Interaction of Lead(II) with Highly-Dentate Linear and Cyclic Polyamines†

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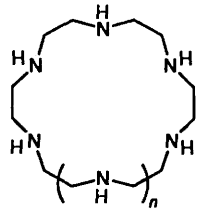
The interaction of Pb^{2+} with the macrocyclic amines 1,4,7,10,13,16-hexaazacyclooctadecane (L^1), 1,4,7,10,13,16,19-heptaazacyclohenicosane (L^2), 1,4,7,10,13,16,19,22-octaazacyclotetracosane (L^3), 1,4,7,10,13,16,19,22,25-nonaazacycloheptacosane (L^4), 1,4,7,10,13,16,19,22,25,28-decaazacyclotriacontane (L^5), 1,4,7,10,13,16,19,22,25,28,31-undecaazacyclotritriacontane (L^6) and 1,4,7,10,13,16,19,22,25,28,31,34-dodecaazacyclohexatriacontane (L^7) belonging to the [3*k*]aneN_k series and with their related open-chain, terminally methylated polyamines 1,14-bis(methylamino)-3,6,9,12-tetraazatetradecane (L^8), 1,17-bis(methylamino)-3,6,9,12,15-pentaazaheptadecane (L^9), 1,20-bis(methylamino)-3,6,9,12,15,18-hexaazaicosane (L^{10}) and 1,23-bis(methylamino)-3,6,9,12,15,18,21-heptaazatricosane (L^{11}) has been studied by potentiometry at 298.1 K in 0.15 mol dm^{-3} $NaClO_4$. The cyclic amines L^1 and L^2 form only mononuclear complexes, while L^3–L^5 can form both mono- and bi-nuclear species. The largest amines of this series L^6 and L^7 form bi- and tri-nuclear lead(II) complexes. Of the open-chain ligands, L^8 forms only mononuclear complexes, while L^9–L^{11} form both mono- and bi-nuclear species. The crystal structure of the solid compound $[Pb_2L^5][ClO_4]_4$ has been solved by X-ray diffraction analysis [space group $P2_1/n$, $Z = 2$, $a = 9.052(9)$, $b = 11.400(9)$, $c = 18.689(8)$ Å, $\beta = 94.42(6)°$, $R = 0.082$ and $R' = 0.068$]. It shows that both Pb^{2+} ions are tightly co-ordinated to four nitrogens of the macrocycle (Pb–N ranging from 2.27 to 2.71 Å). A fifth nitrogen and three oxygens of two perchlorate anions are weakly interacting at much larger distances (Pb–N 3.04; Pb–O 2.98, 3.38, 3.41 Å). The complex cation is situated around a crystallographic symmetry centre. The arrangement of the eight atoms around the lead ion is rather asymmetric leaving a zone free from co-ordinated donor atoms which is believed to be occupied by a lone pair of electrons.

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. The toxic effect of lead on the human body is reflected in general behavioural disturbances such as anaemia, alteration in membrane permeability and inhibition of oxidative phosphorylation and protein synthesis.[1] Most of the pharmacological treatments for metal poisoning use chelating agents. This therapy is based on the formation of stable, soluble, non-toxic compounds which are readily excreted from the body.

In this work we have devoted our attention to the chelation of lead(II) by the macrocyclic ligands 1,4,7,10,13,16-hexaazacyclooctadecane ([18]aneN_6, L^1), 1,4,7,10,13,16,19-heptaazacyclohenicosane ([21]aneN_7, L^2), 1,4,7,10,13,16,19,22-octaazacyclotetracosane ([24]aneN_8, L^3), 1,4,7,10,13,16,19,22,25-nonaazacycloheptacosane([27]aneN_9,L^4),1,4,7,10,13,16,19,22,25,28-decaazacyclotriacontane([30]aneN_{10},L^5),1,4,7,10,13,16,19,22,25,28,31-undecaazacyclotritriacontane ([33]aneN_{11}, L^6) and 1,4,7,10,13,16,19,22,25,28,31,34-dodecaazacyclohexatriacontane ([36]aneN_{12}, L^7) belonging to the [3*k*]aneN_k series of polyazacycloalkanes. These macrocycles, due to their large number of nitrogens, are able to form very stable complexes, containing one or more metal ions,[2–11] which are very soluble in aqueous solution. For comparison, we have also studied the co-ordinative behaviour towards lead(II) of the series of long open-chain polyamines 1,14-bis(methylamino)-3,6,9,12-tetraazatetradecane (L^8), 1,17-bis(methylamino)-3,6,-9,12,15-pentaazaheptadecane (L^9), 1,20-bis(methylamino)-3,6,-9,12,15,18-hexaazaicosane (L^{10}) and 1,23-bis(methylamino)-3,6,9,12,15,18,21-heptaazatricosane (L^{11}). These also form water-soluble, stable mono- and bi-nuclear complexes.[12–14] The influence of the ligand topology on the chelating ability towards



n		*n*	
1	[18]aneN_6, L^1	5	[30]aneN_{10}, L^5
2	[21]aneN_7, L^2	6	[33]aneN_{11}, L^6
3	[24]aneN_8, L^3	7	[36]aneN_{12}, L^7
4	[27]aneN_9, L^4		

$CH_3NHCH_2CH_2NH(CH_2CH_2NH)_nCH_2CH_2NHCH_2CH_2NHCH_3$

n	
2	L^8
3	L^9
4	L^{10}
5	L^{11}

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

lead(II) is considered. We also report the molecular and crystal structure of the solid compound $[Pb_2L^5][ClO_4]_4$ in which the presence of a stereochemically active lone pair on each metal centre is inferred.

