) | 144.0(3) | N(9)–Pb(2)–N(10) | 67.3(4) |
| N(9)–Pb(2)–Br(2) | 147.0(3) | N(7)–Pb(2)–N(10) | 118.7(4) |
| N(8)–Pb(2)–Br(2) | 77.2(3) | N(8)–Pb(2)–N(10) | 136.9(4) |
| N(7)–Pb(2)–Br(2) | 83.9(3) | N(6)–Pb(2)–N(10) | 60.3(4) |
| N(6)–Pb(2)–Br(2) | 117.1(3) | N(9)–Pb(2)–Br(3) | 81.5(3) |
| N(9)–Pb(2)–N(7) | 85.5(4) | N(7)–Pb(2)–Br(3) | 148.2(3) |
| N(9)–Pb(2)–N(8) | 70.1(4) | N(8)–Pb(2)–Br(3) | 85.5(3) |
| N(7)–Pb(2)–N(8) | 62.8(4) | N(6)–Pb(2)–Br(3) | 142.8(3) |
| N(9)–Pb(2)–N(6) | 85.3(4) | N(10)–Pb(2)–Br(3) | 82.5(3) |
| N(7)–Pb(2)–N(6) | 63.7(4) | | |

**Table 2** Selected bond lengths (Å) and angles (°) for [PbL$^3$][ClO$_4$]-[BPh$_4$]

| | | | |
|---|---|---|---|
| Pb–N(1) | 2.77(1) | Pb–N(5) | 2.60(2) |
| Pb–N(2) | 2.86(1) | Pb–N(6) | 2.46(2) |
| Pb–N(3) | 2.87(1) | Pb–N(7) | 2.68(1) |
| Pb–N(4) | 2.88(2) | | |
| N(6)–Pb–N(7) | 68.1(6) | N(2)–Pb–N(6) | 91.3(5) |
| N(5)–Pb–N(7) | 78.4(5) | N(2)–Pb–N(5) | 152.5(5) |
| N(5)–Pb–N(6) | 68.4(6) | N(2)–Pb–N(4) | 108.8(5) |
| N(4)–Pb–N(7) | 139.2(5) | N(2)–Pb–N(3) | 58.6(5) |
| N(4)–Pb–N(6) | 110.4(6) | N(1)–Pb–N(7) | 60.5(5) |
| N(4)–Pb–N(5) | 64.7(5) | N(1)–Pb–N(6) | 90.0(6) |
| N(3)–Pb–N(7) | 143.8(5) | N(1)–Pb–N(5) | 138.5(5) |
| N(3)–Pb–N(6) | 76.9(6) | N(1)–Pb–N(4) | 155.3(5) |
| N(3)–Pb–N(5) | 97.5(5) | N(1)–Pb–N(3) | 112.0(5) |
| N(3)–Pb–N(4) | 62.2(5) | N(1)–Pb–N(2) | 55.3(4) |
| N(2)–Pb–N(7) | 112.0(4) | | |

Finally, similarly to the L$^1$ complex, the crystal packing shows that symmetry related macrocyclic complexes are coupled by π-stacking interactions between the phenanthroline moieties. The aromatic systems are parallel, with a plane to plane distance of 3.49 Å.

**Table 3** Formation constants and corresponding thermodynamic parameters for the lead(II) complexes with ligands $L^1$–$L^3$ (0.1 mol dm$^{-3}$ $NMe_4NO_3$, 298.1 K)

| | log $K$ | $-\Delta G°$/kJ mol$^{-1}$ | $-\Delta H°$/kJ mol$^{-1}$ | $T\Delta S°$/kJ K$^{-1}$ mol$^{-1}$ |
|---|---|---|---|---|
| $Pb^{2+} + L^1 \rightleftharpoons [PbL^1]^{2+}$ | 18.70(1)[a] | 106.6 | 73.4(4) | 33.2 |
| $[PbL^1]^{2+} + H^+ \rightleftharpoons [Pb(HL^1)]^{3+}$ | 1.9(1) | 10.8 | 4.9(8) | 5.9 |
| $Pb^{2+} + L^2 \rightleftharpoons [PbL^2]^{2+}$ | 15.62(6) | 89.0 | 46.0(4) | 41.0 |
| $[PbL^2]^{2+} + H^+ \rightleftharpoons [Pb(HL^2)]^{3+}$ | 4.90(1) | 27.9 | 25.2(4) | 2.7 |
| $Pb^{2+} + L^3 \rightleftharpoons [PbL^3]^{2+}$ | 13.09(6) | 74.6 | 36.4(3) | 38.1 |
| $[PbL^3]^{2+} + H^+ \rightleftharpoons [Pb(HL^3)]^{3+}$ | 6.17(6) | 35.1 | 28.8(3) | 6.3 |
| $[Pb(HL^3)]^{3+} + H^+ \rightleftharpoons [Pb(H_2L^3)]^{4+}$ | 5.85(2) | 33.3 | 36.7(4) | −3.4 |

[a] Values in parentheses are standard deviations on the last significant figure.

