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Unusual binding of exogenous anions in some lead(II) complexes with a functionalized macrocycle

Massimo Di Vaira, Matteo Guerra, Fabrizio Mani and Piero Stoppioni

Dipartimento di Chimica, Università di Firenze, Via Maragliano 77, 50144 Firenze, Italy

The potentially hexadentate compound 1,4,7-tris(pyrazol-1-ylmethyl)-1,4,7-triazacyclononane (L) gave the complexes $[\{PbL(O_2CMe)\}_2][BPh_4]_2\cdot2EtOH$ **1**, $[PbL(ClO_4)]ClO_4$ **2** and $[PbL(BPh_4)]BPh_4$ **3**. The crystal structures of the three complexes have been determined by single-crystal X-ray diffraction. In all, the lead(II) ion is co-ordinated by the six nitrogen donors of the ligand and is bound in addition by three oxygen atoms from bridging acetate (**1**) or perchlorate (**2**) anions, or interacts at a large distance with all the carbon atoms of a phenyl group from a tetraphenylborate anion (**3**). The access to the metal by the exogenous anions is allowed by the co-ordination requirements of the large lead(II) ion which cannot be completely satisfied by the flexible L ligand.

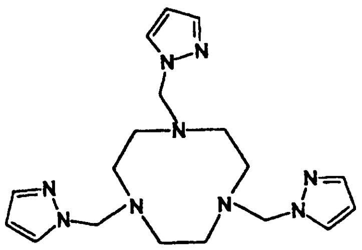
The problems posed by contamination of the environment by the heavy metals Cd, Hg and Pb are of outstanding importance. Amongst these metals, much of the attention in recent years has focused on Pb, due to its extensive industrial use and its toxicity to humans.[1] Even if the decreased use of leaded gasoline has reduced the release of lead into the atmosphere, other anthropogenic sources of lead contamination are pigment making, lead battery manufacturing and, especially, their disposal. The study of the co-ordination chemistry of Pb^{II} has been of crucial importance over the last few years in the search for chelating agents which may serve as metal-sequestring agents not only for environmental applications but also for biomedical purposes.[2,3]

We have previously reported on the synthesis of triazamacrocycles which have pyrazole groups appended to the nitrogen atoms and on their complexes with some transition[4,5] and alkali metals.[6] The information obtained on the solid-state structures of the complexes and their solution behaviour indicates that 1,4,7-tris(pyrazol-1-ylmethyl)-1,4,7-triazacyclononane (L) is a strong and versatile ligand which may bind metal atoms of different sizes and electronic requirements due to the flexibility of its pendant arms and to the sterically favourable arrangement of the nitrogen atoms.

Now we report on the synthesis and structural characterization of three lead(II) complexes which analyse as $PbL(O_2CMe)(BPh_4)\cdot EtOH$ **1**, $PbL(ClO_4)_2$ **2** and $PbL(BPh_4)_2$ **3**. Their crystal structures have revealed unusual binding behaviour of the macrocyclic ligand as well as of the exogenous anions towards Pb^{II}. In particular, it has been found that **3** contains one BPh_4^- anion loosely co-ordinated to Pb^{II} through a phenyl ring. We believe that these compounds may provide useful starting points for the design and synthesis of polydentate ligands which may serve as strong and selective chelating agents for Pb^{II}.

Experimental

All chemicals were reagent grade; solvents, when required by the synthetic procedures, were dried according to standard methods just before use. 1,4,7-Tris(pyrazol-1-ylmethyl)-1,4,7-triazacyclononane was prepared from 1,4,7-triazacyclononane[7] and 1-(hydroxymethyl)pyrazole[8] as previously described.[6,9] Lead(II) nitrate and acetate trihydrate, sodium perchlorate and tetraphenylborate were available commercially. Infrared spectra were recorded with a Perkin-Elmer 283 grating spectrophotometer as Nujol mulls between KBr plates. The ^{13}C NMR spectra of L and of the complexes were recorded with a Varian CFT 80 spectrometer operating at 20.00 MHz; chemical shifts are reported in ppm downfield with respect to the internal standard $SiMe_4$. ^{13}C NMR (L, $CDCl_3$): δ 139.0 (C^3, C^5), 129.1 (C^3, C^5), 105.3 (C^4), 72.5 (CH_2 bridge) and 52.8 (CH_2 macrocycle). The ^1H NMR spectrum of L in CH_2Cl_2 has been reported.[6]



L

Synthesis of the complexes

$[PbL(O_2CMe)(BPh_4)]\cdot EtOH$. The salt $Pb(O_2CMe)_2\cdot3H_2O$ (0.230 g, 0.50 mmol) dissolved in methanol (20 cm^3) was added to a warm solution of compound L (0.185 g, 0.50 mmol) in absolute ethanol (20 cm^3). Addition of sodium tetraphenylborate (0.342 g, 1.00 mmol) in acetone (20 cm^3) and concentration of the resulting solution to small volume yielded colourless crystals of the complex. The product contains ethanol of crystallization as inferred from the IR data [ν(OH) 3340 cm^{-1}] and confirmed by the X-ray analysis. The crystals used for the latter were obtained by slow evaporation at room temperature of a dilute solution of the complex in acetone–ethanol (50:50) (Found: C, 55.6; H, 5.60; N, 11.8. Calc. for $C_{46}H_{56}BN_9O_3Pb$: C, 55.2; H, 5.65; N, 12.6%). ^{13}C NMR [$(CD_3)_2CO$]: δ 142.5 (C^3, C^5), 133.1 (C^3, C^5), 107.2 (C^4), 72.6 (bridge-CH_2), 50.6 (macrocycle-CH_2), 137.1, 126.1 and 122.3 (BPh_4).

$[PbL(ClO_4)_2]$. A warm solution in water (50 cm^3) of both $Pb(NO_3)_2$ (0.166 g, 0.50 mmol) and $NaClO_4\cdot H_2O$ (0.140 g, 1.0 mmol) was added to a warm solution of compound L (0.185 g, 0.50 mmol) in ethanol–methanol (50:50, 30 cm^3). The colourless solid compound which immediately formed was discarded by filtration and slow evaporation at room temperature of the solution gave colourless crystals suitable for X-ray analysis.