Experimental

Materials.—The compounds L^1–L^{11} were synthesised as described previously and handled as their hydrochloride salts.[2-6,12] Crystals of $[Pb_2L^5][ClO_4]_4$ suitable for X-ray analysis were obtained by evaporation at room temperature of solutions containing the ligand and Pb^{2+} in 1:2 molar ratio and a ten-fold excess of $NaClO_4 \cdot H_2O$. Satisfactory elemental analyses were obtained for all the compounds. All the potentiometric measurements were carried out in 0.15 mol dm^{-3} $NaClO_4$. Sodium perchlorate used as a supporting electrolyte was purified as described.[15] Stock solutions of lead(II) were prepared by dissolving $Pb(NO_3)_2 \cdot 4H_2O$ in doubly distilled water and their concentration determined by standard gravimetric methods. Under our experimental conditions, interferences due to the formation of lead(II) chloro complexes or precipitation of lead(II) chloride can be neglected. The CO_2-free NaOH solutions and HCl solutions were prepared following the procedure in ref. 16.

Electromotive Force Measurements.—All the potentiometric measurements were carried out in 0.15 mol dm^{-3} $NaClO_4$ at 298.1 K, by using equipment previously described.[17] The data acquisition was by means of the computer program PASAT.[18] The reference electrode was an Ag–AgCl electrode in saturated KCl solution. The 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[19] which allows one to determine the standard potential E^0 and the ionic product of water [pK_w = 13.73(1) at 298.1 K in 0.15 mol dm^{-3} $NaClO_4$]. In the case of the system Pb^{2+}–L^2, 0.15 mol dm^{-3} NaCl instead of 0.15 mol dm^{-3} $NaClO_4$ was used to maintain the ionic strength to avoid precipitation observed with the latter.

The complexation equilibria of Pb^{2+} and the compounds considered were studied in the range pH 2.5–10 by means of common potentiometric titrations. At least three measurements (300 data points) were performed for each system. The amine concentration was about 2×10^{-3} mol dm^{-3} in all measurements while the metal-ion concentration was varied from 1×10^{-3} to 5×10^{-3} mol dm^{-3} according to the formation of mono-, bi- and tri-nuclear complexes. The computer program SUPERQUAD[20] was used to calculate stability constants from the electromotive force data. The titration curves for each system were treated either as a single set or as separated entities without significant variations in the values of the stability constants. The protonation constants of the [3*k*]aneN_k series and of the linear polyamines employed in all the calculations were previously determined.[2-5,12,21] The distribution diagrams for the binary and ternary systems were calculated by means of the computer program DISPO.[22]

Crystallography.—*Crystal data.* $C_{20}H_{50}Cl_4N_{10}O_{16}Pb_2$, M = 1242.9, monoclinic, space group $P2_1/n$ (alt. $P2_1/c$, no. 14), a = 9.052(9), b = 11.400(9), c = 18.689(8) Å, β = 94.42(6)°, U = 1923(3) $Å^3$ (by least-squares refinement of diffractometer angles for 25 automatically centred reflections, λ = 0.7107 Å), Z = 2, D_c = 2.15 g cm^{-3}, $F(000)$ = 1200, prismatic colourless crystals, dimensions 0.2 × 0.2 × 0.15 mm, μ (Mo-Kα) = 91.65 cm^{-1}.

Data collection and processing. CAD4 diffractometer, θ–2θ mode with scan width = 1.00 + 0.35 tanθ, variable scan speed, Mo-Kα, graphite-monochromated radiation; 1765 reflections measured ($5 \leqslant 2\theta \leqslant 40°$, $\pm h$, $\pm k$, $+l$) giving 817 unique reflections with $I > 3\sigma(I)$. Absorption correction applied by using the DIFABS[23] program.

Structure analysis and refinement. Heavy-atom method (Pb atom). Full-matrix least-squares refinement with only the lead and chlorine atoms anisotropic because of the very low number of observed reflections. The poor quality of the data collected is probably due to some disorder in the perchlorate anions as well as in the macrocyclic ligand. The small dimensions of the crystal also contribute to this loss of observations.

As a consequence, high standard deviations on bond distances, angles and atomic coordinates result. Owing to the disorder in the ligand, the thermal parameters of nitrogen and carbon atoms of the macrocyclic framework are rather high and some intramolecular distances are not realistic. However the electron-density map did not show any maximum better to model the ligand. On account of this disorder the hydrogen atoms were not included in the calculation. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, with $w = a/\sigma^2(F)$, where a is an adjustable parameter. Final R and R' values were 0.082 and 0.068, respectively.

All calculations were performed on an IBM PS2/80 computer with the SHELX 76[24] set of programs which use the analytical approximation for the atomic scattering factors and anomalous dispersion corrections for all atoms from ref. 25. Table 1 lists the final atomic coordinates for the non-hydrogen atoms. The molecular plots were produced by the program ORTEP.[26]

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Results and Discussion

Description of the Structure.—Table 2 shows bond distances and angles involving the metal ion calculated by the program PARST.[27] In the crystal packing there are centrosymmetric $[Pb_2L^5]^{4+}$ cations and perchlorate anions.

