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Lead(II) tetrafluoroborate and hexafluorophosphate complexes with crown ethers, mixed O/S- and O/Se-donor macrocycles and unusual $[BF_4]^-$ and $[PF_6]^-$ coordination†

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The reaction of $Pb[BF_4]_2$ in H_2O/MeCN solution with the macrocycle 18-crown-6 gave the dinuclear complex $[\{Pb(18\text{-crown-6})(H_2O)(\mu^2\text{-}BF_4)\}_2][BF_4]_2$, containing two nine-coordinate lead centres, each bound to all six oxygens of a crown ligand, one water molecule and bridged by two μ^2-BF_4 groups. In contrast, the oxa-thia crown $[18]aneO_4S_2$ gave the mononuclear $[Pb([18]aneO_4S_2)(H_2O)_2(BF_4)][BF_4]$ in which the lead is coordinated O_4S_2 within the puckered ring of the macrocycle, and with two water molecules on one side of the plane and a chelating (κ^2) BF_4^- on the other. The $[Pb([18]aneO_4Se_2)(BF_4)_2]$ has the two BF_4^- groups arranged mutually *cis* and with the macrocycle folded; within each BF_4^- group the Pb–F distances differ by ~0.5 Å, producing a very unsymmetrical chelate. The 15-membered ring macrocycles 15-crown-5 and $[15]aneO_3S_2$ produce sandwich complexes $[Pb(macrocycle)_2][BF_4]_2$ which contain 10-coordinate lead centres. $Pb[PF_6]_2$ in H_2O/MeCN solution formed $[Pb(18\text{-crown-6})(H_2O)_2(PF_6)][PF_6]$ and $[Pb([18]aneO_4S_2)(H_2O)_2(PF_6)][PF_6]$ which contain weak κ^2-coordination of the PF_6^- group on the opposite side of the macrocyclic ring to two coordinated water molecules, giving 10-coordinate lead. In contrast, $[Pb([18]aneO_4Se_2)(PF_6)_2]$ has two κ^2-coordinated PF_6^- groups disposed *cis*, with a very folded macrocycle conformation. In $[Pb(18\text{-crown-6})(NO_3)(PF_6)]$ a chelating nitrate group occupies the coordination sites at Pb(II) instead of the two water molecules, and the weakly coordinating PF_6^- group is tridentate. The crystal structures of the lead nitrate complexes, $[Pb(15\text{-crown-5})(NO_3)_2]$ and $[Pb([18]aneO_4Se_2)(NO_3)_2]$, containing nine- and 10-coordinate lead respectively, are also reported. In solution the complexes are labile, and both conductivity and ^{19}F NMR spectroscopic studies show the BF_4^- and PF_6^- groups are dissociated, whereas in the nitrate complexes the anion coordination is retained in solution. The identification of the coordination modes of the NO_3^- and BF_4^- groups in the solid complexes by IR spectroscopy is discussed.

Introduction

Lead(II) has an extensive chemistry forming complexes with charged and neutral donor ligands from Groups 14–17.[1–3] As a large metal centre (covalent radius 1.46 Å),[4] it is able to form compounds with coordination numbers ranging from two (in diaryllead compounds with bulky substituted aryl groups) to nine (in $Pb(OAc)_2\cdot 3H_2O$),[5] ten in $[Pb(18\text{-crown-6})(NO_3)_2]$,[6] and eleven in $[Pb(15\text{-crown-5})(NO_3)_3]^-$.[6] The complexes often display irregular geometries, reflecting both the steric demands of the ligands and inter-ligand repulsions. The presence of a formal lone pair, which may or may not be stereochemically active, also needs to be considered, although in the higher coordinated complexes with polydentate or macrocyclic ligands the very irregular coordination geometries make it difficult to assess the influence of the lone pair. Unusually for a p-block metal, due to the insoluble and intractable nature of the lead dihalides, the coordination chemistry with neutral ligands is largely based upon oxo-salts such as acetate, nitrate or perchlorate, which are commonly found in the first coordination sphere of the lead.[2,3] Rare examples of lead halide complexes are the 18-crown-6 derivatives, $[PbCl_2(18\text{-crown-6})]$, $[Pb_2I_3(18\text{-crown-6})_2][SnI_5]$, the polymer $[Pb_2Br_4(18\text{-crown-6})]$ and $[PbCl(18\text{-crown-6})]SbCl_6$.[7–10] Due to its large radius and

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†Electronic supplementary information (ESI) available: The ESI contains improved preparations for several of the macrocycles, and crystallographic data for $[Pb(15\text{-crown-5})_2][H_3O][BF_4]_3$. CCDC 900327–900332, 912764, 912765 and 913970. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt32999b

modest charge (and hence low charge/radius ratio), many lead(ii) complexes are extensively dissociated in solution, and this has resulted in significant effort devoted to lead(ii) complexes with aza-, oxa- (crown ether) or thia-macrocycles.[3,11,12] Lead is a toxic element, widely distributed due to its many industrial applications, and this has led to the use of macrocyclic ligands in heavy metal sensors and extraction.[13] Examples of the types of complex found are [Pb(18-crown-6)$(NO_3)_2$] (10-coordinate with bidentate nitrates), and the cation-anion complexes [Pb(15-crown-5)$_2$][Pb(15-crown-5)$(NO_3)_3$]$_2$ and [Pb(12-crown-4)$_2$-(NO_3)][Pb(12-crown-4)$(NO_3)_3$], which also contain 10-coordinate cations and 10- or 11-coordinate anions.[6,14] Ten-coordinate lead is also present in [Pb(18-crown-6)$(O_2CMe)_2$]·$3H_2O$,[15] whilst the thiocyanates [Pb(crown)$(NCS)_2$] (crown = 18-crown-6 or dicyclohexane-18-crown-6) are eight-coordinate.[16] Thia-macrocycle complexes of lead are fewer, but include [Pb([9]aneS_3)$_2$$(ClO_4)_2$] (eight-coordinate, S_6O_2),[17] [Pb([10]aneS_3)(H_2O)-$(ClO_4)_2$] (nine-coordinate, S_3O_6),[18] and [Pb_2([28]aneS_8)$(ClO_4)_4$] (dinuclear, eight-coordinate, S_4O_4).[19]

Here we report the reactions of Pb(ii) with crown ether, oxa-thia and oxa-selena macrocycles, focusing mainly on Pb$[BF_4]_2$ or Pb$[PF_6]_2$ as the lead(ii) source. Oxa-selena macrocycle coordination chemistry has been little studied due to the relative unavailability of the ligands,[20,21] and the only oxa-thia macrocycle compounds of Pb(ii) are [Pb([18]aneO_4S_2)$(ClO_4)_2$], [Pb([18]aneO_4S_2)$(NO_3)_2$] and [Pb([18]aneO_4S_2)$(NCS)_2$] ([18]-aneO_4S_2 = 1,4,10,13-tetraoxa-7,16-dithiacyclooctadecane).[22] Tetrafluoroborate and hexafluorophosphate are markedly weaker coordinating anions than either ClO_4^- or NO_3^-.[23] In the present study we have explored the affinity of the lead(ii) macrocycle fragments (both 15- and 18-membered rings) towards these fluoro-anions and the resulting structures.

Results and discussion

As a result of the labile nature of Pb(ii) in solution and the unpredictable geometries present, spectroscopic techniques provide limited characterisation. The key characterisation technique for complexes of this type is X-ray crystallography, and thus the synthesis and structures of the new complexes are described first, followed by discussion of the spectroscopic data.

