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FULL PAPER

Tetraphenylborate adducts of lead(II) co-ordinated by imidazole-functionalized 1,4,7-triazacyclononanes: crystal and molecular structures

Massimo Di Vaira, Fabrizio Mani and Piero Stoppioni

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

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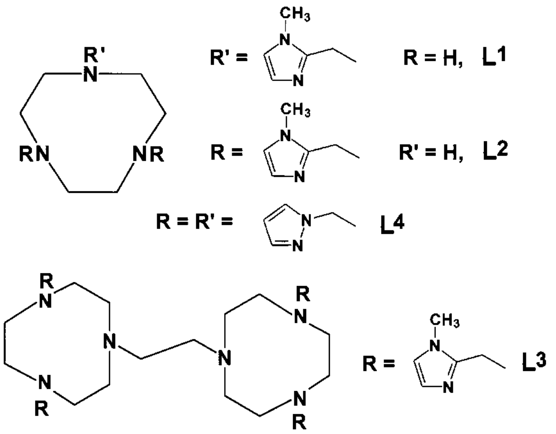
The new functionalized macrocycles 1-(1-methylimidazol-2-ylmethyl)-1,4,7-triazacyclononane, L^1, 1,4-bis(1-methylimidazol-2-ylmethyl)-1,4,7-triazacyclononane, L^2, and 1,2-bis[4,7-bis(1-methylimidazol-2-ylmethyl)-1,4,7-triazacyclonon-1-yl]ethane, L^3, have been synthesized. The reaction of hydrated lead(II) acetate with these compounds in the presence of sodium tetraphenylborate afforded the complexes $[PbL^1Cl(BPh_4)]\cdot 0.5MeCN$, $[PbL^2(BPh_4)]BPh_4$ and $[Pb_2L^3(BPh_4)_2][BPh_4]_2\cdot 4MeCN$ which were characterized in the solid state by elemental analyses and X-ray crystallography. The lead(II) atoms are co-ordinated by the nitrogens of the macrocyclic ring, by the nitrogen donor(s) of the pendant imidazole group(s) and, in the complex with the L^1 ligand, also by a chlorine atom. In each of the three complexes a phenyl group of a tetraphenylborate anion lies at close contact distance from the lead and completes its co-ordination.

Compared to other toxic elements such as arsenic, cadmium and mercury, lead plays a prominent role as environmental contaminant owing to its toxicity, worldwide extensive use, and production in large amounts.[1] For these reasons there recently has been renewed interest in the co-ordination chemistry of lead(II) and a number of lead complexes have been characterized with a variety of ligands.[2]

In the search for chelating ligands which may be suitable as heavy-metal sequestring agents we are interested in the preparation and characterization of lead(II) complexes with functionalized macrocycles. The nine-membered macrocycle 1,4,7-triazacyclononane functionalized with three N-bound imidazole or pyrazole groups provides some versatile and efficient ligands. Owing to the flexibility of the pendant arms employed, to the sterically favourable arrangement of the donor atoms and to the donor ability of the nitrogen atoms of both the macrocyclic and heterocyclic rings, these molecules can bind metal ions with different steric and electronic requirements.[3] The resulting complexes are, in general, remarkably stable and inert towards metal dissociation. We have recently reported on the synthesis and single-crystal X-ray determination of some lead(II) complexes with the potentially hexadentate ligand 1,4,7-tris(pyrazol-1-ylmethyl)-1,4,7-triazacyclononane (L^4).[4] In the course of that study we found that in the solid state structure of the compound $[PbL^4(BPh_4)]BPh_4$ one BPh_4^- phenyl group interacted in η^6 fashion at contact distance from the metal centre.[4] To the best of our knowledge that type of interaction was unprecedented. In order to understand which conditions favour it we have allowed the lead(II) ion to react with some functionalized macrocycles, having different denticity and steric requirements with respect to the L^4 ligand as well as to each other, in the presence of sodium tetraphenylborate. Here we report on the syntheses and structural characterizations of the three lead(II) complexes which analyse as $PbL^1Cl(BPh_4)\cdot 0.5MeCN$ [L^1 = 1-(1-methylimidazol-2-ylmethyl)-1,4,7-triazacyclononane], $PbL^2(BPh_4)_2$ [L^2 = 1,4-bis(1-methylimidazol-2-ylmethyl)-1,4,7-triazacyclononane] and $Pb_2L^3(BPh_4)_4\cdot 4MeCN$ {L^3 = 1,2-bis[4,7-bis(1-methylimidazol-2-ylmethyl)-1,4,7-triazacyclonon-1-yl]ethane}. The crystal structure determinations have revealed that in all of these complexes an η^6 interaction occurs between each Pb^{II} and a phenyl group of a BPh_4^- anion.