The macrocyclic complex is situated around a crystallographic symmetry centre. In the cation $[Pb_2L^5]^{4+}$ the Pb^{2+} ion is co-ordinated by four nitrogen atoms of the macrocyclic ligand (mean Pb–N distance 2.5 Å), which describe a mean plane with the metal ion located 1.363(2) Å above (Fig. 1). The metal ion further interacts with another nitrogen atom N(1) and one oxygen atom of a perchlorate anion [O(1)] at very long distance [O(1)–Pb 2.98(7) and N(1)–Pb 3.04(6) Å]. The plane passing through N(1)–Pb–O(1) forms an angle of 141(2)° with that involving the fully co-ordinated nitrogen atoms. There are two further weak interactions between the lead ion and two oxygen atoms of another perchlorate anion [related by $1 - x$, $1 - y$, $1 - z$; Pb–O(2') 3.38(4) and Pb–O(3') 3.41(6) Å]. Taking into account all these interactions the arrangement of the eight donor atoms around the lead ion is rather asymmetric, leaving a zone free from co-ordinated donor atoms (Fig. 2) which we suppose to be occupied by the lone pair of Pb^{2+}. The presence of a 'gap' in the co-ordination sphere of the cation is

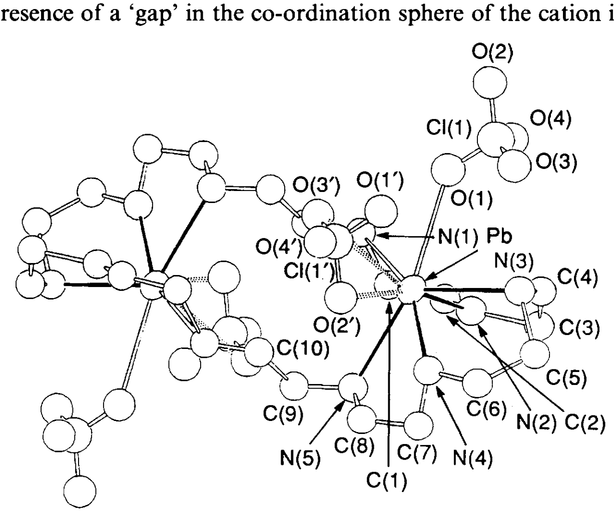

Fig. 1 An ORTEP drawing of the compound $[Pb_2L^5][ClO_4]_4$

Table 1 Atomic coordinates ($\times 10^3$) with estimated standard deviations (e.s.d.s) in parentheses for $[Pb_2L^5][ClO_4]_4$

Atom	*x*	*y*	*z*
Pb	276(1)	625(1)	435(1)
Cl(1)	617(3)	688(2)	579(1)
O(1)	480(9)	653(7)	567(4)
O(2)	697(4)	646(4)	637(2)
O(3)	669(6)	661(5)	517(3)
O(4)	576(10)	783(8)	611(5)
Cl(2)	622(2)	421(2)	192(1)
O(5)	638(5)	344(4)	133(3)
O(6)	687(7)	357(6)	258(4)
O(7)	711(7)	523(6)	179(4)
O(8)	487(7)	445(5)	190(3)
N(1)	139(6)	668(5)	577(3)
C(1)	57(8)	791(7)	541(4)
C(2)	161(11)	846(10)	496(6)
N(2)	234(9)	837(7)	453(5)
C(3)	356(9)	904(6)	405(4)
C(4)	468(8)	828(7)	411(4)
N(3)	501(10)	723(9)	382(6)
C(5)	478(11)	727(9)	289(6)
C(6)	356(13)	645(12)	265(6)
N(4)	251(9)	618(9)	313(4)
C(7)	164(10)	618(10)	252(5)
C(8)	52(9)	560(7)	285(5)
N(5)	6(4)	617(5)	362(2)
C(9)	−107(7)	546(6)	385(4)
C(10)	−51(10)	405(9)	395(5)

Table 2 Bond distances (Å) and angles (°) in the coordination sphere, with e.s.d.s in parentheses

Pb–N(1)	3.04(6)	Pb–N(4)	2.27(8)
Pb–N(2)	2.47(8)	Pb–N(5)	2.71(4)
Pb–N(3)	2.60(10)	Pb–O(1)	2.98(7)
N(3)–Pb–N(4)	70(3)	N(4)–Pb–O(1)	147(2)
N(3)–Pb–N(5)	121(2)	N(5)–Pb–N(1)	92(1)
N(3)–Pb–N(1)	130(3)	N(5)–Pb–N(2)	88(2)
N(3)–Pb–N(2)	76(3)	N(5)–Pb–O(1)	154(2)
N(3)–Pb–O(1)	79(3)	N(1)–Pb–N(2)	69(2)
N(4)–Pb–N(5)	58(2)	N(1)–Pb–O(1)	62(2)
N(4)–Pb–N(1)	149(2)	N(2)–Pb–O(1)	83(2)
N(4)–Pb–N(2)	100(3)		

one of the structural effects ascribed to the stereochemical activity of the lone pair.[28,29] It has also been noted[28,29] that when the lone pair of Pb^{2+} is active the Pb–N bonds opposite to it are shorter than expected (2.6–2.9 Å) for Pb–N bonds in non-active complexes. Accordingly, very short Pb–N distances are observed in the present structure opposite to the gap in the co-ordination environment of the Pb^{2+}, the bond distances between Pb^{2+} and the donor atoms defining the gap [N(5), N(1), O(1), O(2′), O(3′)] being the longest.