Synthesis and X-ray crystal structures

The coordination geometries observed are generally highly irregular, reflecting the constraints of the macrocyclic rings and, in some cases, the small chelate bites of the coordinated anions, and therefore are not easily described in terms of Euclidean shapes. The lead–donor bond lengths also show a range of values, described by some authors as a mixture of normal coordinate bonds and longer directional (weak) interactions.[21,22] The distinction between the two descriptions is not clear-cut and all Pb–donor atom bond distances in the present systems are significantly within the sum of the appropriate Van der Waals radii. In this work we have described the coordination number of the lead based upon all the Pb–donor atom contacts within the Van der Waals sum, while emphasising particularly disparate bond lengths in the individual cases. The relevant Van der Waals radii sums are Pb···O = 3.54, Pb···S = 3.82, Pb···Se = 3.92 and Pb···F = 3.49 Å.[4]

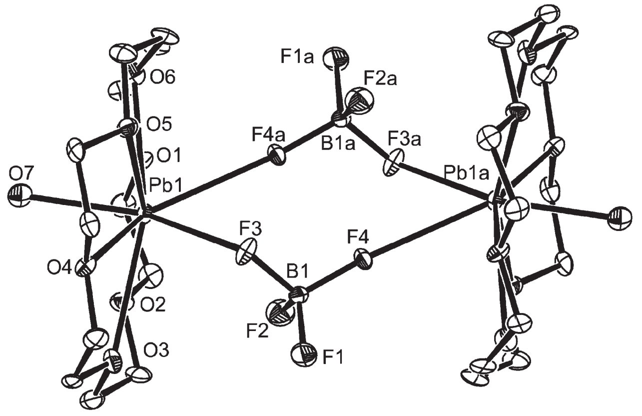

Fig. 1 Crystal structure of the dimer cation in [{Pb(18-crown-6)(H_2O)(μ^2-BF_4)}$_2$]-$[BF_4]_2$ showing the bridging BF_4 groups. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Symmetry operation: $a = -x, -y, 2 - z$. Selected bond lengths (Å) and angles (°): Pb1–O1 = 2.744(5), Pb1–O2 = 2.803(5), Pb1–O3 = 2.894(5), Pb1–O4 = 2.732(5), Pb1–O5 = 2.710(5), Pb1–O6 = 2.701(5), Pb1–O7 = 2.406(6), Pb1···F3 = 2.677(5), Pb1···F4a = 2.813(4), O1–Pb1–O2 = 58.93(14), O2–Pb1–O3 = 57.69(14), O3–Pb1–O4 = 57.75(14), O4–Pb1–O5 = 61.11(14), O5–Pb1–O6 = 60.80(14), O1–Pb1–O6 = 60.13(14).

Reaction of a 50% aqueous solution of Pb$[BF_4]_2$ with one mol. equiv. of 18-crown-6 in MeCN solution afforded the complex [{Pb(18-crown-6)(H_2O)(μ^2-BF_4)}$_2$]$[BF_4]_2$ as a colourless crystalline solid. A crystal structure determination showed (Fig. 1) the Pb(ii) ion within the ring of the 18-crown-6 coordinated to all six ether oxygens (2.744(5)–2.894(5) Å), a coordinated H_2O (2.406(6) Å), and with two μ^2-BF_4^- groups linking two Pb atoms to form a dinuclear species, and giving overall nine-coordination at lead(ii). Two other $[BF_4]^-$ anions provide charge balance. The most unusual feature of this complex is the presence of the asymmetrically bridging $[BF_4]^-$ groups, with Pb–F distances Pb1–F3 = 2.677(5), Pb1–F4a = 2.813(4) Å, and <F3–B1–F4 = 111.5(3)°. The only other example of Pb(ii) with bridging BF_4^- groups is in the organolead complex, [(η^5-C_5Me_5)Pb(μ^2-BF_4)$_2$Pb(η^5-C_5Me_5)], with d(Pb–F) = 2.901(9) and 2.831(9) Å.[24] The coordinated water molecule, which has a significantly shorter Pb–O bond (Pb1–O7 = 2.406(6) Å) than those involving the crown ether, also forms two H-bonds to F atoms of adjacent $[BF_4]^-$ anions, O7···F8′ = 2.722(7), and O7···F5′ = 2.689(7) Å. The known [Pb(18-crown-6)$(NO_3)_2$] is mononuclear with κ^2-NO_3^- groups on opposite sides of the PbO_6 plane.[6,14]

[Pb(15-crown-5)$_2$]$[BF_4]_2$ was obtained using either a 1 : 1 or 1 : 2 Pb$[BF_4]_2$: 15-crown-5 molar ratio. Colourless crystals grown from the filtrate from the 1 : 1 reaction revealed a [Pb-(15-crown-5)$_2$][H_3O]$[BF_4]_3$ constitution, with a disordered lead dication which precludes detailed structural comparison (see ESI†). However, the partial structure does indicate a 10-coordinate Pb(ii) centre, with anionic tetrafluoroborate, and with a hydroxonium cation also present in the asymmetric unit to

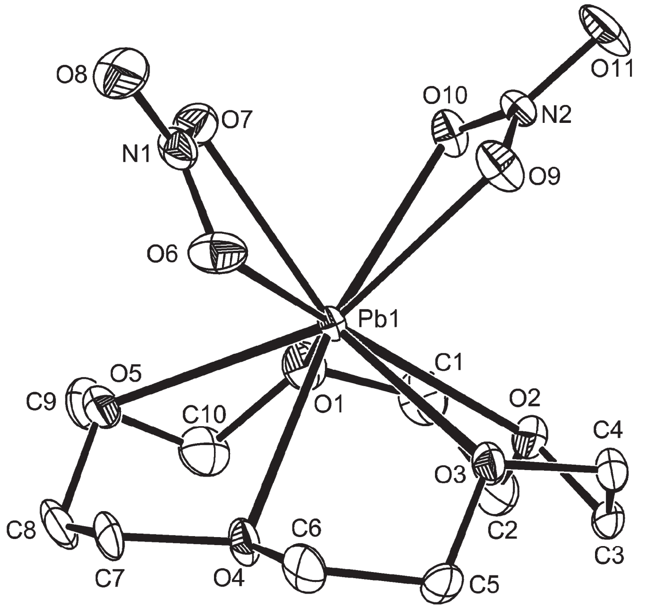

Fig. 2 Crystal structure of the [Pb(15-crown-5)$(NO_3)_2$] showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Pb to crown O atoms are shown as open bonds. Selected bond lengths (Å) and angles (°): Pb1–O1 = 2.691(3), Pb1–O2 = 2.712(3), Pb1–O3 = 2.711(3), Pb1–O4 2.709(3), Pb1–O5 = 2.716(3), Pb1–O6 = 2.574(4), Pb1–O7 = 2.596(3), Pb1–O9 = 2.586(3), Pb1–O10 = 2.681(3), O6–Pb1–O7 = 49.93(11), O9–Pb1–O10 = 48.84(9), O1–Pb1–O2 = 64.18(10), O2–Pb1–O3 = 62.78(10), O3–Pb1–O4 = 61.36(9), O4–Pb1–O5 = 61.79(9), O5–Pb1–O6 = 85.33(12), O6–Pb1–O1 = 144.50(11).