Experimental

Materials and methods

All reagents were reagent grade; commercial solvents, when required by the synthetic procedures, were dried according to standard methods and distilled just before their use. Hydrated lead(II) acetate (Baker), sodium tetraphenylborate (Baker), and 1,8-bis(dimethylamino)naphthalene (Proton Sponge®, Aldrich) were used as received. 1,4-Bis(1-methylimidazol-2-ylmethyl)-1,4,7-tetraazacyclononane (L^2) was prepared from 1,4,7-triazacyclononane,[5] 2-chloromethyl-1-methylimidazole[6] and Proton Sponge®, as previously reported.[7] The purity of the products was checked by means of ^{13}C NMR spectroscopy, verifying that the spectra exhibited the expected resonances. Elemental analyses were performed by the Microanalytical Laboratory of the Department of Chemistry of the University of Florence. The ^{13}C NMR spectra of the compounds were obtained with a Varian FT 80 spectrometer operating at 20.0 MHz, infrared spectra with a Perkin-Elmer 283 grating spectrophotometer as Nujol mulls between KBr plates.

Syntheses

1-(1-Methylimidazol-2-ylmethyl)-1,4,7-triazacyclononane (L^1). Solid 2-chloromethyl-1-methylimidazole hydrochloride

(13.5 g, 80.8 mmol) was slowly added under a nitrogen atmosphere to a solution of 1,4,7-triazacyclononane (10.0 g, 77.5 mmol) in dry dmf (400 ml). The reactants were stirred at room temperature for 5 d, yielding increasing amounts of solid compound with time. The solid compound was filtered off under N_2, washed with ethanol–diethyl ether (1:1 v/v), then with diethyl ether alone and finally dried in a stream of N_2 at about 40 °C. The product so obtained was the bis(hydrochloride) of 1-(1-methylimidazol-2-ylmethyl)-1,4,7-triazacyclononane, L^1, in fairly pure form. Yield 8.5 g (37%). ^{13}C NMR (D_2O): δ 145.0 (C^2), 123.4, 121.6 (C^4, C^5), 48.7 (bridge CH_2), 43.8, 42.5, 42.3 (CH_2 of macrocycle) and 33.3 (CH_3 of imidazole). By working up the dmf solution an amount of the crude L^2 compound was recovered.

1,2-Bis[4,7-bis(1-methylimidazol-2-ylmethyl)-1,4,7-triazacyclonon-1-yl]ethane (L^3). The reaction was carried out under a nitrogen atmosphere with deaerated solvents using a procedure similar to that reported.[8] 1,2-Bis(1-methylimidazol-2-ylmethyl)-1,4,7-triazacyclononane (2.00 g, 6.30 mmol) and 1,2-bis(*p*-tolylsulfonyl)ethane[9] (1.16 g, 3.13 mmol) were dissolved in 50 ml of dry MeCN; solid Na_2CO_3 (2.00 g, 18.9 mmol) was then added. The suspension was refluxed for 6 d. Then the solution, cooled to room temperature, was separated from the solid residue by filtration and rotary evaporated to dryness. The oil so obtained contained impure L^3. The crude product was dissolved in $CHCl_3$ and eluted through a neutral alumina column (Aldrich, type 507C, 150 mesh) with $CHCl_3$–MeOH (19:1 v/v). Yield 1.55 g (75%). ^{13}C NMR ($CDCl_3$): δ 145.5 (C^2), 126.3, 120.9 (C^4, C^5), 56.6 (bridge CH_2), 55.6, 54.9, 54.3 (CH_2 of macrocycle and of connecting chain) and 32.4 (CH_3 of imidazole).