The IR spectrum indicated that the product contains some solvate water [ν(OH) 3540, ν(HOH) 1630 cm^{-1}]. Repeated preparations of the compound under the same experimental conditions gave crystalline products with variable amounts of water content as inferred from the analytical data and the IR spectrum. However, the presence of water molecules was not revealed by the X-ray analysis, presumably due to disordered arrangement of the solvate molecules. Here we report representative values of the elemental analysis data compared with those calculated for the anhydrous compound (Found: C, 27.1; H, 3.60; N, 15.6. Calc. for $C_{18}H_{27}Cl_2N_9O_8Pb$: C, 27.9; H, 3.50; N, 16.2%). ^{13}C NMR (CD_3CN): δ 143.4 (C^3, C^5), 134.0 (C^3, C^5), 108.0 (C^4), 72.6 (bridge-CH_2) and 51.5 (macrocycle-CH_2).

[PbL(BPh$_4$)$_2$]. A solution in water (20 cm^3) of $Pb(NO_3)_2$ (0.166 g, 0.50 mmol) was added to a warm solution of compound L (0.185 g, 0.50 mmol) in ethanol (20 cm^3). A solution of $NaBPh_4$ (0.342 g, 1.00 mmol) in acetone (20 cm^3) was subsequently added to the filtered solution of the reactants. Evaporation at room temperature of the resulting solution gave a colourless crystalline product; its recrystallization from acetone–ethanol (50:50) gave crystals suitable for X-ray analysis. The solid contained acetone from the solvent [ν(CO) 1710 cm^{-1}] which, however, was not revealed by the X-ray analysis (Found: C, 64.7; H, 5.80; N, 9.60. Calc. for $C_{66}H_{67}B_2N_9Pb$: C, 65.2; H, 5.55; N, 10.4%). The complex is not sufficiently soluble in the common deuteriated solvents to give a meaningful ^{13}C NMR spectrum.

Crystal structure determinations

Crystal data and refinement parameters for the compounds [{PbL(O_2CMe)}$_2$][BPh$_4$]$_2$·2EtOH **1**, [PbL(ClO_4)]ClO_4 **2** and [PbL(BPh_4)]BPh_4 **3** are given in Table 1. All operations were performed at 295 K using an Enraf-Nonius CAD4 diffractometer and graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å). Unit-cell parameters were obtained for each compound from the settings of 24 reflections with $13 < \theta < 15°$. The ω–2θ scan mode was used in the data collections. Compound **3** provided worse diffraction data than the others, characterized by a rather rapid decay of the intensities with θ. The intensities of standard reflections monitored periodically failed to reveal any crystal decay during the data collections. An empirical absorption correction was applied to all data after structure solution at isotropic convergence.[10] The principal computer programs used in the crystallographic calculations are listed in refs. 10–14. The atomic scattering factors were from refs. 12 (C, H, B, Cl, N and O) and 15 (Pb), the latter being corrected for anomalous dispersion.[16]

The structures were solved by combinations of direct and heavy-atom methods, which provided the positions of all the non-hydrogen atoms. The atoms of the ethanol solvate molecule in complex **1** were identified on the basis of the peak heights in Δ*F* maps, of the bond lengths, and of possible hydrogen-bond formation by the EtOH oxygen with the acetate ligand. On the other hand, the H_2O (**2**) or Me_2CO (**3**) solvent molecules which, mainly on the basis of the IR data, were expected to be present also in the structures of the other compounds could not be located, probably due to disordered arrangements or poor quality data (**3**). Hydrogen atoms were always introduced in calculated positions (the hydroxyl H atom of the solvent molecule in **1** was not introduced), with C–H 0.96 Å and isotropic $U_H = 1.2U_C$, where U_C is the isotropic or equivalent isotropic thermal parameters of the respective carbon atom. In the final refinement of the model for **1** all the non-hydrogen atoms were assigned anisotropic thermal parameters, except for the atoms of the solvent, which were refined isotropically. The refinement for all the non-hydrogen atoms of **2** was anisotropic.

The structure of complex **3** was initially solved and refined in the triclinic space group $P\bar{1}$ but, following the suggestion of a referee, it was finally refined in the monoclinic *C*2/*c* space group, after the appropriate data transformation. Owing to problems posed by large thermal motion or disorder mostly affecting two pyrazole groups and the connecting chains in the cation, a constrained refinement procedure had to be applied, as in the previous refinement of a zinc complex formed by a closely related ligand.[5] The lengths of the bonds considered to be chemically equivalent within the L ligand (the six macrocyclic N–C distances and the groups of three N–N, C–C and remaining N–C distances) were tied, allowing for rather

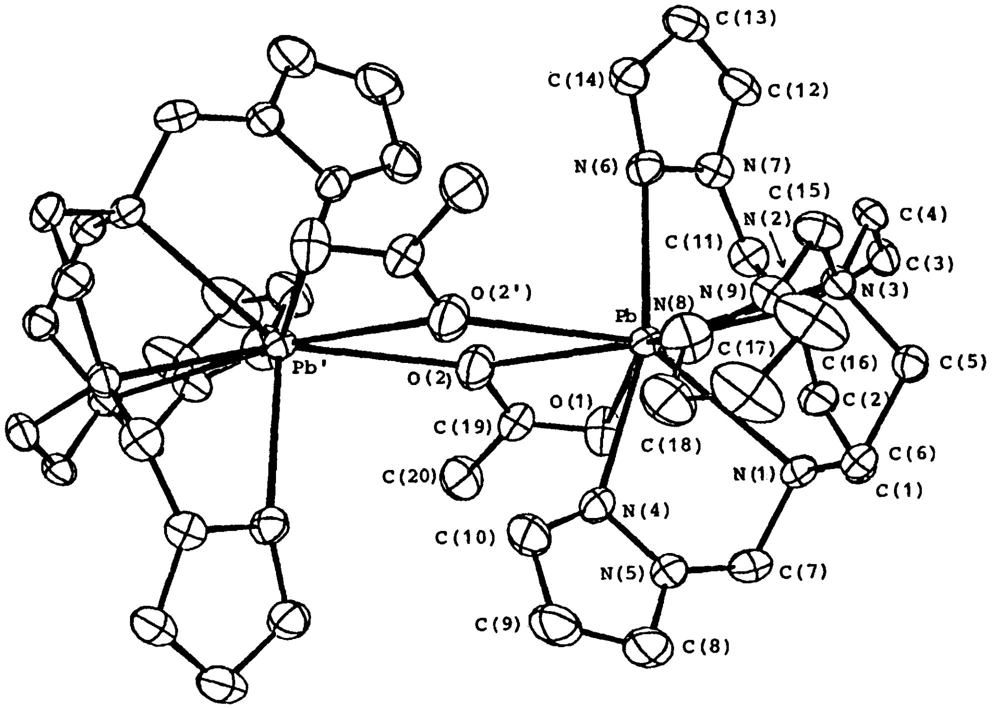


Fig. 1 View of the dimeric cation [{PbL(O_2CMe)}$_2$]$^{2+}$ in the structure of complex **1**, with 20% probability ellipsoids. Primed atoms are related to unprimed ones by an inversion centre