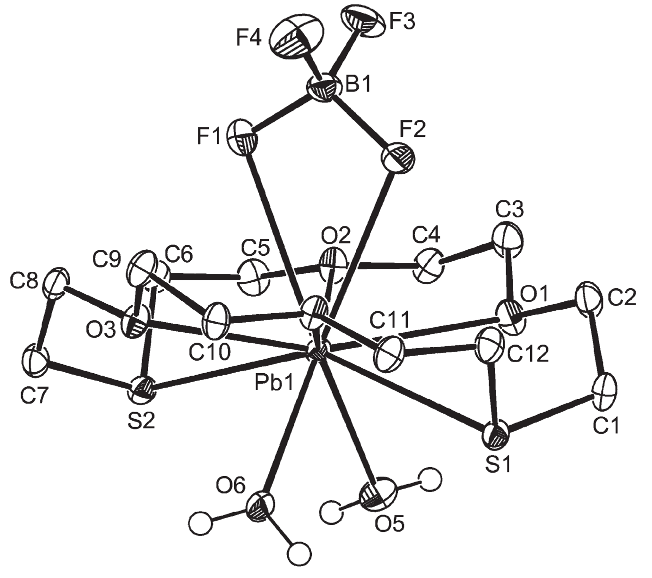

Fig. 3 Crystal structure of the cation in [Pb([18]aneO_4S_2)$(H_2O)_2$$(BF_4)$][$BF_4$] showing the atom numbering scheme and the coordination around Pb1. Ellipsoids are drawn at the 50% probability level and H atoms bonded to C are omitted for clarity. Selected bond lengths (Å) and angles (°): Pb1–O1 = 2.888(2), Pb1–O2 = 2.842(2), Pb1–O3 = 2.726(2), Pb1–O4 = 2.731(2), Pb1–S1 = 3.0151(8), Pb1–S2 = 3.0191(7), Pb1–O5 = 2.559(2), Pb1–O6 = 2.471(2), Pb1⋯F1 = 3.038(2), Pb1⋯F2 = 2.877(2), O5–Pb1–O6 = 73.03(8), O3–Pb1–O4 = 62.68(6), O2–Pb1–O1 = 59.03(5), O4–Pb1–S1 = 66.64(5), O1–Pb1–S1 = 64.42(4), O3–Pb1–S2 = 65.07(4), S1–Pb1–S2 = 147.40(2), F2⋯Pb1⋯F1 = 44.94(4).

balance the charge. In contrast, 15-crown-5 reacted with Pb$[NO_3]_2$ in MeCN solution to give the 1 : 1 complex [Pb(15-crown-5)$(NO_3)_2$]. The crystal structure shows (Fig. 2) pentadentate coordination of the crown and two chelating NO_3^- ligands giving nine-coordinate Pb(II). Unlike the structure of [Pb(18-crown-6)$(NO_3)_2$],[6,14] the 15-crown-5 lies on one side of the Pb ion, with the κ^2-NO_3^- groups *cis*. The Pb–O(crown) distances lie in the range 2.691(3)–2.716(3) Å, while the nitrates are asymmetrically coordinated with Pb–O(nitrate) distances 2.574(4)–2.586(3) Å.

Previous work[6] has reported that the reaction of Pb$[NO_3]_2$ with 15-crown-5 in a 1 : 2 molar ratio in hot MeOH/MeCN solution, gives [Pb(15-crown-5)$_2$][Pb(15-crown-5)$(NO_3)_3$]$_2$ with a badly disordered cation (similar to the problem in [Pb(15-crown-5)$_2$][H_3O][BF_4]$_3$ in this work). We observed only the neutral [Pb(15-crown-5)$(NO_3)_2$] under our conditions.

Aqueous lead tetrafluoroborate reacted with one mol. equiv. of [18]aneO_4S_2 in MeCN to give colourless crystals formulated as [Pb([18]aneO_4S_2)$(H_2O)_2$$(BF_4)$][$BF_4$], on the basis of microanalytical data. The crystal structure shows (Fig. 3) a complex of 1 : 1 Pb : crown stoichiometry with a [Pb([18]aneO_4S_2)$(H_2O)_2$(κ^2-BF_4)]$^+$ cation and a discrete BF_4^- anion. The lead ion sits within the puckered oxa-thia ring, coordinated *via* all six donor atoms (Pb–S = 3.0151(8), 3.0191(7) Å, Pb–O = 2.726(2)–2.888(2) Å). One BF_4^- behaves as a bidentate chelate to Pb(II), with Pb⋯F = 3.038(2), 2.877(2) Å, F2–B1–F1 = 108.1(2)°. Two mutually *cis* coordinated water molecules lie *trans* to the chelating BF_4^- completing the 10-coordinate environment at lead, Pb–O$_{water}$ = 2.471(2), 2.559(2) Å. The OH_2 molecules (O5 and O6) are involved in H-bonds to O and S atoms in the crown and to F in the fluoroborates.

The structure can be compared with that found in [Pb([18]aneO_4S_2)$(ClO_4)_2$][22] in which the lead sits in the plane of the macrocycle with κ^1-perchlorate groups arranged *trans* across the plane (eight-coordinate Pb). The Pb–O distances of 2.662 (2) and 2.744(2) Å, and Pb–OClO_3 = 2.680(2) Å are slightly shorter, but with a longer *d*(Pb–S) = 3.091(1) Å. In contrast, [Pb([18]aneO_4S_2)$(NO_3)_2$][22] is different again, with a 10-coordinate lead environment composed of two *cis* κ^2-NO_3^- groups. Here *d*(Pb–O) = 2.716(10)–2.879(11) Å, *d*(Pb–ONO_2) = 2.553(17)–2.877(16) Å and *d*(Pb–S) = 3.114(6), 3.131(6) Å.

Repeating this reaction with the smaller 15-membered macrocycle, [15]aneO_3S_2 (1,4,7-trioxa-10,13-dithiacyclopentadecane), with a 2 : 1 crown : Pb ratio gave [Pb([15]aneO_3S_2)$_2$][BF_4]$_2$. The X-ray crystallographic analysis revealed a discrete [Pb([15]aneO_3S_2)$_2$]$^{2+}$ sandwich dication (Fig. 4) with the $[BF_4]^-$ anions. Within the cation the Pb(II) centre can be considered to be in a very distorted 10-coordinate environment. Although all the Pb–O and Pb–S distances in both rings lie well within the sum of the Van der Waals radii for the respective elements, two of the Pb–O distances, Pb–O3 and Pb–O4 (2.898(5), 3.055(5) Å), are substantially longer compared to the others and therefore an alternative description would be to consider these as weaker, directional long contacts. The shorter Pb–O distances are 2.688(5), 2.725(5), 2.761(4) and 2.750(4) Å, while