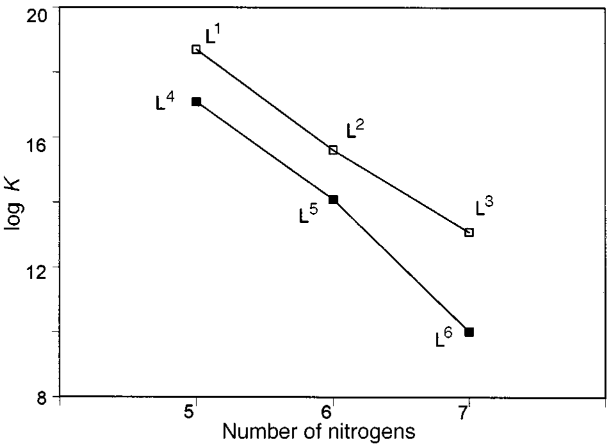


**Fig. 4** Plot of the stability constants of lead(II) complexes with phenanthroline-containing ligands $L^1$–$L^3$ (□) and with [3*k*]aneN$_k$ macrocycles (■) as a function of the number of nitrogen donors.

## Lead(II) co-ordination in aqueous solution

The formation of the lead(II) complexes with $L^1$–$L^3$ has been investigated by means of potentiometric and microcalorimetric measurements in aqueous solution (0.1 mol dm$^{-3}$ $NMe_4NO_3$, 298.1 K).‡ The complexes formed and the corresponding thermodynamic parameters are reported in Table 3. In Fig. 4 the logarithms of the stability constants corresponding to the general reaction $Pb^{2+} + L \rightleftharpoons PbL^{2+}$ are plotted for the phenanthroline-containing polyamines $L^1$–$L^3$ and for the macrocycles of the [3*k*]aneN$_k$ series containing the same number of nitrogen donors ($L^4$–$L^6$).[9] Considering the data in Table 3 and Fig. 4, some general trends may be inferred.

Phenanthroline-containing macrocycles are strong lead(II) binders in aqueous solution. The thermodynamic stability of their complexes is higher than that found for the complexes with saturated macrocycles of the [3*k*]aneN$_k$ series with the same number of nitrogen donors (Fig. 4). The stability of the complexes with $L^1$–$L^3$ decreases as the dimension of the macrocycle and the number of donors increase. This is mainly due to a marked decrease of the enthalpic contribution from $[PbL^1]^{2+}$ to $[PbL^3]^{2+}$. The protonation constants of the complexes with $L^2$ and $L^3$ are rather high, *i.e.* $[PbL^2]^{2+}$ and $[PbL^3]^{2+}$ complexes can be protonated at slightly acidic pH values. In the case of $[PbL^3]^{2+}$, protonation of the complex takes place even at neutral pH, as shown in Fig. 5.