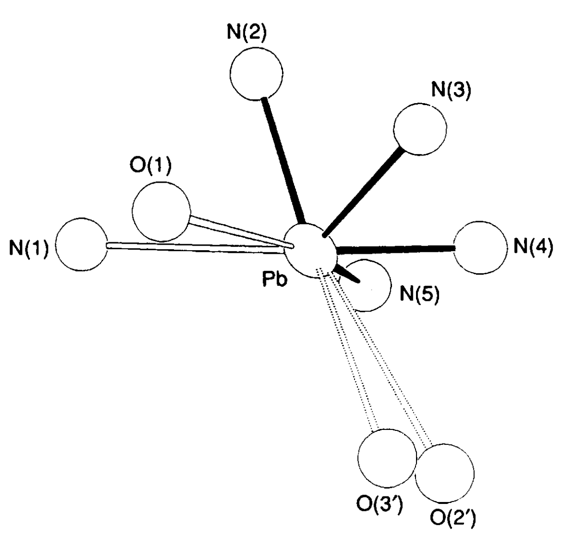

Fig. 2 An ORTEP drawing of the co-ordination site of lead(II) in $[Pb_2L^5][ClO_4]_4$ showing the gap occupied by the lone pair

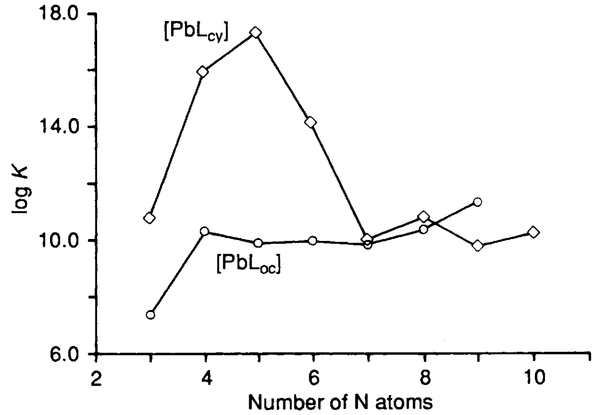

Fig. 3 Plot of the logarithms of the stability constants for the formation of lead(II) mononuclear complexes with the macrocyclic amines (L_{cy}) of the [3*k*]aneN$_k$ series and open-chain polyamines (L_{oc})

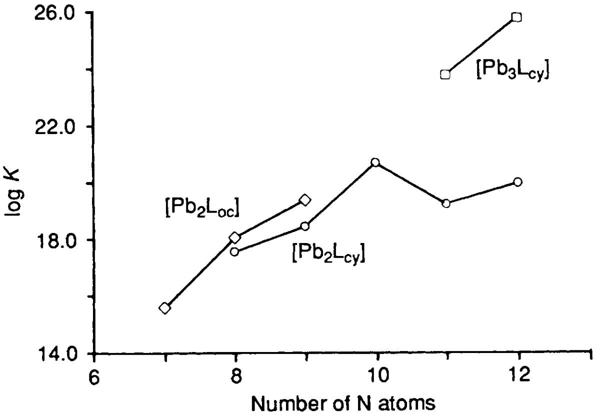

Fig. 4 Plots of the logarithms of the stability constants for the formation of lead(II) bi- and tri-nuclear complexes by the macrocyclic amines of the [3*k*]aneN$_k$ series and open-chain polyamines

Solution Equilibria.—The stability constants for the formation in aqueous solution of lead(II) complexes with the [3*k*]aneN$_k$ (k = 6–12) compounds and with their open-chain counterparts are in Tables 3–7. In Figs. 3 and 4 the logarithms of the stability constants corresponding to the general reaction $pPb^{2+} + L \rightleftharpoons [Pb_pL]^{2p+}$ are plotted for both types of amine L *versus* the number of nitrogen-donor atoms present in each. In Fig. 3 we have also reported the logarithms of the stability constants for the cyclic compounds 1,4,7-triazacyclononane ([9]aneN$_3$, L[12]), 1,4,7,10-tetraazacyclododecane ([12]aneN$_4$, L[13]) and 1,4,7,10,13-pentaazacyclopentadecane ([15]aneN$_5$, L[14]) and the open-chain ones 1,3-azapentane-1,5-diamine (dien), 3,6-diazaoctane-1,8-diamine (trien) and 3,6,9-triazaundecane-1,11-diamine (tetraen).[30,31] Although the stability constants of these compounds have been determined under slightly different experimental conditions and by different techniques and these open-chain compounds are not strictly comparable with those of the present work, since they are not terminally methylated, some general trends may be inferred.

First, the stability of the $[PbL_{oc}]^{2+}$ species (L_{oc} = open-chain ligand) increases from dien to trien, remaining roughly constant for all the other terms of the series of open-chain ligands. For the cyclic ligands (L_{cy}) a maximum in stability is

Table 3 Logarithms of the stability constants for the formation of mononuclear lead(II) complexes by open-chain polyamines in aqueous solution (298.1 K in 0.15 mol dm^{-3} $NaClO_4$)

	log K[b]			
Reaction[a]	L^8	L^9	L^{10}	L^{11}
$Pb + L \rightleftharpoons [PbL]$	9.972(5)	9.86(1)	10.37(1)	11.32(3)
$Pb + L + H \rightleftharpoons [Pb(HL)]$	19.259(3)	19.47(1)	20.328(8)	20.90(3)
$Pb + L + 2H \rightleftharpoons [Pb(H_2L)]$	25.975(5)	27.050(6)	28.912(7)	29.66(3)
$Pb + L + 3H \rightleftharpoons [Pb(H_3L)]$			35.845(4)	37.00(1)
$Pb + L + 4H \rightleftharpoons [Pb(H_4L)]$				42.74(4)
$Pb + L + H_2O \rightleftharpoons [PbL(OH)] + H$	−1.21(1)			
$Pb + HL \rightleftharpoons [Pb(HL)]$	8.98(1)	9.27(2)	9.99(2)	10.32(6)
$PbL + H \rightleftharpoons [Pb(HL)]$	9.29(1)	9.61(2)	9.96(2)	9.58(6)
$Pb + H_2L \rightleftharpoons [Pb(H_2L)]$	6.18(2)	7.24(2)	8.75(2)	9.37(4)
$[Pb(HL)] + H \rightleftharpoons [Pb(H_2L)]$	6.72(2)	7.58(2)	8.58(2)	8.76(5)
$Pb + H_3L \rightleftharpoons [Pb(H_3L)]$			6.41(2)	7.35(3)
$[Pb(H_2L)] + H \rightleftharpoons [Pb(H_3L)]$			6.93(2)	7.34(3)
$Pb + H_4L \rightleftharpoons [Pb(H_4L)]$				4.39(5)
$[Pb(H_3L)] + H \rightleftharpoons [Pb(H_4L)]$				5.74(5)
$[PbL] + OH \rightleftharpoons [PbL(OH)]$	2.55(2)			

[a] Charges have been omitted for clarity. [b] Values in parentheses are standard deviations in the last significant figure.