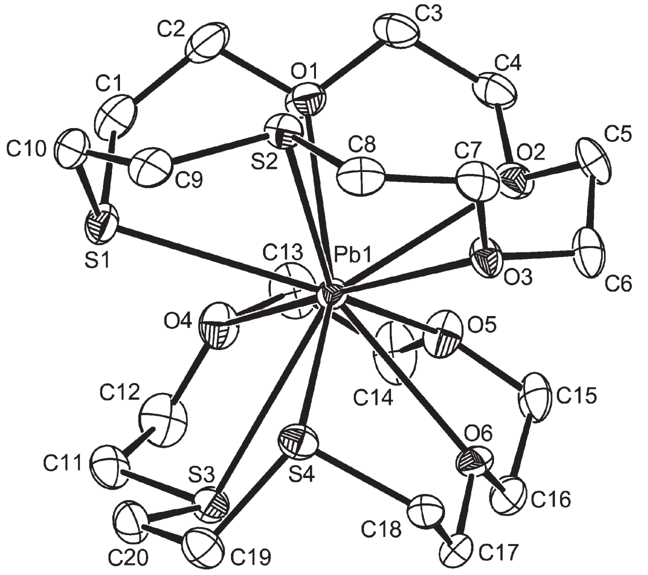

Fig. 4 Crystal structure of the cation in [Pb([15]aneO$_3$S$_2$)$_2$][BF$_4$]$_2$·nCH$_2$Cl$_2$ (n = 1.22) showing the atom numbering scheme and the coordination around Pb1. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Pb1–O1 = 2.688(5), Pb1–O2 = 2.725(5), Pb1–O3 = 2.898(5), Pb1–O4 = 3.055(5), Pb1–O5 = 2.761(4), Pb1–O6 = 2.750(4), Pb1–S1 = 3.022(2), Pb1–S2 = 3.043(2), Pb1–S4 = 3.054(2), Pb1–S3 = 3.116(2), O1–Pb1–O2 = 63.83(14), S1–Pb1–S2 = 66.44(5), O6–Pb1–S4 = 67.66(10), O6–Pb1–S3 = 71.07(10), S3–Pb1–S4 = 65.35(5).

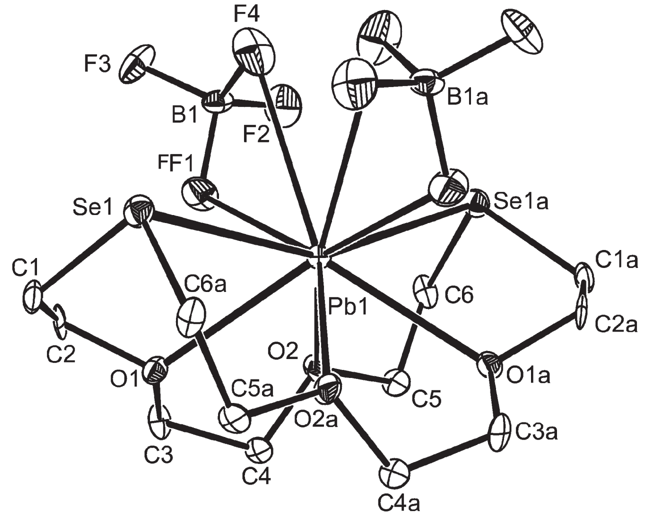

Fig. 5 Structure of [Pb([18]aneO$_4$Se$_2$)(BF$_4$)$_2$] showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level and hydrogen atoms have been omitted for clarity. Symmetry operation: $a = 1 - x, y, 1/2 - z$. Selected bond lengths (Å) and angles (°): Pb1–O2 = 2.584(5), Pb1–O1 = 2.717(4), Pb1···F1 = 2.707(4), Pb1···F4 = 3.223(5), Pb1–Se1 = 3.1820(14), O2–Pb1–O1 = 63.95(14), O2a–Pb1–O1 = 74.62(14), O2a–Pb1–Se1 = 68.67(10), O1–Pb1–Se1 = 65.43(10), Se1–Pb1–Se1a = 155.61(3).

the Pb–S distances are in the range 3.022(2)–3.116(2) Å. On this alternative basis, the lead is coordinated to two S atoms and two O atoms in each ring, giving a "core" coordination number of eight.

Few structurally authenticated complexes containing *endo* coordination of [15]aneO$_3$S$_2$ are known, examples include [Ag([15]aneO$_3$S$_2$)]$^+$,[25] [Ca([15]aneO$_3$S$_2$)I$_2$],[26] and [GeCl([15]aneO$_3$S$_2$)]$^+$,[27] and it is notable that all contain quite a wide range of M–O and M–S bond lengths within each complex, suggesting that these are a characteristic of this particular macrocycle.

The reaction of lead fluoroborate in H$_2$O/MeCN with [18]aneO$_4$Se$_2$ (1,4,10,13-tetraoxa-7,16-diselenacyclooctadecane), reproducibly (by checking unit cell measurements) gave colourless crystals which were found to be [Pb([18]aneO$_4$Se$_2$)(BF$_4$)$_2$] (Fig. 5). This contrasts with the structure of the hydrated thia-crown complex, [Pb([18]aneO$_4$S$_2$)(H$_2$O)$_2$(BF$_4$)][BF$_4$], described above. However, even upon repeated recrystallisations from MeCN, we were unable to obtain pure bulk samples of the anhydrous [18]aneO$_4$Se$_2$ complex; the IR and ^{1}H NMR spectra both reveal some H$_2$O present. There is a marked changed in geometry between the two complexes, the water molecules in [Pb([18]aneO$_4$S$_2$)(H$_2$O)$_2$(BF$_4$)][BF$_4$] are on the opposite side of the Pb-macrocycle plane to the BF$_4^-$, whereas in [Pb([18]aneO$_4$Se$_2$)(BF$_4$)$_2$], which has two-fold symmetry, the BF$_4^-$ groups lie on the same side (mutually *cis*) of the lead. The Pb–O distances are rather shorter in the selenacrown complex (2.584(5), 2.717(4) Å), although the differences between the Pb–S and Pb–Se distances (~0.16 Å) corresponds to the difference in covalent radii of the two donor atoms,[4] suggesting a very similar affinity for the lead. A very noticeable difference is in the coordination of the BF$_4^-$ groups. In both structures the coordination is asymmetric, in [Pb([18]aneO$_4$S$_2$)(H$_2$O)$_2$(BF$_4$)][BF$_4$] Pb1···F1 = 3.038(2), Pb1···F2 = 2.877(2) Å, $\Delta_{\text{Pb–F}}$ = 0.16 Å, whilst in [Pb([18]aneO$_4$Se$_2$)(BF$_4$)$_2$] Pb1···F1 = 2.707(4), Pb1···F4 = 3.223(5) Å, $\Delta_{\text{Pb–F}}$ = 0.52 Å. In the latter, the disparity is sufficiently great that κ^1-coordination may be a better description. Examination of the non-bonded contacts involving the fluoroborate groups provides a possible explanation; in [Pb([18]aneO$_4$Se$_2$)(BF$_4$)$_2$] the F4···F4a is 2.975 Å, very close to the sum of the Van der Waals radius for two fluorines (2 × 1.47 Å)[4] and any attempt at closer approach of F4 to the lead is prevented by this steric interaction. In all the fluoroborate complexes the effect of coordination on the B–F distances or F–B–F angles is small, reflecting the very strong B–F bonding.

The corresponding nitrate complex, [Pb([18]aneO$_4$Se$_2$)(NO$_3$)$_2$], was obtained in high yield, and the crystals are isomorphous with the BF$_4^-$ analogue above. The structure was solved in the space group *C*2/*c* and is shown in Fig. 6. The molecule has two-fold symmetry in which the lead is 10-coordinate with two κ^2-nitrate groups, which are disordered over two sites (see Experimental). The structure was also solved in the non-centrosymmetric *Cc* space group which removed the NO$_3^-$ disorder, but the data failed to converge satisfactorily. This is a well known crystallographic problem,[28–30] and we note that similar problems were apparent in the CIF file deposited for the structure of [Pb([18]aneO$_4$S$_2$)(NO$_3$)$_2$],[22] although not discussed. In that case the structure was reported in space group *Cc* with a large number of restraints.