All ligands show a good ability to co-ordinate Pb$^{II}$. The stability constants for the lead(II) complexes with $L^1$–$L^3$ are remarkably higher than those of the complexes with open-chain polyamines containing the same number of nitrogen donors {for example, log $K = 18.70$ for $[PbL^1]^{2+}$, 9.9 for the lead(II) complex with the linear pentaamine 3,6,9-triazaundeca-1,11-diamine, which contains five amine groups separated by ethylenic chains}.[16] Although this behavior can simply be ascribed to the macrocyclic effect, the larger stability exhibited by the present complexes in comparison with those of corresponding macrocycles of the [3*k*]aneN$_k$ series requires a different explanation and it may be related to insertion of a phenanthroline moiety within the macrocyclic framework. In order to get further information on the role played by the phenanthroline unit, the reaction of complex formation was followed by means of UV spectra recorded on aqueous solutions containing ligands $L^1$–$L^3$ ($1 \times 10^{-4}$ mol dm$^{-3}$) and Pb$^{II}$ in various molar ratios at pH 7. For instance, in the case of $L^1$ the aromatic moiety gives a rather sharp band at 273 nm ($\varepsilon = 21200$ dm$^3$ mol$^{-1}$ cm$^{-1}$). Solutions containing $L^1$ and increasing amounts of Pb$^{II}$, up to 1 : 1 molar ratio, show a marked decrease of the absorbance. A linear correlation between the $\varepsilon$ values and the Pb$^{II}$ : $L^1$ ratio is found up to 1 : 1 ($\lambda_{max} = 274$ nm, $\varepsilon = 14500$ dm$^3$ mol$^{-1}$ cm$^{-1}$). Similar decreases of the $\varepsilon$ values in the presence of Pb$^{II}$ are also found for the $L^2$ and $L^3$ ligands. These data reflect the involvement of the phenanthroline moiety in metal co-ordination in the $[PbL]^{2+}$ complexes in aqueous solution. This suggestion is further confirmed by the crystal structures of the $[PbL^3][ClO_4][BPh_4]$ and $[(PbL^1Br)_2(\mu\text{-}Br)][PbL^1Br_2]Br\cdot5H_2O$ complexes, which show that both the aromatic nitrogens are bound to the metal. Most likely, the different stability of the lead(II) complexes with phenanthroline-containing and [3*k*]aneN$_k$ macrocycles is due to the replacement in the metal co-ordination sphere of two amine groups in the [3*k*]aneN$_k$ complexes with the heteroaromatic nitrogens in the complexes with $L^1$–$L^3$; the latter donor atoms are known to show a better co-ordination ability toward large and "soft" metal cations, such as Pb$^{II}$.

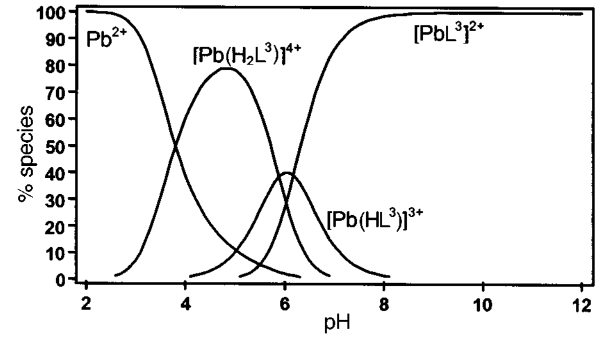


**Fig. 5** Distribution diagram of the species for the system $L^3$–Pb$^{II}$ (0.1 mol dm$^{-3}$ $NMe_4NO_3$, 298.1 K, $[L^3] = [Pb^{2+}] = 1 \times 10^{-3}$ mol dm$^{-3}$).

Fig. 4 also displays a dramatic decrease in stability of the lead(II) complexes with ligands $L^1$–$L^3$ as the dimensions of the macrocycle increase. Such behavior is rather surprising, considering that the number of nitrogen donors available for the co-ordination increases from $L^1$ to $L^3$. On the other hand, Table 3 clearly shows that this effect is mainly due to a marked

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‡ Equilibrium constants and thermodynamic parameters for ligand protonation have been deposited (SUP 57468). Their values are as expected for polyamine macrocyclic compounds.[2b,c]

decrease of the enthalpy change related to the formation of the complexes ($-\Delta H^\circ = 73.4$ and 36.4 kJ mol$^{-1}$ for $[PbL^1]^{2+}$ and $[PbL^3]^{2+}$, respectively). The decreasing enthalpy contributions from $L^1$ to $L^3$ clearly show that the overall metal–ligand interaction decreases with the enlargement of the macrocyclic framework.