$[PbL^1Cl(BPh_4)]\cdot 0.5MeCN$ 1. The salt $Pb(O_2CMe)_2\cdot 3H_2O$ (0.460 g, 1.00 mmol) dissolved in absolute ethanol (20 ml) was added to a warm solution (10 ml) of the compound $L^1\cdot 2HCl$ (0.296 g, 1.00 mmol) in the same solvent. Sodium tetraphenylborate (0.684 g, 2.00 mmol) in acetone (20 ml) was added and the resulting solution concentrated to a small volume; colourless crystals of the complex were obtained. The crystals used for X-ray analysis were obtained by slow evaporation at room temperature of a dilute acetonitrile solution of the complex. The compound so obtained contains acetonitrile of crystallization as inferred from the IR data [ν(CN) 2230 cm^{-1}] and confirmed by the X-ray analysis (Found: C, 53.5; H, 5.3; N, 9.76. Calc. for $C_{36}H_{42.5}BClN_{5.5}Pb$: C, 53.7; H, 5.3; N, 9.56%).

$[PbL^2(BPh_4)]BPh_4$ 2. The complex was synthesized as above using an ethanol solution (20 ml) of the ligand L^2 (0.317 g, 1.00 mmol) and the stoichiometric amounts of lead(II) acetate trihydrate and sodium tetraphenylborate. Crystals suitable for X-ray analysis were obtained by slow evaporation at room temperature of a dilute solution of the complex in acetone–acetonitrile (1:1) (Found: C, 65.8; H, 5.7; N, 8.37. Calc. for $C_{64}H_{67}B_2N_7Pb$: C, 66.1; H, 5.8; N, 8.42%).

$[Pb_2L^3(BPh_4)_2][BPh_4]_2\cdot 4MeCN$ 3. The complex was prepared as for **1** using solutions of L^3 (0.330 g, 0.500 mmol) in ethanol (20 ml), of $Pb(O_2CMe)_2\cdot 3H_2O$ (0.460 g, 1.00 mmol) in methanol (20 ml), and of sodium tetraphenylborate (1.37 g, 4.00 mmol) in acetone (10 ml). Crystals suitable for X-ray analysis were obtained by slow evaporation at room temperature of a dilute solution of the complex in acetonitrile–ethanol (1:1). The compound contains acetonitrile of crystallization as inferred from the IR data [ν(CN) 2245 cm^{-1}] and confirmed by the X-ray analysis (Found: C, 65.8; H, 6.0; N, 9.93. Calc. for $C_{69}H_{74}B_2N_9Pb$: C, 65.9; H, 5.9; N, 10.0%).

The complexes are not sufficiently soluble in the common deuteriated solvents to give meaningful ^{13}C NMR spectra.

Crystallography

Crystal data and refinement parameters for the compounds $[PbL^1Cl(BPh_4)]\cdot 0.5MeCN$ **1**, $[PbL^2(BPh_4)]BPh_4$ **2** and $[Pb_2L^3(BPh_4)_2][BPh_4]_2\cdot 4MeCN$ **3** are given in Table 1. Crystals of **3** provided rather poorly diffracting material. All operations were performed at 295 K using an Enraf-Nonius CAD4 diffractometer and graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\,69$ Å). Unit-cell parameters were obtained for each compound from the settings of 24 reflections with $14 < \theta < 16$ **1**, $13 < \theta < 15$ **2** and $15 < \theta < 17°$ **3**. The crystals used for the final data collections had the shapes of a flattened octahedron **1**, of a prism **2** and of a needle **3**. The ω–2θ scan mode was used in all data collections. The crystals of compounds **1** and **3** were protected by a thin coating of paraffin to prevent slight decomposition. The intensities of standard reflections monitored periodically during the data collections revealed that no correction for decay had to be applied. Empirical absorption corrections were applied to all data sets after structure solutions 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 ref. 12.

The structures were solved by combinations of direct[11] and heavy-atom[12] methods, which provided the positions of all the non-hydrogen atoms. Since the $[Pb_2L^3(BPh_4)_2]^{2+}$ moiety of **3** is centrosymmetric only one half of it forms the symmetry-independent fraction. One MeCN solvate molecule was found to lie in special position, along a twofold axis, in the structure of **1** and two such molecules were in general positions in the structure of **3**. In the final refinement cycles all non-hydrogen atoms were assigned anisotropic thermal parameters. The hydrogen atoms were introduced in positions calculated by the program with isotropic $U_H = 1.2U_{C,N}$ ($U_H = 1.5U_C$ for methyl hydrogens) where $U_{C,N}$ is the equivalent isotropic thermal parameter of the respective carbon or nitrogen atom.