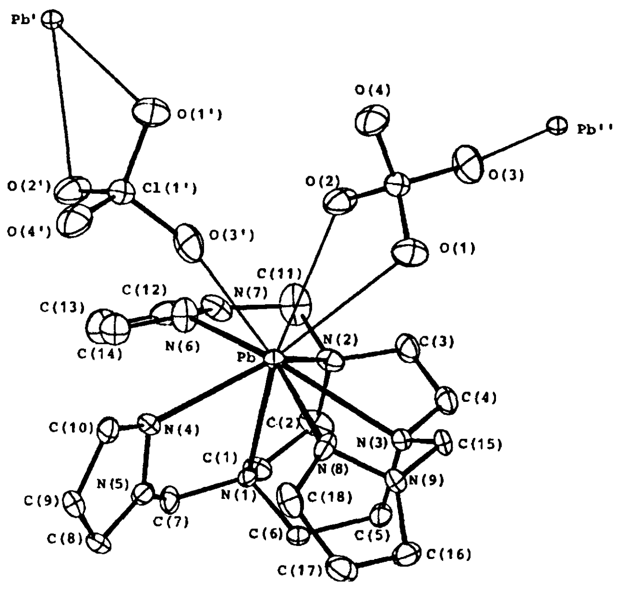


Fig. 2 View of part of the chain of $[PbL(ClO_4)]^+$ units in the structure of complex **2**, with 20% probability ellipsoids. Primed atoms are related to unprimed ones by a glide plane; Pb″ is related to Pb′ by a unit translation along the *c* axis

large estimated standard deviations, to unique values, which were refined. A small damping factor was applied to improve convergence. In the final model all non-hydrogen atoms were refined anisotropically, except for the boron atoms and the *ipso*-carbon atoms of the phenyl rings. In spite of the constraints on the L ligand geometry, some bond angles in a pyrazole group lie outside the ranges of values usually found. However, this should not invalidate the chemically significant information on the lead atom environment. The least-squares refinements for **1** and **3** were performed in two blocks due to the large numbers of parameters.

The atomic coordinates are given in Tables 5–6 and selected bond lengths and angles in Tables 1–3. The structures of the cations are shown in Figs. 1–3.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Results and Discussion

The potentially hexadentate compound 1,4,7-tris(pyrazol-1-ylmethyl)-1,4,7-triazacyclononane (L) was obtained by the one-step reaction of the macrocycle 1,4,7-triazacyclononane[7] with 1-(hydroxymethyl)pyrazole[8] in anhydrous MeCN solution.[6,9] Its reaction with lead(II) salts in equimolar ratio and in the appropriate solvents gave crystalline compounds $[\{PbL(O_2CMe)\}_2][BPh_4]_2\cdot 2EtOH$ **1**, $[PbL(ClO_4)]ClO_4$ **2** and $[PbL(BPh_4)]BPh_4$ **3**. The solid-state structures of the complexes have been established by X-ray diffraction methods. The ^{13}C NMR spectra of **1** and **2** are very similar (apart from the signals due to the BPh_4^- anion in **1**). In both compounds the complexation reaction produces significant shifts of the resonances of the ligand carbons; most of these shifts are downfield with respect to those of free L. The single signal observed for each carbon atom might be accounted for by the presence of only one species in solution. Owing to the poor solubility of complex **3** in common deuteriated solvents, its ^{13}C NMR spectrum is meaningless.

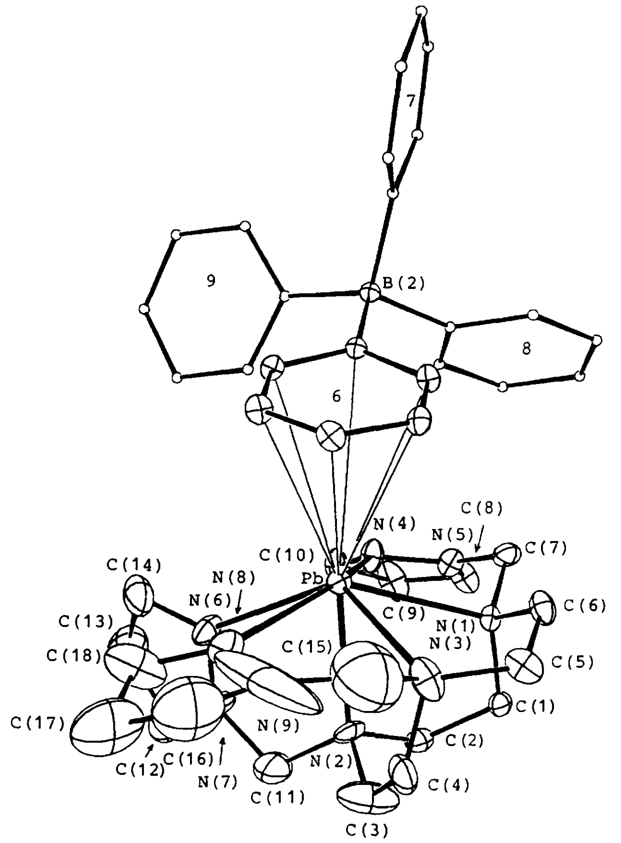


Fig. 3 A view of the $[PbL(BPh_4)]^+$ cation in the structure of **3**. Due to large thermal motion or disordered arrangement of some atoms, 10% probability ellipsoids are shown. For clarity the carbon atoms of three BPh_4^- phenyl groups have been assigned fixed radii and only serial numbers of all phenyl groups are given. Thin connecting lines mark the long Pb ··· C(Ph) interactions

Table 1 Selected bond distances (Å) and angles (°) for $[\{PbL(O_2CMe)\}_2][BPh_4]_2\cdot 2EtOH$ **1** *