The analysis of the protonation of the complexes can give further information about the co-ordination modes of these ligands in their lead(II) complexes. As shown in Table 3, the value for the first stepwise protonation constant $[PbL]^{2+} + H^+ \rightleftharpoons [Pb(LH)]^{3+}$ increases from $L^1$ to $L^3$. In particular, the $[PbL^1]^{2+}$ complex exhibits a very low tendency to protonate ($\log K = 1.9$), indicating that protonation implies detachment of a nitrogen donor bound to the metal. In the $[PbL^1]^{2+}$ complex therefore all five nitrogens co-ordinate to the lead(II) ion. The $[PbL^2]^{2+}$ and $[PbL^3]^{2+}$ complexes show markedly higher values of the first protonation constant. In particular, the latter complex can bind up to two protons in aqueous solution with rather high protonation constants {$\log K = 6.17$ and 5.85 for the equilibria $[PbL^3]^{2+} + H^+ \rightleftharpoons [Pb(HL^3)]^{3+}$ and $[Pb(HL^3)]^{3+} + H^+ \rightleftharpoons [Pb(H_2L^3)]^{4+}$, respectively}. As a consequence, protonated species of the complex are present in aqueous solution in a wide pH range (3–7), while the $[PbL^3]^{2+}$ complex is formed from neutral to alkaline pH, as shown by the distribution diagram in Fig. 5. The high values of the two protonation constants of the $[PbL^3]^{2+}$ complex suggest that at least two amine nitrogens are weakly bound, or not bound, to the metal cation. It is also of interest that the electronic spectrum recorded on a solution containing $Pb^{II}$ and $L^3$ in 1 : 1 molar ratio at pH 5, where the $[Pb(H_2L^3)]^{4+}$ species is prevalent, is almost equal to that recorded at pH 8, where the unprotonated $[PbL^3]^{2+}$ complex is present (Fig. 5). This observation indicates that protonation of the complex takes place on two amine groups and does not involve the aromatic nitrogens co-ordinated to the metal.

These thermodynamic observations lead us to suppose that in $L^1$ the five nitrogen donors are in an optimum disposition to co-ordinate the lead(II) cation, giving strong Pb–N interactions, while in the $[PbL^2]^{2+}$ and $[PbL^3]^{2+}$ complexes some nitrogen donors are weakly bound, or not bound, to the metal. The crystal structures of the $[(PbL^1Br)_2(\mu\text{-}Br)][PbL^1Br_2]Br\cdot 5H_2O$ and $[PbL^3][ClO_4][BPh_4]$ complexes can be used to infer further information on lead(II) co-ordination. These structures evidence two main differences between the binding features of $L^1$ and $L^3$.

In the $L^1$ complex all five nitrogens are co-ordinated to the metal and the Pb–N bond lengths range between 2.44 and 2.73 Å, with an average of 2.60 Å. The metal also interacts with two bromide ions at longer distances. Most likely these $Br^-$ anions are replaced by water molecules in aqueous solutions. In the $L^3$ complex all nitrogen donors interact with the metal, with an average Pb–N distance of 2.73 Å. In particular, three bond lengths [Pb–N(2), Pb–N(3) and Pb–N(4), see Table 2] are considerably longer (greater than 2.85 Å), indicating a weak interaction of these nitrogens with the metal. Although in the $L^1$ complex the macrocycle assumes a folded conformation, the macrocyclic framework does not evidence conformational strain. It seems likely that a strong interaction with the metal is achieved without significant conformational changes in the cyclic backbone. On the other hand, in $[PbL^3][ClO_4][BPh_4]$ the ligand "wraps" around the metal ion, in order to interact by using all the donor atoms. This process leads to conformational strain of the macrocyclic framework, as shown by the values of the C–N–C and N–C–C bond angles in the aliphatic chain.

Although conclusions on co-ordination properties of ligands in solution derived from solid state observations may sometimes be misleading, the high values of some Pb–N distances and the rather strained structure of the macrocycle in $[PbL^3][ClO_4][BPh_4]$ can reasonably explain the lower heat of formation and, therefore, the lower stability of the $[PbL^3]^{2+}$ complex than that of $[PbL^1]^{2+}$ in aqueous solution.

## Concluding remarks

Phenanthroline-containing macrocycles $L^1$–$L^3$ form stable water-soluble 1 : 1 lead(II) complexes. They are effective chelating agents for this metal. Two main effects can be related to the insertion of a phenanthroline moiety within a macrocyclic framework.

First, it enhances the thermodynamic stability of the complexes. The stability constants are higher than those reported for lead(II) complexes with acyclic or cyclic polyamines containing the same number of nitrogen donors. This effect is mainly due to the involvement of the phenanthroline moiety in metal co-ordination. Among the three ligands, the stability of the complexes decreases from $L^1$ to $L^3$. This effect is mainly due to a marked decrease of the enthalpic contribution to the formation of the complexes, indicating that the overall metal–ligand interaction decreases from $L^1$ to $L^3$. Both thermodynamic and structural data suggest that in the $[PbL^1]^{2+}$ complex strong Pb–N interactions take place, while in $[PbL^2]^{2+}$ and $[PbL^3]^{2+}$ some of the amine groups are weakly bound to the metal.