Table 4 Logarithms of the stability constants for the formation of mononuclear lead(II) complexes by macrocyclic polyamines in aqueous solution (298.1 K in 0.15 mol dm^{-3} $NaClO_4$, 0.15 mol dm^{-3} NaCl with L^2)

	log K				
Reaction	L^1	L^2	L^3	L^4	L^5
$Pb + L \rightleftharpoons [PbL]$	14.13(1)	10.02(5)	10.83(1)	9.77(1)	10.24(7)
$Pb + L + H \rightleftharpoons [Pb(HL)]$	19.86(2)	18.06(6)	19.48(1)	19.15(2)	19.83(5)
$Pb + L + 2H \rightleftharpoons [Pb(H_2L)]$		25.65(4)	26.92(1)	27.81(1)	28.74(5)
$Pb + L + 3H \rightleftharpoons [Pb(H_3L)]$		31.88(6)	31.68(9)	34.28(1)	36.29(3)
$[PbL] + H \rightleftharpoons [Pb(HL)]$	5.73(3)	8.0(1)	8.65(2)	9.38(3)	9.6(1)
$[Pb(HL)] + H \rightleftharpoons [Pb(H_2L)]$		7.6(1)	7.46(2)	8.66(3)	8.9(1)
$[Pb(H_2L)] + H \rightleftharpoons [Pb(H_3L)]$		6.2(1)	4.8(1)	6.47(2)	7.5(1)
$Pb + HL \rightleftharpoons [Pb(HL)]$	9.71(2)	8.30(7)	9.83(2)	9.56(3)	9.98(7)
$Pb + H_2L \rightleftharpoons [Pb(H_2L)]$		6.61(5)	7.94(2)	8.82(2)	9.45(7)
$Pb + H_3L \rightleftharpoons [Pb(H_3L)]$		4.21(7)	3.9(1)	6.52(3)	8.05(5)

Table 5 Logarithms of the stability constants for the formation of binuclear lead(II) complexes with the open-chain polyamines in aqueous solution (298.1 K in 0.15 mol dm^{-3} $NaClO_4$)

	log K		
Reaction	L^9	L^{10}	L^{11}
$2Pb + L \rightleftharpoons [Pb_2L]$	15.61(2)	18.064(9)	19.38(1)
$2Pb + L + H \rightleftharpoons [Pb_2(HL)]$		25.39(1)	26.67(2)
$2Pb + L + H_2O \rightleftharpoons [Pb_2L(OH)] + H$	6.67(3)	8.68(1)	9.74(3)
$2Pb + L + 2H_2O \rightleftharpoons [Pb_2L(OH)_2] + 2H$	−3.67(4)	−2.19(4)	−0.99(3)
$[Pb_2L] + H \rightleftharpoons [Pb_2(HL)]$		7.33(3)	7.29(4)
$2Pb + HL \rightleftharpoons [Pb_2(HL)]$		15.00(3)	16.09(4)
$[Pb_2L] + OH \rightleftharpoons [Pb_2L(OH)]$	4.79(5)	4.35(3)	4.09(5)
$[Pb_2L(OH)] + OH \rightleftharpoons [Pb_2L(OH)_2]$	3.39(7)	2.86(4)	3.00(6)
$[PbL] + Pb \rightleftharpoons [Pb_2L]$	5.76(3)	7.69(2)	8.06(4)

found for $[PbL^{14}]^{2+}$ (log K = 17.3).[30] Then, the stability of these complexes undergoes a sharp decrease when the series from $[PbL^{14}]^{2+}$, $[PbL^1]^{2+}$, $[PbL^2]^{2+}$ (log K = 10.02) is examined. From L^2 to L^5 the stability of the $[PbL_{cy}]^{2+}$ complexes remains practically constant. For the two largest ligands, at least under our experimental conditions, no mononuclear complexes have been detected. Although conclusions on co-ordination numbers derived just from stability constants may sometimes be misleading, these data seem to suggest four-co-ordination for the mononuclear complexes of the open-chain ligands and five-co-ordination for those of the cyclic ones. Four-co-ordination of lead(II) by the open-chain polyamines finds further support in protonation constants of $[PbL_{oc}]^{2+}$ species. The values for the first stepwise protonation constant $[PbL_{oc}]^{2+} + H^+ \rightleftharpoons [Pb(HL_{oc})]^{3+}$ are very high and close to those for the first protonation steps of the free amines indicating that at least one nitrogen atom remains unco-ordinated throughout the series. The constants for the second protonation steps $[Pb(HL_{oc})]^{3+} + H^+ \rightleftharpoons [Pb(H_2L_{oc})]^{4+}$ are still relatively high and compare well with those for the third protonation steps of the free amines ($H_3L_{oc}{}^{3+} + H^+ \rightleftharpoons H_4L_{oc}{}^{4+}$) in which the same overall charges are present. For instance, these constants are 6.72 for the lead(II) complex and 6.52 for the free amine in the case of L^8, indicating that just four of the six nitrogens of the ligand are

Table 6 Logarithms of the stability constants for the formation of binuclear lead(II) complexes with the macrocyclic polyamines in aqueous solution (298.1 K in 0.15 mol dm^{-3} $NaClO_4$)