From a chemical viewpoint the structure of [Pb([18]aneO$_4$Se$_2$)(NO$_3$)$_2$] is not in doubt, but the crystallographic

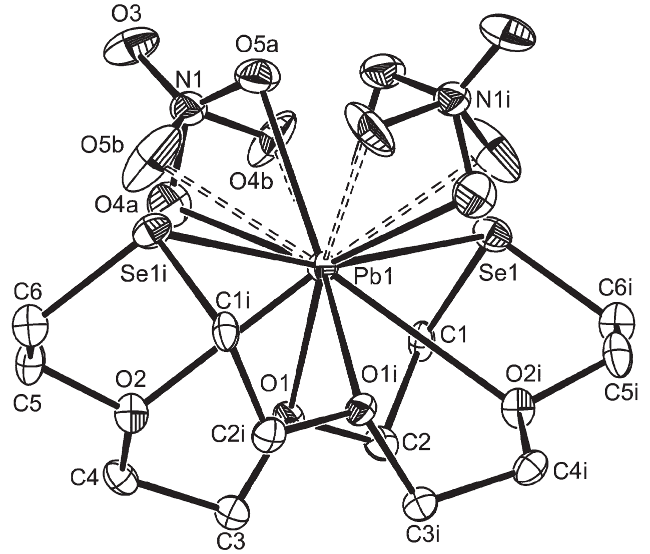

Fig. 6 Structure of $[Pb([18]aneO_4Se_2)(NO_3)_2]$ refined in the space group $C2/c$ showing the atom numbering scheme. The molecule has two-fold symmetry. Atomic displacement ellipsoids are drawn at the 25% probability level and hydrogen atoms have been omitted for clarity. The disordered nitrate was modelled as O4A/B and O5A/B and both components are shown. The bonds to Pb1 involving O4B and O5B are shown dashed. Symmetry operation: $i = -x, y, 1/2 - z$. Selected bond lengths (Å) and angles (°): Pb1–O2 = 2.77(8), Pb1–O2 = 2.929(8), Pb1–O4A = 2.61(2), Pb1–O5A = 2.61(2), Pb1–Se1 = 3.174(2), O1–Pb1–O2 60.3(2), O2–Pb1–Se1 62.72(15), O1–Pb1–Se1 68.01(15), Se1–Pb–Se1i = 165.01(4).

problem precludes detailed comparison of bond lengths and angles between the structures.

Attempts to isolate a complex of the corresponding oxatellura macrocycle $[18]aneO_4Te_2$ with $Pb[BF_4]_2$ in MeCN solution were unsuccessful.

In order to further explore the structural consequences of changing the anions, we also prepared some PF_6^- salts. Attempts to convert $[Pb(18\text{-crown-}6)(NO_3)_2]$ to the bis(hexafluorophosphate) complex by metathesis with excess $[NH_4][PF_6]$ in aqueous solution, gave some colourless crystals which were identified spectroscopically and by their X-ray crystal structure, as $[Pb(18\text{-crown-}6)(NO_3)(PF_6)]$. The structure (Fig. 7) shows the lead in the plane of the crown, κ^2-coordinated to the nitrate group, and with the PF_6^- group on the opposite side of the crown, interacting *via* three fluorines (κ^3), Pb1⋯F2 = 2.975(9), Pb1⋯F4 = 3.174(8) Å (Fig. 7). The Pb⋯F distances are well within the Van der Waals radii sum (3.49 Å),[4] and the three lead-coordinated P–F bonds are slightly lengthened (P1–F2 = 1.605(9), P1–F4 = 1.610(7) Å) compared to the others (P1–F3 = 1.564(9), P1–F1 = 1.586(9) Å).

An alternative approach to the lead hexafluorophosphate complexes was *via* direct reaction of an aqueous solution of $Pb[PF_6]_2$‡ (made by dissolving $PbCO_3$ in aqueous HPF_6) with the macrocycles in MeCN. In this way, $[Pb(18\text{-crown-}6)(H_2O)_2(PF_6)][PF_6]$, $[Pb([18]aneO_4S_2)(H_2O)_2(PF_6)][PF_6]$ and

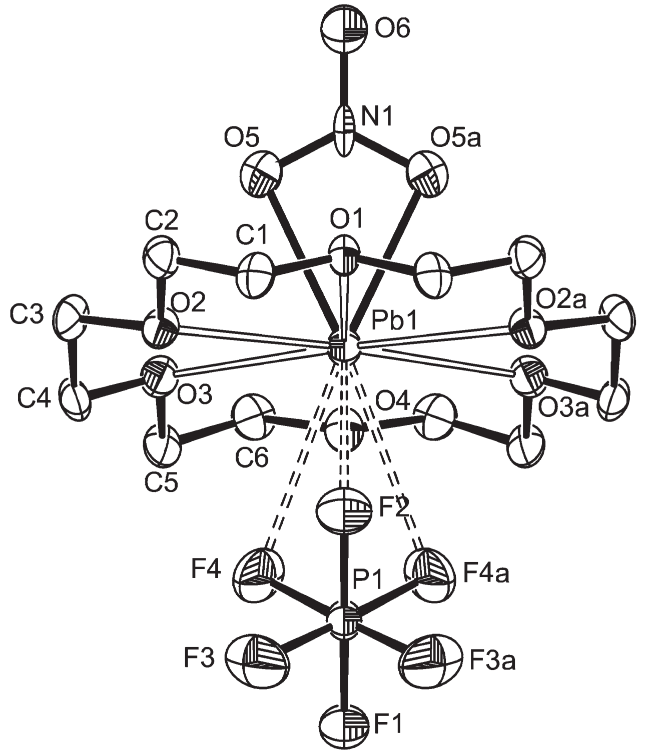

Fig. 7 The structure of $[Pb(18\text{-crown-}6)(NO_3)(PF_6)]$ showing the atom labelling scheme. The displacement ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. The molecule has mirror symmetry with Pb1–O shown as open bonds and the Pb1⋯F contacts shown as dashed lines. Symmetry operation: $a = 1 - x, y, z$. Selected bond lengths (Å) and angles (°): Pb1–O1 = 2.715(9), Pb1–O2 = 2.736(6), Pb1–O4 = 2.801(10), Pb1–O3 = 2.811(6), Pb1–O5 = 2.525(7), Pb1⋯F2 = 2.975(9), Pb1⋯F4 = 3.174(8), O5–Pb1–O5A = 50.6(3), O1–Pb1–O2 = 61.82(13), O2–Pb1–O3 = 60.7(2), O4–Pb1–O3 = 58.85(14).