Secondly, the lead(II) complexes can readily be extracted in organic solvents from aqueous solution at neutral pH, due to the hydrophobic character of the phenanthroline moiety.

These characteristics make these ligands promising extracting agents and/or ionophores for $Pb^{II}$.

## Experimental

### General procedures

The 200.0 MHz $^1H$ and 50.32 MHz $^{13}C$ NMR spectra in $D_2O$ or $CDCl_3$ solutions were recorded at 298 K in a Bruker AC-200 spectrometer. In $^1H$ NMR spectra peak positions are reported relative to TMS ($CDCl_3$ solutions) or to HOD at $\delta$ 4.75 ($D_2O$ solutions). 1,4-Dioxane was used as reference standard in $^{13}C$ NMR spectra ($\delta$ 67.4) in $D_2O$ solutions. The UV-vis spectra were recorded on a Shimadzu UV-2101PC spectrophotometer.

### Syntheses

Ligands $L^1$ and $L^2$ were obtained following the synthetic procedure reported in Scheme 1. 2,9-Bis(bromomethyl)-1,10-phenanthroline **1**,[12] *N*,*N*′,*N*″-tris(*p*-tolylsulfonyl)-3-azapentane-1,5-diamine **2**,[11] *N*,*N*′,*N*″,*N*‴-tetrakis(*p*-tolylsulfonyl)-3,6-dioctane-1,8-diamine **3**,[17] and $L^3$ [18] were prepared as previously described.

**2,5,8-Tris(*p*-tolylsulfonyl)-2,5,8-triaza[9]-[9](2,9)[1,10]-phenanthrolinophane 4.** Compound **2** (5 g, 8.8 mmol) and $K_2CO_3$ (12 g, 88 mmol) were suspended in refluxing $CH_3CN$ (200 mL). To this mixture a solution of **1** (3.22 g, 8.8 mmol) in $CH_3CN$ (400 mL) was added dropwise in 6 h. After the addition was complete the suspension was refluxed for 2 h and then filtered. The solution was vacuum evaporated to yield the crude product which was chromatographed on neutral alumina ($CH_2Cl_2$–ethyl acetate 100 : 3). The eluted fractions were collected and evaporated to dryness to afford **4** as a colorless solid. (2.2 g, 32%): mp 130–132 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 2.21 (s, 3 H), 2.24 (s, 6 H), 2.32 (t, 4 H), 2.43 (t, 4 H), 4.12 (s, 4 H), 7.20 (d, 2 H), 7.32 (d, 4 H), 7.38 (d, 2 H), 7.60 (s, 2 H), 7.68 (d, 2 H), 7.74 (d, 4 H) and 8.31 (d, 2 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 21.5, 21.6, 48.8, 49.5, 55.3, 123.8, 126.6, 127.4, 127.8, 128.2, 129.7, 130.0, 135.7, 136.2, 137.6, 143.3, 143.6, 145.1 and 156.8 (Found: C, 60.7; H, 5.2; N, 9.0. Calc. for $C_{39}H_{39}N_5O_6S_3$: C, 60.84; H, 5.10; N, 9.10%).

**2,5,8-Triaza[9]-[9](2,9)[1,10]-phenanthrolinophane trihydrobromide ($L^1\cdot$3HBr).** Tritosylated macrocycle **4** (2.2 g, 2.9 mmol) and phenol (25 g, 265 mmol) were dissolved in HBr–$MeCO_2H$ (33%, 240 mL). The solution was stirred at 90 °C for 18 h. The resulting suspension was filtered and the solid washed with

$CH_2Cl_2$ several times. The yellowish solid was recrystallized from a water–ethanol mixture to give L$^1$ as its trihydrobromide salt (1.5 g, 95%) (Found: C, 39.1; H, 4.4; N, 12.6. Calc. for $C_{18}H_{24}Br_3N_5$: C, 39.30; H, 4.40; N, 12.73%). $^1$H NMR ($D_2O$ solution, pH 7): $\delta$ 3.08 (t, 4 H), 3.28 (t, 4 H), 4.74 (s, 4 H), 7.76 (d, 2 H), 8.00 (s, 2 H) and 8.50 (d, 2 H). $^{13}$C NMR ($D_2O$ solution, pH 7): $\delta$ 46.4, 48.7, 51.4, 123.6, 128.0, 129.9, 139.9, 145.3 and 152.1. The free amine L$^1$ can be obtained in almost quantitative yield by dissolving the hydrobromide salt in water and eluting the resulting solution through an ionic exchange resin (Dowex 1 × 8, alkaline form). The recovered solution was distilled to dryness in vacuum to yield L$^1$ as a colorless solid, mp 39–42 °C (Found: C, 70.0; H, 6.9; N, 22.6. Calc. for $C_{18}H_{21}N_5$: C, 70.33; H, 6.89; N, 22.78%).