Pb–N(1)	2.770(9)	Pb–O(1)	2.503(8)
Pb–N(2)	2.805(5)	Pb–O(2)	2.725(9)
Pb–N(3)	2.906(7)	Pb–O(2′)	2.925(8)
Pb–N(4)	2.543(8)	Pb ··· Pb′	4.960(2)
Pb–N(6)	2.873(9)	O(2) ··· O(2′)	2.71(1)
Pb–N(8)	3.047(11)		
N(1)–Pb–N(2)	63.2(2)	N(3)–Pb–O(1)	132.9(2)
N(1)–Pb–N(3)	62.4(2)	N(3)–Pb–O(2)	170.2(3)
N(1)–Pb–N(4)	66.2(2)	N(3)–Pb–O(2′)	124.7(3)
N(1)–Pb–N(6)	125.1(2)	N(4)–Pb–N(6)	163.3(3)
N(1)–Pb–N(8)	83.6(3)	N(4)–Pb–N(8)	72.4(3)
N(1)–Pb–O(1)	79.8(3)	N(4)–Pb–O(1)	76.2(3)
N(1)–Pb–O(2)	123.7(3)	N(4)–Pb–O(2)	80.4(3)
N(1)–Pb–O(2′)	137.7(3)	N(4)–Pb–O(2′)	73.2(3)
N(2)–Pb–N(3)	62.5(2)	N(6)–Pb–N(8)	118.6(3)
N(2)–Pb–N(4)	125.5(2)	N(6)–Pb–O(1)	93.1(3)
N(2)–Pb–N(6)	62.3(2)	N(6)–Pb–O(2)	82.9(3)
N(2)–Pb–N(8)	119.3(3)	N(6)–Pb–O(2′)	97.1(3)
N(2)–Pb–O(1)	76.3(2)	N(8)–Pb–O(1)	148.2(3)
N(2)–Pb–O(2)	112.1(2)	N(8)–Pb–O(2)	128.5(3)
N(2)–Pb–O(2′)	158.9(3)	N(8)–Pb–O(2′)	73.2(3)
N(3)–Pb–N(4)	109.4(3)	O(1)–Pb–O(2)	47.8(3)
N(3)–Pb–N(6)	87.3(2)	O(1)–Pb–O(2′)	101.9(2)
N(3)–Pb–N(8)	57.2(2)	O(2)–Pb–O(2′)	57.3(3)

[a] Symmetry operation: ′ $-x, -y, -z$.

The structure of compound **1** consists of dimeric $[\{PbL(O_2CMe)\}_2]^{2+}$ cations, BPh_4^- anions and ethanol solvate molecules. Each metal atom in the dimeric, centrosymmetric, cation (Fig. 1) is co-ordinated by the six N donor atoms of the L ligand (three macrocycle, N_m, and three pyrazole, N_p) and by three oxygen atoms from the two bridging acetate ligands. Each acetate acts as a chelating ligand toward one metal atom and is bridging between the two metals through one of its oxygen atoms. Also in the structure of **2** the lead atom is co-ordinated by six N atoms and three O atoms (Fig. 2), provided by two symmetry-related ClO_4^- anions. One of the anions in this structure is unco-ordinated, whereas the other acts as a bidentate ligand toward one metal and as a monodentate ligand with respect to a second; conversely, an anion symmetry-related to the latter donates one oxygen to the first lead atom considered. In this way chains with the $[PbL(ClO_4)]^+$ repeat unit are formed, parallel to the crystallographic *c* axis, with interspersed, unco-ordinated, ClO_4^- anions. In the structure of compound **3**, containing $[PbL]^{2+}$ cations (Fig. 3) and BPh_4^- anions, the metal atom is co-ordinated by the six N atoms of the ligand. Moreover, a phenyl group of a BPh_4^- anion approaches the metal from the opposite side to that spanned by the L ligand, forming Pb $\cdots$ C distances in the van der Waals range (3.47–3.63 Å; 3.24 Å distance from Pb^{II} to the centroid of the phenyl ring).

The lead–donor atom distances exhibited by the three complexes (Tables 1–3) are spread over a wide range of values, essentially as is found for other lead(II) complexes with related ligands.[3,17–24] In the mean, the Pb–N distances in the present compounds are affected by the space requirements of the coligands. The mean in **1**, where the acetate groups are comparatively tightly bound, is about 0.16 Å larger than in **2**, where the perchlorate anions are rather loosely bound. Finally, the mean in **3**, where the phenyl group interacts from a very large distance, is smaller than in **2**, by 0.05 Å. On comparing the $Pb–N_p$ and $Pb–N_m$ distances within a given cation the mean of the former essentially matches that of the latter in **1** and, separately, in **2**, but it is about 0.12 Å larger than the latter in **3**. Overall, the present $Pb–N_m$ distances are somewhat longer than those formed by unsubstituted macrocycles.[3,19,20] The Pb–O distances in **1** are long compared to those found for lead

Table 2 Selected bond distances (Å) and angles (°) for $[PbL(ClO_4)]ClO_4$ **2***

Pb–N(1)	2.596(8)	Pb–N(8)	2.860(10)
Pb–N(2)	2.663(9)	Pb–O(1)	3.189(10)
Pb–N(3)	2.721(8)	Pb–O(2)	3.135(11)
Pb–N(4)	2.587(9)	Pb–O(3′)	2.950(11)
Pb–N(6)	2.539(10)		
N(1)–Pb–N(2)	67.6(3)	N(3)–Pb–N(8)	63.4(3)
N(1)–Pb–N(3)	68.3(3)	N(3)–Pb–O(1)	76.0(3)
N(1)–Pb–N(4)	67.5(3)	N(3)–Pb–O(2)	99.5(3)
N(1)–Pb–N(6)	79.0(3)	N(3)–Pb–O(3′)	146.5(3)
N(1)–Pb–N(8)	88.8(3)	N(4)–Pb–N(6)	80.4(3)
N(1)–Pb–O(1)	144.2(3)	N(4)–Pb–N(8)	75.1(3)
N(1)–Pb–O(2)	140.1(3)	N(4)–Pb–O(1)	136.4(3)
N(1)–Pb–O(3′)	138.9(3)	N(4)–Pb–O(2)	141.4(3)
N(2)–Pb–N(3)	63.9(3)	N(4)–Pb–O(3′)	73.5(3)
N(2)–Pb–N(4)	128.6(3)	N(6)–Pb–N(8)	155.3(3)
N(2)–Pb–N(6)	67.7(3)	N(6)–Pb–O(1)	124.7(3)
N(2)–Pb–N(8)	127.1(3)	N(6)–Pb–O(2)	81.1(3)
N(2)–Pb–O(1)	95.0(3)	N(6)–Pb–O(3′)	82.5(3)
N(2)–Pb–O(2)	73.0(3)	N(8)–Pb–O(1)	77.0(3)
N(2)–Pb–O(3′)	135.7(3)	N(8)–Pb–O(2)	120.6(3)
N(3)–Pb–N(4)	118.4(3)	N(8)–Pb–O(3′)	93.3(3)
N(3)–Pb–N(6)	128.8(3)		

* Symmetry operation: ′ $x, \frac{1}{2} - y, \frac{1}{2} + z$.