$[Pb([18]aneO_4Se_2)(PF_6)_2]$ were obtained. In all three cases colourless crystals grew from the concentrated reaction mixture, and these were carefully separated and dried *in vacuo.* It proved impossible to recrystallise the compounds without decomposition, and examination of the mother liquors from the preparations showed large amounts of decomposition products, identified by a combination of ^{19}F and ^{31}P NMR spectroscopy as $[PO_3F]^{2-}$, $[PO_2F_2]^-$, F^- and $[PO_4H_{3-n}]^{n-}$.[31] The isolated solids also degrade (and blacken) considerably over a few days. For these reasons it has not been possible to obtain satisfactory microanalytical data for the hexafluorophosphate salts. Although $[PF_6]^-$ is usually viewed as a stable anion, degradation/hydrolysis in the presence of some metal salts has been reported previously.[23,31,32]

In the structure of $[Pb(18\text{-crown-}6)(H_2O)_2(PF_6)][PF_6]$ (Fig. 8) the two water molecules are on the opposite side of the Pb-crown unit to the PF_6^- group which is coordinated as a bidentate, with shorter Pb⋯F (Pb1⋯F2 = 2.881(9) Å) bonds than in the tridentate example in $[Pb(18\text{-crown-}6)(NO_3)(PF_6)]$. The water molecules are hydrogen bonded to a (partially occupied) lattice water, and charge is balanced by an ionic PF_6^- group. The similarity to the structure of $[Pb([18]aneO_4S_2)(H_2O)_2(BF_4)][BF_4]$ is

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‡It is important to note that ^{207}Pb, ^{19}F and ^{31}P NMR spectroscopy showed only $[Pb(H_2O)_x]^{2+}$ and PF_6^- ions present in the initial aqueous solution.

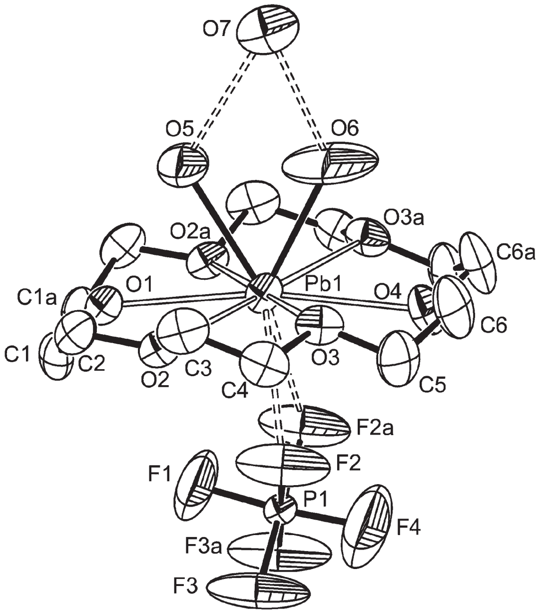

Fig. 8 The structure of the cation in [Pb(18-crown-6)$(H_2O)_2(PF_6)$][PF_6]·H_2O showing the atom labelling scheme. The displacement ellipsoids are drawn at the 40% probability level and H atoms are omitted for clarity. The molecule has crown Pb1–O shown as open bonds and the Pb1···F and O···O contacts shown as dashed lines. Selected bond lengths (Å) and angles (°): Pb1–O1 = 2.704(10), Pb1–O3 = 2.731(7), Pb1–O4 = 2.733(11), Pb1–O2 = 2.77(2), Pb1–O5 = 2.545(19), Pb1–O6 = 2.57(3), Pb1···F2 = 2.881(9), O1–Pb1–O2 = 60.0(1), O3–Pb1–O2 = 60.1(2), O1–Pb1–O2a = 60.0(1), O3–Pb1–O4 = 61.1(2).

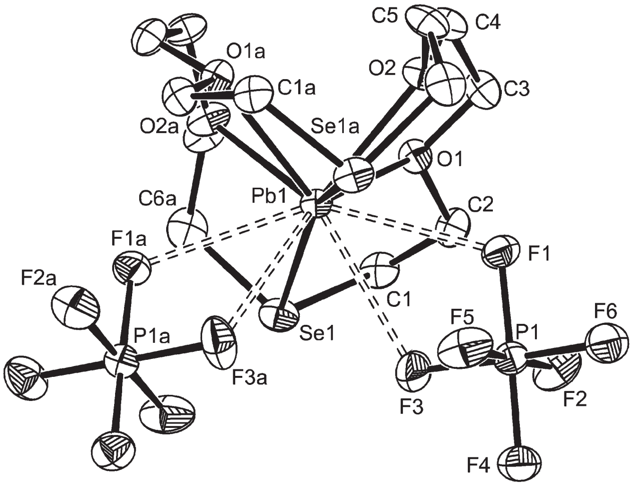

Fig. 9 The structure of [Pb([18]aneO_4Se_2)$(PF_6)_2$] showing the atom labelling scheme. The displacement ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. The molecule has two-fold symmetry and the long F···Pb1 interactions are shown with dashed bonds. Symmetry operation: $a = -x, y, 1/2 - z$. Selected bond lengths (Å) and angles (°): Pb1–O2 = 2.543(4), Pb1–O1 = 2.664(3), Pb1–Se1 = 3.173(1), F3···Pb1 = 2.908(4), F1···Pb1 = 2.920(3). O2–Pb1–O1 = 63.68(10), O2–Pb1–Se1 = 69.60(7), O1–Pb1–Se1 = 65.13(7), Se1–Pb1–Se1 = 156.02(2). (There is a F5···Se1′ contact of 3.167(4) Å).

also notable. Although the X-ray structure was not determined, the similarity of the spectroscopic data strongly suggests that the [18]aneO_4S_2 has the same constitution as the 18-crown-6 complex–[Pb([18]aneO_4S_2)$(H_2O)_2(PF_6)$][PF_6].

Unexpectedly the structure of the colourless crystals obtained from Pb[PF_6]$_2$ and [18]aneO_4Se_2 showed these had the constitution [Pb([18]aneO_4Se_2)$(PF_6)_2$] (Fig. 9) with two *cis* disposed κ^2-PF_6^- groups and a very puckered macrocyclic ring. There is an overall similarity to the structure of [Pb([18]aneO_4Se_2)$(BF_4)_2$] but, whereas the BF_4^- groups are very asymmetrically coordinated to the lead (~κ^1 as discussed above), the PF_6^- groups are symmetrically bound. The macrocycle conformation is similar in both compounds.

These lead systems are unusual examples of coordination (albeit weak), of the hexafluorophosphate ion,[23] and it is notable that in the published structure of [PbCl(18-crown-6)]-$SbCl_6$,[10] although the $SbCl_6^-$ anion is on the "open" side of the Pb-crown plane opposite to the axial Cl, the nearest Pb···Cl_{Sb} contact is ~3.80 Å which is greater than the Van der Waals radii sum (3.77 Å),[4] indicating no significant bonding interaction. The very ready hydrolysis of the PF_6^- anions observed for the Pb(II) complexes is very unusual.

Spectroscopic studies

In labile systems the speciation may differ significantly between the solid and solution phases, and this is evident in the present complexes. Molar conductivity measurements carried out in 10^{-3} mol dm^{-3} MeCN showed that the nitrate complexes exhibited molar conductivities[33] much less than those of 1 : 1 electrolytes (see Experimental), showing the nitrates remain coordinated in solution. However, the fluoroborates had much higher values, indicating the anions dissociate in solution. The MeCN does not however compete as a ligand for the lead in the solid state, since the complexes are recovered unchanged from MeCN solution. They could also be recrystallised from acetone, but were decomposed by $MeNO_2$.