**2,5,8,11-Tetrakis(*p*-tolylsulfonyl)-2,5,8,11-tetraaza[12]-[12](2,9)[1,10]-phenanthrolinophane 5.** This compound was synthesized from **3** (6.7 g, 8.8 mmol) and **1** (3.22 g, 8.8 mmol) following the procedure reported for **4**, as a colorless solid (2.7 g, 31%): mp 152–154 °C; $^1$H NMR ($CDCl_3$) $\delta$ 2.23 (s, 12 H), 2.38 (s, 4 H), 2.44 (t, 4 H), 2.56 (t, 4 H), 4.36 (s, 4 H), 7.26 (d, 2 H), 7.35 (d, 4 H), 7.39 (d, 4 H), 7.68 (d, 4 H), 7.71 (s, 2 H), 7.77 (d, 4 H) and 8.32 (d, 2 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 21.3, 21.4, 47.3, 49.2, 49.7, 55.7, 122.9, 126.5, 127.3, 127.5, 128.3, 129.7, 129.8, 134.5, 134.9, 135.9, 137.2, 143.5, 145.1 and 156.7 (Found: C, 59.5; H, 5.2; N, 8.6. Calc. for $C_{24}H_{25}N_3O_4S_2$: C, 59.60; H, 5.21; N, 8.69%).

**2,5,8,11-Tetraaza[12]-[12](2,9)[1,10]-phenanthrolinophane tetrahydrobromide (L$^2$·4HBr).** This compound was synthesized from **5** (2.7 g, 2.9 mmol) following the procedure reported for L$^1$, as a colorless solid (1.82 g, 97%). $^1$H NMR ($D_2O$, pH 4): $\delta$ 3.22 (s, 4 H), 3.45 (t, 4 H), 3.64 (t, 4 H), 4.82 (s, 4 H), 7.83 (d, 2 H), 7.99 (s, 2 H) and 8.54 (d, 2 H). $^{13}$C NMR ($D_2O$, pH 4): $\delta$ 45.8, 47.6, 47.8, 53.0, 124.3, 128.3, 130.1, 140.3, 145.1 and 152.5 (Found: C, 35.5; H, 4.9; N, 12.3. Calc. for $C_{10}H_{15}N_3Br_2$: C, 35.63; H, 4.48; N, 12.47%). The free amine L$^2$ was obtained from the tetrahydrobromide salt in almost quantitative yield as reported for L$^1$, mp 48–51 °C (Found: C, 68.3; H, 7.6; N, 23.8. Calc. for $C_{10}H_{13}N_3$: C, 68.54; H, 7.48; N, 23.98%).

**[PbL$^1$][NO$_3$]$_2$.** A solution of $Pb(NO_3)_2$ (33 mg, 0.1 mmol) in water (5 cm$^3$) was added to a solution of L$^1$ (55 mg, 0.1 mmol) in water (10 cm$^3$). The pH was adjusted to 7 and the reaction mixture stirred for 15 min. To the resulting solution $CHCl_3$ (10 cm$^3$) was added and the mixture stirred for 10 min. The organic layer was separated and dried over $Na_2SO_4$. On addition of hexane (20 cm$^3$) a white precipitate separated. Yield: 38 mg (60%). MS (ESI): *m*/*z* 577, [PbL$^1$(NO$_3$)]$^+$; 514, [PbL$^1$(NO$_3$)$^+$ − HNO$_3$] (Found: C, 33.6; H, 3.3; N, 15.2. Calc. for $C_{18}H_{21}N_7O_6Pb$: C, 33.85; H, 3.31; N, 15.35%).

**[PbL$^2$][NO$_3$]$_2$.** This compound was synthesized from L$^2$ (35 mg, 0.1 mmol) and $Pb(NO_3)_2$ (33 mg, 0.1 mmol) following the procedure reported for [PbL$^1$][NO$_3$]$_2$. Yield 56 mg (82%). MS (ESI): *m*/*z* 620, [PbL$^2$(NO$_3$)]$^+$; 558, [PbL$^2$(NO$_3$)$^+$ − HNO$_3$] (Found: C, 35.3; H, 3.9; N, 16.6. Calc. for $C_{20}H_{26}N_8O_6Pb$: C, 35.24; H, 3.84; N, 16.44%).