CCDC reference number 186/1106.

Results and discussion

The addition of BPh_4^- to solutions containing lead(II) acetate and, in turn, one of the compounds $L^1\cdot 2HCl$, L^2 or L^3 in equimolar ratios results in the precipitation of crystalline compounds having the formulae $PbL^1Cl(BPh_4)\cdot 0.5MeCN$ **1**, $PbL^2(BPh_4)_2$ **2** and $Pb_2L^3(BPh_4)_4\cdot 4MeCN$ **3**. All of these are scarcely soluble in the common organic solvents. For this reason their ^{13}C NMR spectra in deuteriated solvents do not provide useful information. Both the IR and the analytical data suggested that in no case acetate anions were present in the solid compounds, being apparently displaced by the tetraphenylborate anions added to the reactant solutions, a feature confirmed by the structure determinations.

The crystal structures of the compounds **1**, **2** and **3** have been determined in order to know whether the BPh_4^- anions play the simple role of counter ions in the structures or take part in the co-ordination to the metal centre as previously found for a lead(II) complex formed by the trisubstituted triazacyclononane L^4 ligand.[4] Bond distance and angles about the metal atoms in the three compounds are given in Tables 2–4. Views of relevant parts of the structures appear in Figs. 1–3.

The metal atom in compound **1** is co-ordinated by the macrocycle nitrogens, by the nitrogen donor of the methylimidazole group, and by the chlorine atom. In addition to these five donors forming bond distances to the metal atom in the normal range there is a phenyl group from the tetraphenylborate anion lying at contact distance from the lead(II) atom. Its carbon atoms form distances in the 3.56–3.87 Å range to the metal and the centroid of the ring lies at 3.44 Å from the metal position. The environments of the lead(II) atom in **2** and of the two metal atoms in the centrosymmetric cation of **3** are closely similar to each other, being formed by five nitrogen atoms, three of which

Table 1 Crystallographic data for [PbL^{1}Cl(BPh$_4$)]·0.5MeCN **1**, [PbL^2(BPh$_4$)]BPh$_4$ **2** and [Pb$_2$L^3(BPh$_4$)$_2$][BPh$_4$]$_2$·4MeCN **3**

	1	**2**	**3**
Formula	$C_{36}H_{42.5}BClN_{5.5}Pb$	$C_{64}H_{67}B_2N_7Pb$	$C_{138}H_{148}B_4N_{18}Pb_2$
M	805.71	1163.06	2516.36
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$C2/c$ (no. 15)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a/Å	36.239(11)	12.092(2)	11.674(6)
b/Å	10.405(2)	13.346(3)	13.738(4)
c/Å	18.058(6)	17.453(4)	21.449(3)
α/°^{a}		87.96(2)	102.00(2)
β/°	100.61(2)	77.00(2)	94.08(4)
γ/°^{a}		89.65(2)	114.16(4)
U/Å^3	6693(3)	2743(1)	3022(2)
Z	8	2	1
D_c/g cm^{-3}	1.599	1.408	1.382
Crystal size/mm	0.13 × 0.27 × 0.33	0.30 × 0.40 × 0.70	0.15 × 0.15 × 1.10
μ/mm^{-1}	5.16	3.12	2.84
Collection range/°	$5 \leq 2\theta \leq 50$	$5 \leq 2\theta \leq 50$	$5 \leq 2\theta \leq 50$
No. measured reflections	6446	9259	10249
No. unique data	5880	9259	10249
Absorption correction factors^b	0.82–1.42	0.86–1.16	0.86–1.23
No. parameters	405	669	730
Goodness of fit	1.031	1.018	1.424
$R1 = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|^c$	0.057	0.047	0.073
$wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$	0.161	0.120	0.256
Largest features in final difference map/e Å^{-3}	0.96, −0.97	1.80, −2.87	1.71, −1.86

[a] For compound **1**: $a = \gamma = 90°$. [b] From DIFABS.[10] [c] Based on the 3642 **1**, 7480 **2** and 8250 **3** reflections with $F_o > 4\sigma F_o$; $R1 = 0.125$ **1**, 0.069 **2** and 0.101 **3** for all unique reflections.