The solution ($CDCl_3$ or CD_3CN) ^1H NMR data of all the complexes at 295 K show resonances for the geometrically distinct CH_2 units in the macrocycles, slightly shifted to higher frequency as a result of coordination to the lead, but either with ill-defined splittings or as broad singlets showing the dynamic nature of the complexes, which are probably undergoing reversible ligand dissociation. In the case of [Pb(15-crown-5)$_2$][BF_4]$_2$ cooling the CD_3CN solution, showed some ill-defined second order patterns, and then at 230 K an AB quartet pattern as the ligand exchange slowed. Several of the other complexes showed similar but less well-defined spectra at low temperatures. We were unable to observe ^{207}Pb or (for the [18]aneO_4Se_2 complexes) $^{77}Se\{^1H\}$ NMR resonances over the temperature range 295–220 K, again attributed to dynamic processes. Similarly, although several of the tetrafluoroborate complexes contain coordinated anions in the solid state, in CD_3CN or $CDCl_3$ solution the $^{19}F\{^1H\}$ NMR spectra each show a singlet due to one BF_4^- environment. Coordinated tetrafluoroborate has been identified by $^{19}F\{^1H\}$ NMR spectroscopy in some kinetically inert organometallic species.[22]

In the solid state, the most useful technique was IR spectroscopy, which showed features due to the anions present, as well as water (where present) and the macrocycle. The strong and quite complex absorptions arising from the macrocycles make identification of the anion vibrations difficult, but by comparison of the corresponding nitrate and tetrafluoroborate salts, peaks due to the macrocycle can be identified with reasonable certainty. κ^2-Coordinated nitrate groups identified crystallographically in $[Pb(18\text{-crown-}6)(NO_3)_2]$, $[Pb(15\text{-crown-}5)(NO_3)_2]$ and $[Pb([18]aneO_4Se_2)(NO_3)_2]$ have approximate C_{2v} symmetry§ for which three stretching modes are expected, $2A_1 + B_2$ – all IR active.[34] A good comparison for these are lanthanide nitrate complexes with κ^2-NO_3^- groups which also have high coordination number, large metal centres with no strong stereochemical preferences. Typically C_{2v} coordinated NO_3^- groups on these metals show IR stretching bands ~1470, 1310 and 1030 cm^{-1} and a bending mode ~820 cm^{-1}.[35–37] The ~1470 cm^{-1} band is obscured in the present cases, but the other three features were identified in the spectra (Experimental section), which also show the absence of ionic nitrate ions. Although not assigned, the published IR spectrum of $[Pb([18]aneO_4S_2)(NO_3)_2]$ shows[21] bands at 1357, 1012, and 801 cm^{-1}, also consistent with the nitrate coordination present.

The ionic tetrafluoroborate anion, exhibits a broad, often asymmetric, band at ~1070 cm^{-1} and a sharp band at ~520 cm^{-1} due to the stretching and bending modes respectively,[34] although hydrogen bonding to neighbouring groups or site symmetry can cause some ill-defined splitting in the higher frequency band, as seen in the spectrum of $[Pb([15]aneO_3S_2)_2][BF_4]_2$ (see ESI†). The BF_4^- stretching region of $[\{Pb(18\text{-crown-}6)(H_2O)(BF_4)\}_2][BF_4]_2$ and $[Pb([18]aneO_4S_2)(H_2O)_2(BF_4)][BF_4]$ are clearly different (ESI†), but the broad bands and the occurrence of the ligand modes in the same region make detailed assignment uncertain, and the IR spectra alone would not permit certain identification of the anion coordination mode. The hexafluorophosphate anion shows stretching and bending modes at ~850 and ~560 cm^{-1} respectively.[34] The free, κ^2- and κ^3-coordinated PF_6^- groups in $[Pb(18\text{-crown-}6)(H_2O)_2(PF_6)][PF_6]$, $[Pb([18]aneO_4S_2)(H_2O)_2(PF_6)][PF_6]$ and $[Pb([18]aneO_4Se_2)(PF_6)_2]$ show only broadened vibrations with no resolved splittings, even when two forms, *e.g.* free and κ^2-PF_6^- are present in the same compound, and as with the tetrafluoroborates described above, ^{19}F (and ^{31}P) NMR studies in MeCN or $CDCl_3$ show the anions are dissociated from the metal centre in solution.

Conclusions

The structures of the macrocyclic complexes reported in this work and related literature[6,10,13,14,21] show that lead(II) typically coordinates to all donors of the macrocycle, albeit with a range of bond lengths, and completes a high coordination number environment, 8–11, by ligating to counter anions or water. A combination of the high coordination numbers, different donor groups and the steric constraints of both the macrocycles and the anions, produce irregular geometries, but there is no evidence for a stereochemically active lone pair on the lead centre. The overall picture that emerges from comparing the structures is of a large metal centre with no strong stereochemical preferences, and with the lead geometry/coordination accommodating to the steric demands of the macrocycles and the different anions to maximise the Pb–donor interactions and minimise repulsions between the ligands. Overall the potential well about the lead is probably quite shallow and one should not overinterpret the observed differences in bond lengths, especially set against the different coordination numbers and donor atom geometries.

The 15-membered ring macrocycles adopt sandwich or half-sandwich structures as the ring is too small for the Pb^{2+} to fit in the plane, but the 18-ring macrocycles have a sufficiently large cavity to accommodate the metal centre if desired. The structures observed in individual cases may also reflect crystal packing and (in some cases) H-bonding interactions. Although a range of structures is observed, these are obtained reproducibly under the conditions used, and the same species crystallise from MeCN or acetone (sometimes also CH_2Cl_2); we have no evidence that isomeric forms are obtainable, suggesting the solvent/conditions used are not responsible for the variations observed with different macrocycles. Whether the co-ligands are disposed *trans* across the Pb-macrocycle plane or *cis* with a more folded conformation of the macrocycle, will depend upon the subtle packing forces and inter-ligand interactions (note also the presence of H···O and H···F hydrogen bonds in several structures), and the structures observed will reflect this interplay of individually rather small energy terms. The low charge/radius ratio largely accounts for the relatively weak binding of the ligands and the solution lability observed. A number of different coordination modes of the BF_4^- group have been identified – μ^2, κ^2 and possibly κ^1, as well as examples of κ^2 and κ^3 coordinated PF_6^- groups, and the results show that these groups are less strongly coordinated to lead than nitrate or perchlorate, readily dissociating in solution.

Experimental

Infrared spectra were recorded as Nujol mulls between CsI plates using a Perkin-Elmer Spectrum100 spectrometer over the range 4000–200 cm^{-1}. ^1H NMR spectra were recorded using a Bruker AV300 spectrometer. $^{19}F\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were obtained on a Bruker DPX400 and are referenced to $CFCl_3$ and H_3PO_4 respectively. Microanalyses were undertaken by Medac Ltd. Conductivities were measured for solutions in MeCN using a Cambridge conductivity bridge. Solvents were dried by distillation prior to use, CH_2Cl_2 and MeCN from CaH_2, hexane from sodium benzophenone ketyl. Lead nitrate, lead tetrafluoroborate (50% solution in water),

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§ The coordinated nitrates are bound asymmetrically to the metal, but even allowing for lower actual symmetry three stretching modes are predicted; the frequencies distinguish coordinated from ionic nitrate, but identification of the coordination mode (κ^1 *vs.* κ^2) has been controversial in many systems.[34]

18-crown-6 and 15-crown-5 were obtained from Aldrich and used as received. The oxa-thia crowns [18]aneO_4S_2, [18]aneO_2S_4, [15]aneO_3S_2, and [18]aneO_4Se_2 and [18]aneO_4Te_2 were prepared by the original methods[38–40] or modifications as described in the ESI.† Lead hexafluorophosphate (as an aqueous solution) was made by adding a small excess of basic lead carbonate (Aldrich) to a known volume of aqueous HPF_6 (65%), and after reaction had ceased, filtering off any residual solid, and concentrating the solution *in vacuo*. Aliquots of this solution were used for the syntheses.