**[PbL$^3$][NO$_3$]$_2$.** This compound was synthesized from L$^3$ (39 mg, 0.1 mmol) and $Pb(NO_3)_2$ (33 mg, 0.1 mmol) following the procedure for [PbL$^1$][NO$_3$]$_2$. Yield 64 mg (89%). MS (ESI): *m*/*z* 663, [PbL$^3$(NO$_3$)]$^+$; 601, [PbL$^3$(NO$_3$)$^+$ − HNO$_3$] (Found: C, 36.3; H, 4.3; N, 17.3. Calc. for $C_{22}H_{31}N_9O_6Pb$: C, 36.46; H, 4.31; N, 17.39%).

**[(PbL$^1$Br)$_2$(μ-Br)][PbL$^1$Br$_2$]Br·5H$_2$O.** Sodium bromide (10 mg, 0.1 mmol) was added to an aqueous solution (5 cm$^3$) containing [PbL$^1$][NO$_3$]$_2$ (6.4 mg, 0.01 mmol). Colorless crystals of the complex suitable for X-ray analysis were obtained by slow evaporation at room temperature of this solution. Yield: 5 mg (71%) (Found: C, 30.8; H, 3.3; N, 10.0. Calc. for $C_{54}H_{73}Br_6N_{15}O_5Pb_3$: C, 30.69; H, 3.48; N, 9.94%).

**Table 4** Crystal data for [(PbL$^1$Br)$_2$(μ-Br)][PbL$^1$Br$_2$]Br·5H$_2$O **1** and [PbL$^3$][ClO$_4$][BPh$_4$] **2**

| | **1** | **2** |
|---|---|---|
| Empirical formula | $C_{54}H_{73}Br_6N_{15}O_5Pb_3$ | $C_{46}H_{51}BClN_7O_4Pb$ |
| *M* | 2113.30 | 1019.39 |
| *T*/K | 298 | 298 |
| Crystal system | Triclinic | Triclinic |
| Space group | $P\bar{1}$ | $P\bar{1}$ |
| *a*/Å | 11.260(5) | 9.777(7) |
| *b*/Å | 14.250(5) | 13.700(10) |
| *c*/Å | 21.475(5) | 16.750(10) |
| *α*/° | 74.230(5) | 89.16(7) |
| *β*/° | 79.330(5) | 84.90(10) |
| *γ*/° | 83.720(5) | 71.90(10) |
| *V*/Å$^3$ | 3252(2) | 2124(3) |
| *Z* | 2 | 2 |
| Reflections collected ($5 < 2\theta < 50$) | 11701 | 7724 |
| Refined parameters | 748 | 550 |
| Unique observed reflections [$I > 2\sigma(I)$] | 7145 | 3779 |
| Final *R*1, *wR*2 [$I > 2\sigma(I)$] | 0.0621, 0.1216 | 0.1031, 0.2519 |
| (all data) | 0.1212, 0.1499 | 0.1910, 0.3231 |

**[PbL$^3$][ClO$_4$][BPh$_4$].** The salt $NaClO_4 \cdot H_2O$ (10 mg, 0.1 mmol) and $NaBPh_4$ (34 mg, 0.1 mmol) were added to an aqueous solution (5 cm$^3$) containing [PbL$^3$][NO$_3$]$_2$ (7.2 mg, 0.01 mmol). Colorless crystals of the complex suitable for X-ray analysis were obtained by slow evaporation at room temperature of this solution. Yield: 3 mg (30%) (Found: C, 53.9; H, 5.0, N, 9.5. Calc. for $C_{46}H_{51}BClN_7O_4Pb$: C, 54.20; H, 5.04; N, 9.62%).

**CAUTION:** perchlorate salts of organic ligands and their metal complexes are potentially explosive; these compounds must be handled with great caution!

### X-Ray crystallography

Colorless single crystals of [(PbL$^1$Br)$_2$(μ-Br)][PbL$^1$Br$_2$]Br·5H$_2$O and [PbL$^3$][ClO$_4$][BPh$_4$] were mounted on an Enraf-Nonius CAD4 X-ray diffractometer, equipped with graphite monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å). For both compounds 25 carefully centered reflections were used to determine cell parameters. A summary of crystal data for refining and data collection of both compounds is in Table 4. For both structures, the function minimized was $\Sigma w(|F_o|^2 - |F_c|^2)^2$, with the weighting factors calculated in agreement with the refinement program. The programs used and the source of atomic scattering factors and anomalous dispersion corrections are given in ref. 19.