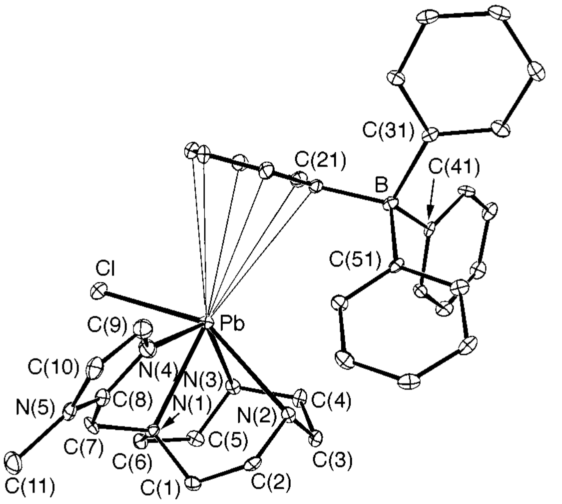


Fig. 1 View of the [PbL^{1}Cl(BPh$_4$)] moiety in the structure of compound **1**. In this and in the following figures 20% probability ellipsoids are shown and only the *ipso*-carbon atoms of phenyl rings are labelled for clarity.

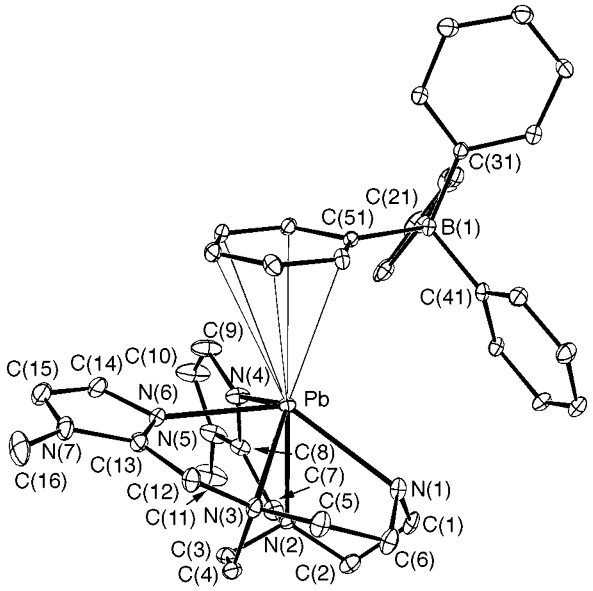


Fig. 2 View of the [PbL^2(BPh$_4$)]$^+$ cation in the structure of compound **2**.

are provided by the macrocycle and two by the methylimidazole groups. Also in the structures of these two compounds a tetraphenylborate phenyl group completes the co-ordination about each metal atom, lying at close contact distance from it. The distances of the centroids of the rings from the metal centres are 3.10 (**2**) and 3.06 Å (**3**). It may be worth noting that in the structure of **2**, which exhibits the (relatively) longer of these two Pb···Ph distances, the mean Pb–N bond distance is shorter than in the other structure, by *ca.* 0.04 Å; the shortening affects mostly the bonds formed by the macrocycle nitrogens.

The co-ordination geometry presents grossly similar features for all the metal centres of these compounds in spite of the difference in the nature of the donor set between **1** and the other two compounds. In each case there is a nitrogen atom (N$_{ax}$) of the macrocycle lying almost opposite the phenyl ring. The N$_{ax}$ atom may be assumed to define an "axial" direction, together with the ring centroid. The remaining four N donors, or three N and one Cl donor for **1**, are approximately arranged in a plane which is essentially perpendicular to the "axial" direction. The metal atom lies out of that (least-squares) plane by a considerably larger amount than any of the defining atoms, in the direction of the phenyl group. As a result of this arrangement, the nitrogen donor atoms in **2** and **3**, as well as the chlorine and nitrogen atoms in **1**, span regions of space about the metal atom which are definitely narrower than a hemisphere, thus favouring the approach by the bulky counter ion. The macrocycle N$_{ax}$ nitrogen is invariably one of those bearing a dangling group, being in particular the only nitrogen of that type present in **1**. The position occupied by the N$_{ax}$ atom in the co-ordination sphere allows a reduction of the interactions between its methylimidazole and the co-ordinating phenyl group. The second methylimidazole group, when present, takes on an arrangement in which its plane is almost parallel to that of the phenyl group.