Table 3 Selected bond distances (Å) and angles (°) for $[PbL(BPh_4)]BPh_4$ **3**

Pb–N(1)	2.564(9)	Pb–N(4)	2.722(13)
Pb–N(2)	2.516(11)	Pb–N(6)	2.513(12)
Pb–N(3)	2.581(16)	Pb–N(8)	2.770(16)
N(1)–Pb–N(2)	68.6(3)	N(2)–Pb–N(8)	85.9(4)
N(1)–Pb–N(3)	66.8(4)	N(3)–Pb–N(4)	128.8(4)
N(1)–Pb–N(4)	64.1(3)	N(3)–Pb–N(6)	123.5(5)
N(1)–Pb–N(6)	124.6(3)	N(3)–Pb–N(8)	68.4(4)
N(1)–Pb–N(8)	134.0(4)	N(4)–Pb–N(6)	76.4(4)
N(2)–Pb–N(3)	68.5(4)	N(4)–Pb–N(8)	150.3(4)
N(2)–Pb–N(4)	80.8(4)	N(6)–Pb–N(8)	74.1(4)
N(2)–Pb–N(6)	68.1(4)		

Table 4 Crystallographic data for $[\{PbL(O_2CMe)\}_2][BPh_4]_2 \cdot 2EtOH$ **1**, $[PbL(ClO_4)]ClO_4$ **2** and $[PbL(BPh_4)]BPh_4$ **3**

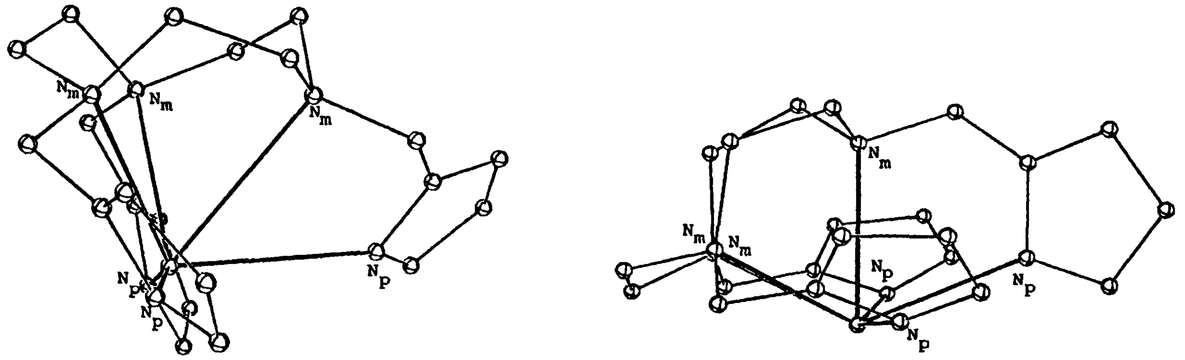
	1	**2**	**3**
Formula	$C_{92}H_{112}B_2N_{18}O_6Pb_2$	$C_{18}H_{27}Cl_2N_9O_8Pb$	$C_{66}H_{67}B_2N_9Pb$
M	2002.04	775.57	1215.14
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$C2/c$
a/Å	11.845(6)	8.853(2)	34.006(4)
b/Å	12.166(5)	30.303(7)	13.241(4)
c/Å	17.439(6)	9.557(9)	26.445(3)
α/°	101.43(4)		
β/°	103.28(4)	92.29(7)	107.84(8)
γ/°	107.48(4)		
U/Å^3	2234(2)	2562(3)	11 335(7)
Z	1	4	8
D_c/g cm^{-3}	1.487	2.010	1.424
F(000)	1012	1512	4944
Crystal size/mm	0.10 × 0.30 × 0.40	0.10 × 0.20 × 0.80	0.10 × 0.40 × 0.80
μ/mm^{-1}	7.71	6.90	3.05
Range of absorption correction factor[a]	1.11–0.79	1.01–0.93	1.06–0.86
Scan width[b]/°	1.10	1.10	0.90
Scan speed/° min^{-1}	1.5–5	1.5–5	3–8
Collection range/°	$5 \leqslant 2\theta \leqslant 54$	$5 \leqslant 2\theta \leqslant 52$	$5 \leqslant 2\theta \leqslant 46$
Data collected	$\pm h, \pm k, +l$	$\pm h, +k, +l$	$\pm h, \pm k, +l$[c]
No. unique data	8510	4123	7362
No. observed data[d]	6199	3403	4427
No. parameters	532	343	669
g[e]	0.0025	0.0005	0.0010
R[f]	0.050	0.049	0.065
R'[g]	0.066	0.057	0.073
Maximum, minimum electron density/e Å^{-3}[h]	0.9, −1.2	1.7, −1.3	1.7, −1.3

[a] Empirical correction applied, see text. In the case of complex **3** the correction was applied before the transformation from the triclinic to the monoclinic model. [b] Value of the *a* parameter in the formula $(a + 0.35 \tan \theta)°$ for the scan width. [c] Data collected in triclinic setting (13 012 unique reflections), see text. [d] Reflections with $I > 3\sigma_I$. [e] Value of *g* in the formula $w^{-1} = \sigma^2(F_o) + gF_o^2$ for the weighting scheme. [f] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [g] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$. [h] The highest peaks in the final Fourier-difference maps were near the metal atom position and had no chemical meaning.