Reaction	log K				
	L^3	L^4	L^5	L^6	L^7
$2Pb + L \rightleftharpoons [Pb_2L]$	17.57(1)	18.46(1)	20.70(2)	19.24(1)	19.97(2)
$2Pb + L + H \rightleftharpoons [Pb_2(HL)]$	23.73(2)	24.89(2)	27.35(4)	27.02(1)	28.36(2)
$2Pb + L + 2H \rightleftharpoons [Pb_2(H_2L)]$			33.79(3)	33.78(2)	35.66(2)
$2Pb + L + 3H \rightleftharpoons [Pb_2(H_3L)]$			39.34(5)	40.14(1)	41.83(3)
$2Pb + L + 4H \rightleftharpoons [Pb_2(H_4L)]$			45.20(2)	45.73(1)	48.23(1)
$2Pb + L + H_2O \rightleftharpoons [Pb_2L(OH)] + H$	7.87(3)	8.59(2)	10.79(2)	8.43(6)	9.48(3)
$2Pb + L + 2H_2O \rightleftharpoons [Pb_2L(OH)_2] + 2H$		−2.17(2)	−0.28(2)	−2.62(7)	−1.45(3)
$[Pb_2L] + H \rightleftharpoons [Pb_2(HL)]$	6.16(3)	6.43(3)	6.65(6)	7.78(2)	8.39(4)
$[Pb_2(HL)] + H \rightleftharpoons [Pb_2(H_2L)]$			6.44(7)	6.76(3)	7.30(4)
$[Pb_2(H_2L)] + H \rightleftharpoons [Pb_2(H_3L)]$			5.55(8)	6.36(3)	6.17(5)
$[Pb_2(H_3L) + H \rightleftharpoons [Pb_2(H_4L)]$			5.86(7)	5.59(2)	6.40(4)
$[PbL] + Pb \rightleftharpoons [Pb_2L]$	6.74(2)	8.69(2)	10.46(9)		
$2Pb + HL \rightleftharpoons [Pb_2(HL)]$	14.08(4)	15.30(4)	17.50(6)	17.23(3)	18.61(4)
$2Pb + H_2L \rightleftharpoons [Pb_2(H_2L)]$			14.50(5)	14.51(4)	16.26(4)
$2Pb + H_3L \rightleftharpoons [Pb_2(H_3L)]$			11.10(7)	11.85(3)	13.55(5)
$2Pb + H_4L \rightleftharpoons [Pb_2(H_4L)]$			8.40(4)	8.80(3)	10.99(3)
$[Pb_2L] + OH \rightleftharpoons Pb_2L(OH)]$	4.03(5)	3.86(4)	3.82(4)	2.9(1)	3.24(5)
$[Pb_2L(OH)] + OH \rightleftharpoons [Pb_2L(OH)_2]$		2.97(5)	2.66(5)	2.7(1)	2.80(5)

Table 7 Logarithms of the stability constants for the formation of trinuclear lead(II) complexes with the macrocyclic polyamines in aqueous solution (298.1 K in 0.15 mol dm^{-3} $NaClO_4$)

Reaction	log K	
	L^6	L^7
$3Pb + L \rightleftharpoons [Pb_3L]$	23.76(2)	25.77(3)
$3Pb + L + H \rightleftharpoons [Pb_3(HL)]$	30.44(3)	32.78(4)
$3Pb + L + H_2O \rightleftharpoons [Pb_3L(OH)] + H$	16.05(2)	16.71(4)
$3Pb + L + 2H_2O \rightleftharpoons [Pb_3L(OH)_2] + 2H$	6.92(5)	6.97(4)
$3Pb + L + 3H_2O \rightleftharpoons [Pb_3L(OH)_3] + 3H$		−3.65(7)
$3Pb + HL \rightleftharpoons [Pb_3(HL)]$	20.65(5)	23.03(6)
$[Pb_3L] + H \rightleftharpoons [Pb_3(HL)]$	6.68(5)	7.01(7)
$[Pb_3L] + OH \rightleftharpoons [Pb_3L(OH)]$	6.02(4)	4.67(6)
$[Pb_3L(OH)] + OH \rightleftharpoons [Pb_3L(OH)_2]$	4.60(7)	3.99(6)
$[Pb_3L(OH)_2] + OH \rightleftharpoons [Pb_3L(OH)_3]$		3.1(1)
$[Pb_2L] + Pb \rightleftharpoons [Pb_3L]$	4.52(3)	5.80(5)

involved in co-ordination to the metal ion. In the system Cu^{2+}–L^8 in which five-co-ordination of copper(II) was ascertained, the corresponding stability constant was just 3.90.[12] The constant enthalpic contributions reported in the literature for the formation of lead(II) complexes with trien and tetraen[30] also support the four-co-ordination of lead(II) by the nitrogens of the open-chain ligands.

Correlation between protonation constants of the $[PbL]^{2+}$ complexes and co-ordination numbers is much more difficult for the cyclic amines since the special conformations they adopt upon co-ordination make these data scarcely amenable to analysis. While some of the stability data for these amines seem to indicate five-co-ordination, others can be accounted for assuming four-co-ordination. For instance, the maximum in stability found for $[PbL^{14}]^{2+}$ and the fact that only a monoprotonated form of $[PbL^1]^{2+}$ is present in solution could indicate five-co-ordination whereas the low stabilities found for the lead(II) complexes of L^2–L^5 which, on the other hand, are similar to those of the open-chain polyamines, could imply four-co-ordination.