In the structure of the compound [PbL^4(BPh$_4$)]BPh$_4$ **4**

Table 2 Selected bond distances (Å) and angles (°) for [PbL^{1}Cl(BPh$_4$)]·0.5MeCN **1**

Pb–N(1)	2.563(8)	Pb–N(4)	2.609(11)
Pb–N(2)	2.639(9)	Pb–Cl	2.742(3)
Pb–N(3)	2.541(9)		
N(1)–Pb–N(2)	68.3(3)	N(3)–Pb–N(4)	133.3(3)
N(1)–Pb–N(3)	68.1(3)	N(3)–Pb–Cl	88.5(2)
N(1)–Pb–N(4)	66.1(3)	N(1)–Pb–Cl	81.8(2)
N(2)–Pb–N(3)	67.0(3)	N(4)–Pb–Cl	93.8(2)
N(2)–Pb–N(4)	87.8(3)	N(2)–Pb–Cl	146.5(2)

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

Pb–N(1)	2.694(6)	Pb–N(4)	2.477(6)
Pb–N(2)	2.609(5)	Pb–N(6)	2.501(6)
Pb–N(3)	2.590(6)		
N(1)–Pb–N(2)	67.0(2)	N(2)–Pb–N(4)	68.0(2)
N(1)–Pb–N(3)	66.0(2)	N(2)–Pb–N(6)	90.0(2)
N(1)–Pb–N(4)	125.7(2)	N(3)–Pb–N(4)	123.4(2)
N(1)–Pb–N(6)	130.8(2)	N(3)–Pb–N(6)	65.5(2)
N(2)–Pb–N(3)	71.1(2)	N(4)–Pb–N(6)	77.0(2)

Table 4 Selected bond distances (Å) and angles (°) for [Pb$_2$L^3(BPh$_4$)$_2$][BPh$_4$]$_2$·4MeCN **3**

Pb–N(1)	2.806(8)	Pb–N(4)	2.465(9)
Pb–N(2)	2.617(8)	Pb–N(6)	2.534(8)
Pb–N(3)	2.640(7)		
N(1)–Pb–N(2)	65.3(3)	N(2)–Pb–N(4)	68.8(3)
N(1)–Pb–N(3)	65.5(3)	N(2)–Pb–N(6)	94.5(3)
N(1)–Pb–N(4)	128.3(3)	N(3)–Pb–N(4)	118.2(3)
N(1)–Pb–N(6)	130.3(3)	N(3)–Pb–N(6)	65.0(3)
N(2)–Pb–N(3)	70.1(3)	N(4)–Pb–N(6)	74.7(3)

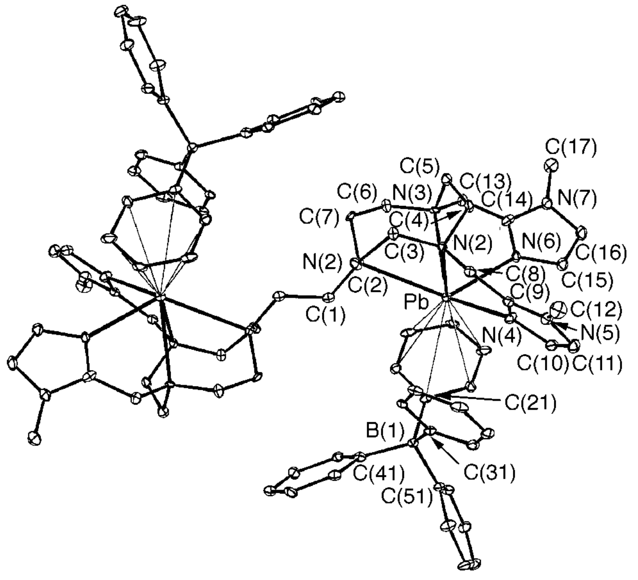


Fig. 3 View of the centrosymmetric [Pb$_2$L^3(BPh$_4$)$_2$]$^{2+}$ cation in the structure of compound **3**. Only symmetry-independent atoms are labelled.