Table 5 Fractional coordinates of the non-hydrogen atoms of $[\{PbL(O_2CMe)\}_2][BPh_4]_2{\cdot}2EtOH$ **1** *

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pb	0.111 29(3)	0.017 20(3)	0.143 44(2)	C(19)	0.216 6(9)	0.117 4(9)	0.022 2(6)
N(1)	0.303 7(6)	−0.043 5(7)	0.224 2(4)	C(20)	0.279 9(14)	0.147 9(16)	−0.039 4(8)
N(2)	0.290 3(6)	0.192 6(6)	0.283 7(4)	C(21)	−0.305 7(8)	−0.350 6(8)	0.368 3(5)
N(3)	0.112 6(7)	−0.023 5(6)	0.302 2(4)	C(22)	−0.334 1(8)	−0.473 3(8)	0.334 7(5)
N(4)	0.145 3(7)	−0.154 8(7)	0.054 3(4)	C(23)	−0.253 2(9)	−0.530 9(9)	0.361 0(6)
N(5)	0.234 5(8)	−0.188 3(8)	0.090 5(5)	C(24)	−0.143 1(10)	−0.467 9(11)	0.422 2(7)
N(6)	0.067 3(7)	0.233 8(7)	0.201 6(5)	C(25)	−0.113 3(10)	−0.349 4(11)	0.455 6(7)
N(7)	0.167 3(7)	0.314 4(6)	0.262 5(5)	C(26)	−0.191 3(9)	−0.290 8(10)	0.429 0(6)
N(8)	−0.052 5(10)	−0.216 9(9)	0.161 3(7)	C(31)	−0.331 6(8)	−0.146 1(8)	0.337 6(5)
N(9)	−0.051 5(8)	−0.210 7(8)	0.234 8(5)	C(32)	−0.338 7(9)	−0.111 5(9)	0.264 7(6)
C(1)	0.412 5(8)	0.057 5(10)	0.281 3(6)	C(33)	−0.277 3(12)	0.008 4(11)	0.266 4(9)
C(2)	0.406 2(8)	0.179 3(9)	0.276 5(6)	C(34)	−0.209 8(12)	0.096 6(11)	0.339 6(9)
C(3)	0.270 1(8)	0.186 8(8)	0.363 6(5)	C(35)	−0.199 5(10)	0.066 3(9)	0.410 7(8)
C(4)	0.143 7(8)	0.098 3(7)	0.354 4(5)	C(36)	−0.260 8(10)	−0.053 7(9)	0.408 6(6)
C(5)	0.200 4(9)	−0.080 4(8)	0.331 1(5)	C(41)	−0.479 4(7)	−0.274 7(7)	0.408 6(4)
C(6)	0.247 4(9)	−0.133 3(9)	0.264 5(6)	C(42)	−0.519 1(7)	−0.370 8(7)	0.441 5(5)
C(7)	0.342 1(10)	−0.104 0(11)	0.158 5(7)	C(43)	−0.596 7(8)	−0.375 3(8)	0.490 6(5)
C(8)	0.215 7(16)	−0.303 6(12)	0.050 0(8)	C(44)	−0.635 3(8)	−0.280 1(9)	0.510 5(5)
C(9)	0.108 4(14)	−0.342 2(11)	−0.013 5(8)	C(45)	−0.596 7(9)	−0.182 2(9)	0.480 6(6)
C(10)	0.068 3(12)	−0.248 5(9)	−0.007 4(7)	C(46)	−0.521 1(8)	−0.179 9(8)	0.430 4(5)
C(11)	0.286 3(9)	0.306 5(8)	0.267 8(6)	C(51)	−0.507 9(9)	−0.367 4(8)	0.250 2(5)
C(12)	0.140 4(11)	0.396 0(9)	0.311 2(6)	C(52)	−0.633 4(10)	−0.409 0(8)	0.235 0(6)
C(13)	0.013 3(12)	0.365 6(10)	0.280 6(7)	C(53)	−0.717 4(13)	−0.488 8(11)	0.162 9(9)
C(14)	−0.026 6(10)	0.265 9(10)	0.214 2(7)	C(54)	−0.672 9(21)	−0.524 8(14)	0.099 7(10)
C(15)	−0.013 4(10)	−0.097 0(8)	0.291 5(7)	C(55)	−0.551 0(20)	−0.484 9(16)	0.107 8(8)
C(16)	−0.088 8(15)	−0.318 3(12)	0.245 8(10)	C(56)	−0.467 4(13)	−0.404 9(11)	0.183 8(6)
C(17)	−0.108 5(16)	−0.402 9(11)	0.178 5(10)	**B**	−0.404 2(10)	−0.283 1(9)	0.340 0(6)
C(18)	−0.088 7(14)	−0.340 1(12)	0.125 4(9)	O(61)	0.518 0(24)	0.076 8(22)	0.078 0(14)
O(1)	0.279 5(7)	0.121 0(7)	0.089 6(4)	C(62)	0.614(3)	0.159(3)	0.078 4(19)
O(2)	0.104 2(8)	0.090 6(8)	0.005 2(5)	C(63)	0.623 2(22)	0.268 5(20)	0.129 0(14)

* Atoms N(1)–C(18) belong to the L ligand, O(1)–C(20) to the acetate ligand, C(21)–**B** to the tetraphenylborate anion and O(61)–C(63) to the ethanol solvate molecule. The coordinates of a symmetry-independent set of atoms in the complex, which is centrosymmetric, are listed.



(*a*) (*b*)

Fig. 4 Schematic representations of the PbL part of (*a*) the centrosymmetric $[\{PbL(O_2CMe)\}_2]^{2+}$ cation in **1** (N_m = macrocycle N atom, N_p = pyrazole N atom) and (*b*) the $[PbL]^{2+}$ cation in **2**; the arrangement about the metal atom in **3** is closely similar to that found for **2**

carboxylates, in the absence of macrocyclic coligands (2.32–2.79 Å in refs. 21 and 22), and are also longer than those formed by a chelating acetate (2.49 Å, mean in ref. 23) in the presence of a large but unsubstituted macrocycle. Finally, the Pb–O distances formed by the co-ordinating perchlorate anion in **2** are in the (wide) range of those reported for related structures.[3,18,20,24]

According to Figs. 1–3 the L ligand spans essentially half of the space around the metal atom, allowing access to the metal by other ligands. Such an arrangement appears to be imposed by the size of the lead atom and differs significantly from that, with approximate three-fold symmetry, previously detected for complexes with smaller metal atoms formed by the present L ligand[6] or by a related[5] functionalized macrocycle. Moreover, as should be apparent from the schematic representations in Fig. 4, there are also differences in the conformation attained by L in complex **1**, compared to that in **2** or **3**. Essentially, the three $Pb–N_p$ bonds, which are almost coplanar in all cases, lie on one side of the metal atom in **2** and **3**, but not in **1**, the mean of the two acute $N_p–Pb–N_p$ angles being 95.5 (**1**), 77.7 (**2**) and 75.1° (**3**). The difference between **1** and the other two compounds may be caused by the fact that the group of O-donor atoms in **2** or the phenyl group in **3** spans a rather large cone with its vertex at the metal atom, whereas the O-donor atoms in **1** approximately lie in a plane containing also the metal atom. Fig. 4 also shows that the metal atom approximately lies in a plane with five of the N donor atoms in the structures of **2** and **3**, but not in that of **1**.