**[(PbL$^1$Br)$_2$(μ-Br)][PbL$^1$Br$_2$]Br·5H$_2$O.** The structure was solved by the Patterson method. An absorption correction was then applied. Refinement was performed by full-matrix least squares with all the non-hydrogen atoms anisotropic, except the O5 and O5′ atoms of a disordered solvent molecule, and the hydrogen atoms in calculated positions with isotropic thermal parameters refined to the final value $U = 0.050(6)$ Å$^2$. Two peaks in the electronic density map have been attributed to a disordered water molecule and introduced with population parameters 0.66 and 0.33 for O5 and O5′, respectively.

**[PbL$^3$][ClO$_4$][BPh$_4$].** The structure was solved by the heavy atom technique. An absorption correction was then applied. Refinement was performed by full-matrix least-squares with all the non-hydrogen atoms anisotropic and the hydrogen atoms in calculated position with isotropic thermal parameters fixed at

$U = 0.05$ Å$^2$. A significantly high degree of disorder affects the aliphatic chain of the macrocyclic molecule, giving rise to remarkably high values for the thermal factors of almost all the carbon and the nitrogen atoms of the chain. Only for one carbon atom could we localize the double position (C20 and C20′; population parameters 0.7 and 0.3, respectively).

As often found in crystal structures containing lead atoms, several residual peaks are present in the electron density map around the metal. The poor quality of the data, mainly due to disorder and the absorption effect of the lead atom, gives rise to rather high values obtained at the end of refinement for agreement factors, thermal parameters of several atoms and e.s.d.s of cell parameters, atomic coordinates and bond distances and angles.

CCDC reference number 186/1265.

See http://www.rsc.org/suppdata/dt/1999/393/ for crystallographic files in .cif format.

### Potentiometric measurements

Equilibrium constants for complexation reactions with L[1], L[2] and L[3] were determined by pH-metric measurements ($\mathrm{pH} = -\log\,[\mathrm{H}^+]$) in 0.1 mol dm$^{-3}$ $NMe_4NO_3$ at 298.1 ± 0.1 K, by using potentiometric equipment that has been described.[20] The combined glass electrode was calibrated as a hydrogen concentration probe by titrating known amounts of HCl with $CO_2$-free NaOH solutions and determining the equivalence point by Gran's method[21] which allows one to determine the standard potential $E°$, and the ionic product of water [p$K_w$ = 13.83(1) at 298.1 K in 0.1 mol dm$^{-3}$ $NMe_4NO_3$]. $1 \times 10^{-3}$–$2 \times 10^{-3}$ mol dm$^{-3}$ Ligands and metal ion concentrations were employed in the potentiometric measurements, performing three titration experiments (about 100 data points each) in the pH range 2–11. The computer program SUPERQUAD[22] was used to calculate equilibrium constants from emf data. All titrations were treated either as single sets or as separated entities, for each system, without significant variation in the values of the determined constants.

### Microcalorimetric measurements

The enthalpies of protonation of L[1], L[2] and L[3] were determined in 0.1 mol dm$^{-3}$ $NMe_4NO_3$ aqueous solutions by means of an automated system composed of a Thermometric AB thermal activity monitor (model 2277) equipped with perfusion-titration device and Hamilton Pump (model Microlab M) coupled with a 0.250 cm$^3$ gas-tight Hamilton syringe (model 1759 LT). Typically 1.2 cm$^3$ of $5 \times 10^{-3}$ mol dm$^{-3}$ acidic ligand solution in 0.1 mol dm$^{-3}$ $NMe_4NO_3$ were charged into the calorimetric ampoule. After thermal equilibration, 0.015 cm$^3$ additions of a 0.1 mol dm$^{-3}$ $NMe_4OH$ standard solution were delivered. Under the reaction conditions and employing the determined protonation constant, the concentrations of the species present in solution before and after addition were calculated and the corresponding enthalpies of reaction were determined from the calorimetric data by means of the KK88 program.[23] At least three titrations were performed for each system. The titration curves for each system were treated either as a single set or as separated entities without significant variation in the values of the enthalpy changes.

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