formed by the triazamacrocycle substituted with three dangling pyrazole groups[4] the centroid of the co-ordinating phenyl group was at 3.24 Å from the metal atom and also in that case a macrocycle nitrogen lay almost in *trans* position with respect to the phenyl group. The remaining five donors of the hexadentate L^4 ligand were all reasonably close to an "equatorial" plane, normal to the axial direction defined as above by the positions of N$_{ax}$ and of the phenyl centroid. Although both pyrazole groups attached to the macrocycle nitrogens lying in the equatorial plane were not far from being parallel to that plane, as well as to the plane of the phenyl ring, the pyrazole group which approached the phenyl ring more closely (viewing along the axial direction) was also more closely coplanar with it, compared to the other pyrazole group.

Such arrangements of the dangling groups in these compounds and the trend in the mean values of the Pb–N distances noted above for the metal environments in **2** and **3** suggest that the repulsive interactions between the BPh$_4^-$ phenyl group and parts of the flexible ligand surrounding the metal atom are not negligible, which in turn would suggest that the attractive forces holding the phenyl group on top of the lead(II) atom should also be significant.

In an attempt further to investigate the nature of this interaction molecular orbital calculations at the extended-Hückel level[15] have been performed with the program CACAO[16] on a simplified model for compound **2**, similar to that previously used for **4**,[4] however taking into account the differences in co-ordination number and geometry between the two compounds. The results of the two sets of calculations are substantially similar. The phenyl bonding orbital of a$_1$ symmetry interacts, rather weakly due to the large separation between the two fragments formed by the metal–ligand moiety and the phenyl ring, with two orbitals of the metal fragment. One of these, lying at low energy, has a predominant lead(II) s contribution, whereas the other one, which lies at higher energy and undergoes the comparatively stronger interaction with the phenyl orbital, has a substantial lead(II) p component and forms the "lead(II) lone pair". The latter fragment orbital is oriented toward the phenyl ring due to antibonding with nitrogen orbitals and eventually forms the HOMO of the [PbL^2(BPh$_4$)]$^+$ system. The above three-orbital interaction involving filled orbitals is a destabilizing one: the energy of the lone pair steadily increases as the distance between the two fragments decreases. On the other hand, stabilizing interactions are provided by empty orbitals on the metal [essentially antibonding combinations of lead(II) p and nitrogen orbitals] which mix with the e-type bonding combinations of the ring, of C$_{p_z}$ origin. The slight mixing of functions produced by these and additional, even weaker, orbital interactions, suggests that the two parts forming the [PbL^2(BPh$_4$)]$^+$ cation are essentially held by polarization forces,[4] enhanced by the participation of relatively numerous atoms and by the favourable geometrical features. Of course, the role of the electrostatic forces should not be neglected. However, the fact that the geometries of the co-ordinating phenyl groups in **1**–**4** do not exhibit significant distortions or systematic differences from expected values indicates that the interactions under discussion, although significant, are not of a strength comparable to that of bonding interactions.

Although apparently the lead(II) interaction with a BPh$_4^-$ phenyl group had not been described before our previous report,[4] a few examples exist of η^6 aromatic co-ordination to lead(II)[17] and, particularly, tin(II).[18] Such interactions seem to be attained in the presence of electron-withdrawing coligands[17] or are given by phenyl groups anchored in proximity of the metal atom as a part of a normally co-ordinating ligand.[18]

The results here and previously[4] reported show that the interaction of a phenyl group of the BPh$_4^-$ anion with lead(II) should not be considered to be exceptional. The weak co-ordination of BPh$_4^-$ to lead(II) in the co-ordinatively unsaturated PbL^{2+} moieties (L = L^1, L^2, 0.5L^3 or L^4) is favoured by the large size of the metal atom, the common co-ordination numbers of which exceed the denticity of the ligands used in these studies, and by the flexibility of the dangling groups. It is evident that the geometry of the environment provided by the above L ligands in the PbL^{2+} moieties favours the approach of extra ligands to the metal centre in order to satisfy its co-ordination requirements. However, the reasons why a generally considered non-co-ordinating species like the tetraphenylborate anion successfully competes with the much more strongly coordinating acetate for the lead(II) centre are not readily apparent. Presumably, the van der Waals interactions, which are exerted by the former anion under suitable geometrical circumstances, provide the decisive contribution, when added to the ionic forces which are active in both cases.