In an attempt to understand the nature of the interaction between the LPb^{2+} metal fragment and the co-ordinating phenyl group in **3**, extended-Hückel calculations with the program CACAO[25] were performed on a model with the L ligand replaced by six properly arranged NH_3 groups and the BPh_4^- phenyl group by a benzene molecule. Favourable

Table 6 Fractional coordinates of the non-hydrogen atoms of $[PbL(ClO_4)]ClO_4$ **2***

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pb	0.350 97(4)	0.162 63(1)	−0.254 46(4)	C(10)	0.462 7(14)	0.100 2(4)	0.058 0(11)
N(1)	0.171 4(10)	0.095 4(3)	−0.287 9(9)	C(11)	0.042 8(17)	0.213 9(6)	−0.373 8(16)
N(2)	0.122 1(11)	0.178 9(3)	−0.436 4(11)	C(12)	−0.137 5(16)	0.203 3(5)	−0.166 7(23)
N(3)	0.371 8(10)	0.125 8(3)	−0.512 7(9)	C(13)	−0.114 3(19)	0.186 2(7)	−0.031 4(21)
N(4)	0.357 0(10)	0.111 1(3)	−0.038 5(10)	C(14)	0.044 1(17)	0.177 9(5)	−0.022 5(17)
N(5)	0.281 9(10)	0.072 8(3)	−0.063 3(9)	C(15)	0.533 1(12)	0.121 6(4)	−0.533 3(11)
N(6)	0.117 7(11)	0.190 2(4)	−0.135 5(12)	C(16)	0.665 2(13)	0.051 8(4)	−0.443 0(14)
N(7)	0.004 3(12)	0.204 7(4)	−0.227 0(14)	C(17)	0.704 6(14)	0.037 1(5)	−0.316 0(16)
N(8)	0.601 7(11)	0.105 0(3)	−0.292 9(10)	C(18)	0.666 0(13)	0.070 9(5)	−0.222 9(13)
N(9)	0.601 9(10)	0.093 2(3)	−0.428 5(9)	Cl(1)	0.519 4(3)	0.267 85(10)	−0.391 5(3)
C(1)	0.019 6(13)	0.106 6(4)	−0.349 8(14)	O(1)	0.586 0(12)	0.224 2(3)	−0.406 6(11)
C(2)	0.015 2(16)	0.141 1(5)	−0.458 8(18)	O(2)	0.370 1(10)	0.262 7(3)	−0.335 5(11)
C(3)	0.197 4(16)	0.190 9(5)	−0.563 7(13)	O(3)	0.508 0(13)	0.288 4(4)	−0.524 9(10)
C(4)	0.304 6(15)	0.157 5(4)	−0.615 2(12)	O(4)	0.611 1(11)	0.294 5(3)	−0.299 1(10)
C(5)	0.292 5(13)	0.082 3(4)	−0.519 3(11)	Cl(2)	−0.085 3(4)	0.064 4(1)	0.205 0(3)
C(6)	0.254 2(12)	0.063 9(4)	−0.375 6(11)	O(5)	0.036 8(16)	0.091 9(5)	0.190 5(13)
C(7)	0.145 9(13)	0.074 7(4)	−0.149 1(11)	O(6)	−0.042 7(21)	0.034 7(5)	0.310 6(18)
C(8)	0.333 9(16)	0.039 4(4)	0.016 6(12)	O(7)	−0.116 7(16)	0.046 8(5)	0.071 8(13)
C(9)	0.453 9(17)	0.056 1(4)	0.096 7(13)	O(8)	−0.206 2(20)	0.086 9(9)	0.245 0(18)

* Atoms Pb–C(18) belong to the cation and the other atoms to the anions.

Table 7 Fractional coordinates of the non-hydrogen atoms of $[PbL(BPh_4)]BPh_4$ **3***