While L^8 just forms mononuclear species, L^9–L^{11} are able to incorporate a second lead(II) ion, forming binuclear complexes. The stepwise stability constant for the addition of the second metal ion ($Pb^{2+} + [PbL]^{2+} \rightleftharpoons [Pb_2L]^{4+}$) clearly increases from L^9 to L^{10} (log K = 5.76 and 7.69, respectively, Table 5) indicating the co-ordination of another nitrogen in L^{10} (four nitrogen atoms per Pb^{2+} ion). The increase, however, is very much reduced, for the addition of a second Pb^{2+} ion to L^{11} (log K = 8.06, Table 5), which contains nine nitrogen atoms. Such an increase seems too small to be ascribed to the co-ordination of the ninth nitrogen, but, most likely, it might be related to a greater facility of the longer ligand to dispose its co-ordination sites around the large lead(II) ion. Therefore, these data suggest that also in the binuclear complexes of open-chain polyamines the lead(II) metal ions are at most four-co-ordinated.

Unlike the open-chain amines for which formation of binuclear complexes is already detected with the heptadentate ligand L^9, octadentate L^3 is the first cyclic ligand forming such species. The stability of these species increases steadily from L^3 to L^5, dropping slightly for the largest two terms of the series (Table 6, Fig. 4). As already commented upon for the mononuclear complexes, also for binuclear ones to hypothesize on co-ordination numbers is rather difficult. The maximum in stability found for L^5 could suggest five-co-ordination of both metal ions by the nitrogens of the macrocycle in $[Pb_2L^5]^{4+}$. However, as previously discussed, the crystal structure of the solid compound $[Pb_2L^5][ClO_4]_4$ clearly shows that in each co-ordination site four nitrogens are much closer to the metal ion than the other. From the structural features of this structure the presence of a stereoactive lone pair on Pb^{2+} has been inferred. The lone pair can reside in the spherically symmetric 6s orbital or in a localized hybrid orbital, exhibiting in the latter case stereochemical activity in accord with the valence-shell electron-pair repulsion model.[32] The transition from a stereochemically inactive to an active lone pair seems to be accompanied by a noticeable decrease in size of the cation and an increase in covalency of the metal–ligand bonds at the expense of a reduced overall co-ordination number.[28]

The largest two amines of the [3*k*]aneN$_k$ series, L^6 and L^7, bind a third metal ion to form trinuclear complexes. As expected for the involvement of all the donor atoms of both amines in co-ordination to the three metal ions, an evident gain in stability is observed from L^6 to L^7 (Fig. 4). The distribution diagrams for the species existing in equilibria in the systems Pb^{2+}–L^6 and –L^7 calculated for metal : ligand ratios 2 : 1 and 3 : 1 are presented in Fig. 5. It can be seen that for both systems bi- or tri-nuclear species clearly predominate throughout the studied pH range as a function of the metal : ligand molar ratio. For transition-metal ions, analogous formation of trinuclear complexes has been reported only for copper(II).[6]

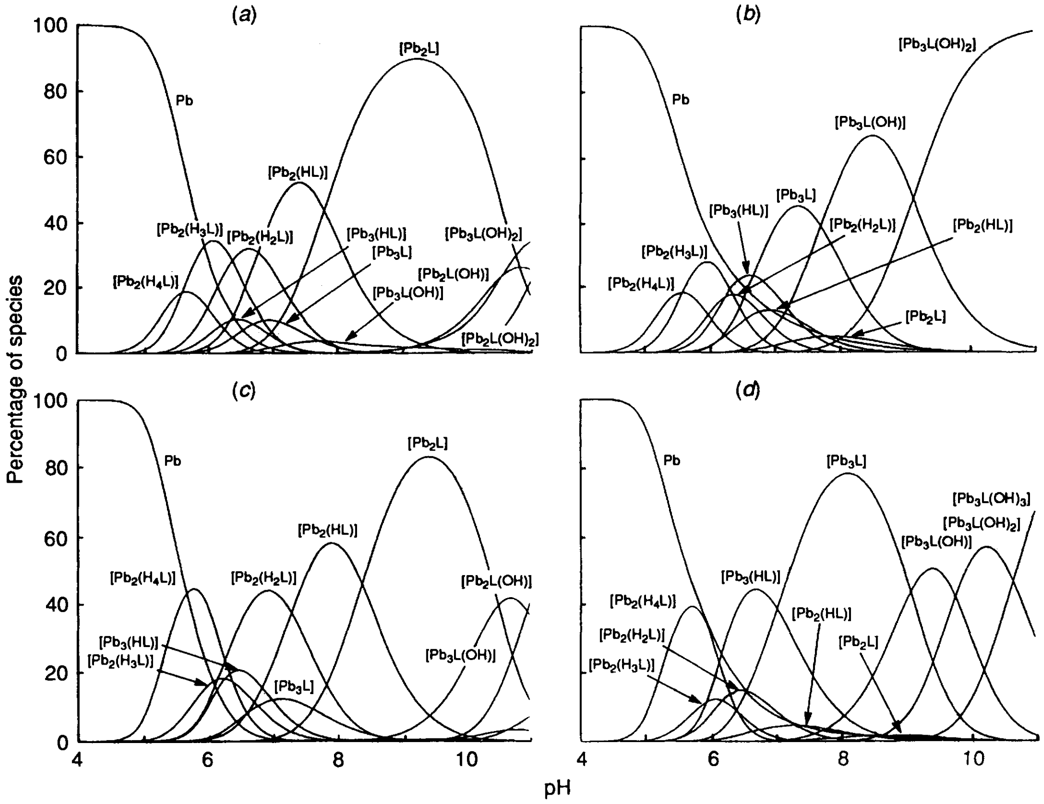

Fig. 5 Calculated distribution diagrams for the system: (*a*) Pb^{2+}(2×10^{-3} mol dm^{-3})–L^6 (1×10^{-3} mol dm^{-3}), (*b*) Pb^{2+} (3×10^{-3} mol dm^{-3})–L^6 (1×10^{-3} mol dm^{-3}), (*c*) Pb^{2+} (2×10^{-3} mol dm^{-3})–L^7 (1×10^{-3} mol dm^{-3}) and (*d*) Pb^{2+} (3×10^{-3} mol dm^{-3})–L^7 (1×10^{-3} mol dm^{-3}). Percentages are calculated with respect to Pb^{2+}