Acknowledgements

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References

1 M. J. Hynes and B. Jonson, *Chem. Soc. Rev.*, 1997, **26**, 133; K. Abu-Dari, F. E. Hahn and K. N. Raymond, *J. Am. Chem. Soc.*, 1990, **112**, 1519.

2 D. L. Reger, J. E. Collins, A. L. Rheingold, L. M. Liable-Sands and G. P. A. Yap, *Inorg. Chem.*, 1997, **36**, 345; J. Parr, A. T. Ross and A. M. Z. Slawin, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 1509; A. Andres, A. Bencini, A. Carachalios, A. Bianchi, P. Dapporto, E. Garcia-España, P. Paoletti and P. Poli, *J. Chem. Soc.*, *Dalton Trans.*, 1993, 3507; K. Abu-Dari, T. B. Karpishin and K. N. Raymond, *Inorg. Chem.*, 1993, **32**, 3052; D. L. Reger, M. F. Huff, A. L. Rheingold and B. S. Haggerty, *J. Am. Chem. Soc.*, 1992, **114**, 579; K. Wieghardt, M. Kleine-Boymann, B. Nuber, J. Weiss, L. Zsolnai and G. Hutter, *Inorg. Chem.*, 1986, **25**, 1647; N. W. Alcock, E. H. Curzon and P. Moore, *J. Chem. Soc.*, *Dalton Trans.*, 1984, 2813.

3 M. Di Vaira, F. Mani and P. Stoppioni, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 1375; 1994, 3739; G. de Martino Norante, M. Di Vaira, F. Mani, S. Mazzi and P. Stoppioni, *J. Chem. Soc.*, *Dalton Trans.*, 1992, 361; M. Di Vaira, B. Cosimelli, F. Mani and P. Stoppioni, *J. Chem. Soc.*, *Dalton Trans.*, 1991, 331.

4 M. Di Vaira, M. Guerra, F. Mani and P. Stoppioni, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 1173.

5 T. J. Atkins, J. E. Richman and W. F. Oettle, *Org. Synth.*, 1978, **58**, 86; K. Wieghardt, W. Schmid, B. Nuber and I. Weiss, *Chem. Ber.*, 1978, **112**, 2220.

6 R. G. Jones, *J. Am. Chem. Soc.*, 1949, **71**, 383.

7 M. Di Vaira, F. Mani and P. Stoppioni, *Inorg. Chim. Acta*, 1998, **273**, 151.

8 K. Wieghardt, I. Tolksdorf and W. Herrmann, *Inorg. Chem.*, 1985, **24**, 1230.

9 A. Buttafava, L. Fabbrizzi, A. Perotti, G. Poggi and B. Seghi, *Inorg. Chem.*, 1986, **25**, 1456.

10 DIFABS, N. Walker and D. Stuart, *Acta Crystallogr.*, *Sect. A*, 1983, **39**, 158.

11 SIR 92, A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi and G. Polidori, *J. Appl. Crystallogr.*, 1994, **27**, 435.

12 G. M. Sheldrick, SHELXL 93, Program for Crystal Structure Refinement, University of Göttingen, 1993.

13 PARST, M. Nardelli, *J. Appl. Crystallogr.*, 1995, **28**, 659.

14 C. K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

15 R. Hoffmann, *Angew. Chem.*, *Int. Ed. Engl.*, 1982, **21**, 711.

16 CACAO, C. Mealli and D. M. Proserpio, *J. Chem. Educ.*, 1990, **67**, 399.

17 A. G. Gash, P. F. Rodesiler and E. L. Amma, *Inorg. Chem.*, 1974, **13**, 2429.

18 J. L. Lefferts, K. C. Molloy, M. B. Hossain, D. van der Helm and J. J. Zuckerman, *Inorg. Chem.*, 1982, **21**, 1410 and refs. therein.

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