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pb	0.163 75(2)	0.302 23(4)	0.164 04(2)	C(36)	0.032 8(4)	0.823 4(10)	0.012 9(5)
N(1)	0.158 1(3)	0.477 7(7)	0.121 3(3)	C(41)	0.121 9(4)	0.737 6(9)	−0.007 8(5)
N(2)	0.091 7(4)	0.336 0(9)	0.104 1(5)	C(42)	0.134 9(4)	0.766 4(9)	0.045 5(5)
N(3)	0.125 9(5)	0.431 7(11)	0.205 6(5)	C(43)	0.176 7(4)	0.770 6(9)	0.077 2(5)
N(4)	0.179 5(4)	0.311 4(8)	0.069 3(4)	C(44)	0.206 6(4)	0.743 1(10)	0.055 4(5)
N(5)	0.182 8(3)	0.405 9(8)	0.055 5(4)	C(45)	0.195 1(4)	0.714 0(9)	0.003 9(5)
N(6)	0.130 2(4)	0.145 2(9)	0.116 6(5)	C(46)	0.153 9(4)	0.712 3(10)	−0.027 1(5)
N(7)	0.094 0(4)	0.163 2(11)	0.083 5(6)	C(51)	0.064 8(4)	0.652 4(10)	−0.089 5(5)
N(8)	0.126 0(4)	0.209 8(10)	0.231 0(5)	C(52)	0.079 5(4)	0.555 2(11)	−0.075 0(6)
N(9)	0.112 8(10)	0.265 6(15)	0.263 3(12)	C(53)	0.071 4(5)	0.470 6(12)	−0.107 4(7)
C(1)	0.117 3(3)	0.503 0(8)	0.084 1(5)	C(54)	0.049 2(6)	0.481 2(17)	−0.157 7(9)
C(2)	0.092 2(4)	0.411 3(9)	0.063 8(4)	C(55)	0.031 5(6)	0.572 8(18)	−0.175 9(7)
C(3)	0.064 9(6)	0.379 3(20)	0.132 2(7)	C(56)	0.040 5(5)	0.656 7(14)	−0.142 3(6)
C(4)	0.080 8(5)	0.422 2(13)	0.185 3(9)	C(61)	0.274 8(3)	0.280 0(8)	0.222 4(4)
C(5)	0.139 2(5)	0.535 5(12)	0.201 8(5)	C(62)	0.258 3(3)	0.195 4(10)	0.240 4(4)
C(6)	0.167 4(4)	0.541 4(10)	0.169 1(5)	C(63)	0.235 7(4)	0.202 8(11)	0.276 1(5)
C(7)	0.191 0(4)	0.479 3(10)	0.097 5(5)	C(64)	0.227 9(4)	0.293 4(11)	0.295 2(5)
C(8)	0.177 1(5)	0.416 6(12)	0.003 3(5)	C(65)	0.242 1(4)	0.379 6(10)	0.276 3(5)
C(9)	0.169 0(6)	0.323 6(12)	−0.017 8(6)	C(66)	0.264 6(4)	0.372 6(9)	0.241 7(4)
C(10)	0.172 0(5)	0.259 4(10)	0.024 2(5)	C(71)	0.353 9(4)	0.284 8(9)	0.227 9(5)
C(11)	0.068 6(5)	0.249 3(11)	0.080 4(11)	C(72)	0.387 9(4)	0.292 5(11)	0.207 5(6)
C(12)	0.079 3(9)	0.095 0(19)	0.045 5(12)	C(73)	0.428 7(4)	0.291 6(12)	0.240 6(6)
C(13)	0.110 5(10)	0.029 3(21)	0.063 2(14)	C(74)	0.436 6(5)	0.290 8(14)	0.293 9(7)
C(14)	0.141 2(7)	0.052 2(13)	0.109 3(10)	C(75)	0.404 4(6)	0.287 0(13)	0.314 9(6)
C(15)	0.123 1(16)	0.362 3(25)	0.246 1(14)	C(76)	0.364 1(5)	0.285 4(11)	0.282 0(5)
C(16)	0.095 7(14)	0.194 8(25)	0.286 2(15)	C(81)	0.298 7(3)	0.364 1(9)	0.142 8(5)
C(17)	0.080 9(10)	0.108(3)	0.260 8(14)	C(82)	0.310 3(4)	0.463 9(10)	0.156 8(5)
C(18)	0.110 4(6)	0.119 4(14)	0.235 6(9)	C(83)	0.305 3(5)	0.541 0(10)	0.121 3(7)
C(21)	0.067 6(4)	0.854 0(11)	−0.076 4(5)	C(84)	0.289 8(4)	0.522 9(12)	0.067 3(7)
C(22)	0.099 3(5)	0.920 1(10)	−0.076 4(6)	C(85)	0.279 2(4)	0.426 3(12)	0.051 0(6)
C(23)	0.092 6(6)	1.010 9(12)	−0.100 6(7)	C(86)	0.283 2(4)	0.348 7(10)	0.087 8(5)
C(24)	0.053 5(6)	1.043 0(13)	−0.129 8(8)	C(91)	0.300 7(4)	0.163 1(9)	0.157 7(5)
C(25)	0.020 9(6)	0.981 3(14)	−0.130 0(7)	C(92)	0.262 4(5)	0.128 6(10)	0.127 7(5)
C(26)	0.027 8(5)	0.890 4(13)	−0.104 8(7)	C(93)	0.254 2(5)	0.034 1(10)	0.101 8(5)
C(31)	0.043 9(4)	0.736 2(10)	−0.008 7(5)	C(94)	0.287 0(6)	−0.026 3(11)	0.104 5(6)
C(32)	0.029 4(4)	0.646 3(11)	0.006 2(4)	C(95)	0.326 3(6)	0.003 5(10)	0.132 8(7)
C(33)	0.007 1(4)	0.641 2(12)	0.042 5(5)	C(96)	0.333 4(5)	0.095 7(10)	0.158 8(5)
C(34)	−0.002 5(4)	0.731 8(12)	0.063 8(5)	B(1)	0.074 1(5)	0.745 4(12)	−0.045 9(6)
C(35)	0.009 8(5)	0.820 9(12)	0.049 1(6)	B(2)	0.306 1(4)	0.271 8(10)	0.187 1(5)

* Atoms Pb–C(18) belong to the $[PbL]^{2+}$ cation and the other atoms to the two tetraphenylborate anions.

interactions to the bonding were found to exist between empty combinations of the metal orbitals (in particular one lying in the plane of the five 'equatorial' N atoms and antibonding with respect to the N donors) and some filled benzene orbitals, which are slightly depressed. An interaction of this sort had been discussed for a $Pb(AlCl_4)_2{\cdot}C_6H_6$ complex,[26] where the Pb · · · C distances are slightly shorter than in the present case. On the other hand, the highest occupied molecular orbital

(HOMO) of the LPb^{2+} metal fragment, which is the 'lead(II) lone pair' often referred to [3,19,20,22] (in the present case it points away from the region of the L ligand), has repulsive interactions with filled benzene orbitals, particularly with the a_1 π combination, preventing a closer approach of the two fragments. In view of the large distances involved, such interactions may be interpreted as indications of substantial polarization, rather than of true bonding effects; they should supplement the effect of purely electrostatic attraction.

In conclusion, the interactions of the lead(II) ion with either the acetate or the perchlorate groups in compounds **1** and **2** are imposed by the large size of the metal ion, the co-ordination requirements of which are not satisfied by the six donor atoms of the macrocyclic ligand, also due to its insufficient span despite its flexibility. The co-ordination in **3** by a phenyl group of the BPh_4^- anion, generally considered to have very little co-ordinating ability, which occurs in the presence of competing ligands such as water and the nitrate anion, might be surprising. It may be rationalized in terms of the large number of electrons involved in the (essentially van der Waals) interaction between the two parts of the $[PbL(BPh_4)]^+$ cation.

In spite of the inability of the 1,4,7-tris(pyrazol-1-ylmethyl)-1,4,7-triazacyclononane ligand fully to encapsulate the large lead(II) cation, it has been found to be able to bind the metal ion efficiently, both in the solid state and in solution. We are now undertaking the design of a new pyrazole-functionalized macrocycle of different size and donor atom set, which might exhibit better co-ordinating ability toward lead(II) and, possibly, good selectivity between metal ions.

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