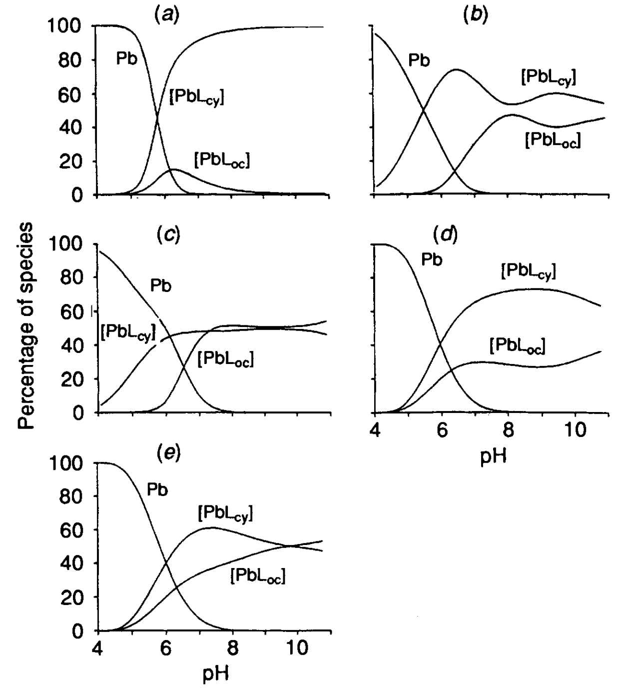

Fig. 6 Overall calculated distribution diagrams for the ternary systems (*a*) L^8–L^1–Pb^{2+} in 1 : 1 : 1 L_{oc} : L_{cy} : Pb^{2+} molar ratio, (*b*) L^9–L^2–Pb^{2+} (1 : 1 : 1), (*c*) as (*b*) but 1 : 1 : 2, (*d*) L^{10}–L^3–Pb^{2+} (1 : 1 : 1) and (*e*) as (*d*) but (1 : 1 : 2). The percentages of free lead and the sums of the percentages of open-chain and cyclic complexes are plotted *vs.* pH. Percentages are calculated with respect to Pb^{2+}

In all the systems the formation of bi- and tri-nuclear species is accompanied by very stable polyhydroxo complexes. This can be explained by the low number of nitrogens bound to each metal ion in the polynuclear complexes.

The high stability of lead(II) complexes of the macrocyclic and open-chain polyamines, as well as the ability to form polynuclear complexes exhibited by most of the amines, indicates these compounds are strong chelating agents towards Pb^{2+} in aqueous solution, suggesting their use for removing Pb^{2+} from contaminated aqueous media.

Considerations on the Macrocyclic Effect.—In order to analyse the macrocyclic effect[33] for the lead(II) complexes, the metathetical reaction $[Pb_nL_{oc}] + L_{cy} \longrightarrow [Pb_nL_{cy}] + L_{oc}$ (n = 1 or 2) has to be considered. This reaction presents clear positive log K values, *i.e.* there is a macrocyclic effect, only for mononuclear complexes of ligands containing six or less nitrogens. For binuclear complexes no such effect is observed. This situation is similar to that observed for complexes of Cu^{2+} and Zn^{2+},[12,13] and differs slightly from that found for Cd^{2+} where a macrocyclic effect was also observed for ligands containing seven nitrogen donor atoms, L^2 and L^9.[13] The relative sizes of the metal ions and co-ordination numbers account for these observations. The higher the co-ordination number and the larger the metal-ion size, the larger the ligand up to which a macrocyclic effect is observed.[12,13] Lead(II), although decreased in size due to the presence of the active lone pair, is still somewhat larger than Cu^{2+} and Zn^{2+} but presents lower co-ordination numbers.

However, in order to establish the identity of the prevailing species (macrocyclic or open-chain complexes) in solution the different basicities of the open-chain and cyclic amines have to be taken into account in addition to the stability constants of the complexes formed. Recently,[34,35] some of us have indicated that the best way to perform this comparison is to calculate distribution diagrams for the mixed-ligand systems L_{oc}–L_{cy}–Pb^{2+} and represent the overall percentages of formation as a function of pH. In Fig. 6 such diagrams have been calculated for a 1:1:1 molar ratio of L_{oc}:L_{cy}:Pb^{2+} for the system L^8–L^1–Pb^{2+} [Fig. 6(*a*)] and in 1:1:1 and 1:1:2 molar ratios for the systems L^9–L^2–Pb^{2+} [Fig. 6(*b*) and 6(*c*)] and L^{10}–L^3–Pb^{2+} [Fig. 6(*d*) and 6(*e*)]. In the system L^8–L^1–Pb^{2+}, as could be expected from the large difference in stability (Tables 3 and 4), the complexes of the cyclic amines clearly predominate over those of L^8. For the systems L^9–L^2–Pb^{2+} and L^{10}–L^3–Pb^{2+} in 1:1:1 ratio, although the differences in stability between the mononuclear complexes are very small, the reduced basicity of the cyclic amines still favours formation of the macrocyclic complexes. Finally, for these two systems in 1:1:2 molar ratio a cross-over is observed in the selectivity patterns; while at lower pH values the formation of cyclic amine complexes is favoured, at higher pH the open-chain amine complexes are preferred.

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