[{Pb(18-crown-6)(H_2O)(BF_4)}$_2$][BF_4]$_2$: $Pb(BF_4)_2$ as a 50% aqueous solution (0.402 g, 0.53 mmol) was added dropwise to 18-crown-6 (0.139 g, 0.53 mmol) dissolved in CH_3CN (5 mL). The resulting colourless mixture was allowed to evaporate at room temperature for 12 h, which afforded colourless crystals that were collected by filtration, washed with CH_3CN (2 mL) and CH_2Cl_2 (2 mL), then dried *in vacuo*. Yield: 0.250 g, 72%. Required for $C_{12}H_{26}B_2F_8O_7Pb$ (633.4): C, 21.7; H, 3.9. Found: C, 21.8; H, 3.4%. ^1H NMR (CD_3CN, 293 K): $\delta = 3.82$ (s, CH_2). $^{19}F\{^1H\}$ NMR (CD_3CN, 293 K): −151.8 (s).¶ IR (Nujol): 3470br (νOH), 1620s (δH_2O), 1143sh, 1090br,m, 969br,m (νBF_4), 517s (δBF_4) cm^{-1}.

[Pb(15-crown-5)$_2$][BF_4]$_2$: $Pb(BF_4)_2$ as a 50% aqueous solution (0.400 g, 0.53 mmol) was added dropwise to 15-crown-5 (0.231 g, 1.05 mmol) dissolved in CH_3CN (5 mL). The colourless reaction mixture was left to stir for 24 h, and upon slow evaporation afforded colourless crystals. These were washed with CH_3CN (2 mL) followed by CH_2Cl_2 (2 mL) and dried *in vacuo*. Yield: 0.21 g, 49%. Required for $C_{20}H_{40}B_2F_8O_{10}Pb\cdot CH_2Cl_2$ (906.3): C, 27.8; H, 4.7. Found: C, 28.2, H, 4.5%. ^1H NMR (CD_3CN, 293 K): $\delta = 3.92$ (m), 3.86 (m), 5.3 (s) (CH_2Cl_2); (230 K): 3.89 (d), 3.77 (d) $^2J_{HH} = 4$ Hz. $^{19}F\{^1H\}$ NMR (CD_3CN, 293 K): −152.2(s). IR (Nujol): 1087sh, 1052br,s (νBF_4), 520s (δBF_4) cm^{-1}. Λ_M (10^{-3} mol dm^{-3}, CH_3CN) = 335 ohm^{-1} cm^2 mol^{-1}.

[Pb(18-crown-6)(NO_3)$_2$]: 18-crown-6 (0.239 g, 0.91 mmol) dissolved in deionised water (3 mL) was added dropwise to a saturated aqueous solution (5 mL) of $Pb(NO_3)_2$ (0.301 g, 0.91 mmol). A white microcrystalline solid precipitated from the reaction mixture after ~1 h stirring at room temperature. The precipitate was collected by vacuum filtration and washed with 5 mL of deionised water and then dried *in vacuo*. Yield: 0.190 g, 72%. Required for $C_{12}H_{24}N_2O_{12}Pb$ (595.3): C, 24.2; H, 4.1; N, 4.7. Found: C, 24.2; H, 4.0; N, 4.7%. ^1H NMR ($CDCl_3$, 293 K): $\delta = 3.79$ (s, CH_2). IR (Nujol): 1350, 1030, 823 (NO_3) cm^{-1}. Λ_M (10^{-3} mol dm^{-3}, CH_3CN) = 50 ohm^{-1} cm^2 mol^{-1}.

[Pb(15-crown-5)(NO_3)$_2$]: 15-crown-5 (0.133 g, 0.60 mmol) dissolved in a minimum amount of dry CH_3CN (5 mL) was slowly added to a suspension of $Pb(NO_3)_2$ (0.200 g, 0.60 mmol) in dry acetonitrile (5 mL). The mixture was left to stir for 2 days and the remaining solids were removed by filtration. The filtrate was left to slowly evaporate for 12 h and afforded colourless crystals which were washed with CH_3CN (2 mL) and CH_2Cl_2 (2 mL), then dried *in vacuo*. Yield: 0.080 g, 25%. Required for $C_{10}H_{20}N_2O_{11}Pb$ (551.3): C, 21.8; H, 3.7; N 5.1. Found: C, 22.1; H, 3.8; N 5.1%. ^1H NMR ($CDCl_3$, 293 K): δ = 3.79 (s, CH_2). IR (Nujol): 1352m, 1025, 805 (NO_3) cm^{-1}. Λ_M (10^{-3} mol dm^{-3}, CH_3CN) = 40 ohm^{-1} cm^2 mol^{-1}.

[Pb([18]aneO_4S_2)(H_2O)$_2$(BF_4)][BF_4]: [18]aneO_4S_2 (0.060 g, 0.20 mmol) dissolved in CH_3CN (2 mL) was added dropwise to $Pb(BF_4)_2$ as a 50% aqueous solution (0.155 g, 0.20 mmol). This was stirred at room temperature for 2 h. before being concentrated *in vacuo* to colourless oil. Dichloromethane (1 mL) was added and afforded a cloudy white suspension which upon slow evaporation afforded colourless crystals. These were washed with CH_3CN (2 mL) followed by CH_2Cl_2 (2 mL) and dried *in vacuo*. Yield: 0.155 g, 97%. Required for $C_{12}H_{28}B_2F_8O_6PbS_2\cdot CH_2Cl_2$ (798.2): C 19.6, H 3.8; found: C 19.2, H 3.4%. ^1H NMR ($CDCl_3$, 293 K): δ = 3.13 (t, [8H], SCH_2), 3.70 (s, [8H], OCH_2), 4.01 (m, [8H], OCH_2), 5.3 (CH_2Cl_2). $^{19}F\{^1H\}$ NMR (CD_3CN, 293 K): −148.5 (s). IR (Nujol): 3470 br (νOH), 1612s (δH_2O), 1081m, 1020m, 990m (νBF_4), 518s (δBF_4) cm^{-1}. Λ_M (10^{-3} mol dm^{-3}, CH_3CN) = 314 ohm^{-1} cm^2 mol^{-1}.

[Pb([15]aneO_3S_2)$_2$][BF_4]$_2$: $Pb(BF_4)_2$ as a 50% aqueous solution (0.300 g, 0.39 mmol) was added dropwise to [15]aneO_3S_2 (0.200 g, 0.79 mmol) dissolved in CH_3CN (3 mL). The colourless reaction solution was left to stir for 24 h and upon slow evaporation of the solvent colourless crystals formed, which were washed with CH_2Cl_2 (2 mL) and dried *in vacuo*. Yield: 0.203 g, 59%. Required for $C_{20}H_{40}B_2F_8O_6PbS_4\cdot 2CH_2Cl_2$ (1055.5): C, 25.0, H 4.2. Found: C, 24.6; H, 3.8%. ^1H NMR ($CDCl_3$, 293 K): δ = 3.31 (t, [4H], SCH_2), 3.36 (s, [4H], SCH_2), 3.86 (br,s, [8H], OCH_2), 3.95 (t, [4H], OCH_2), 5.24 (s, CH_2Cl_2). $^{19}F\{^1H\}$ NMR (CD_3CN, 293 K): −151.3 (s). IR (Nujol): 1051br,m, 1030sh,m (νBF_4), 520s (δBF_4) cm^{-1}. Λ_M (10^{-3} mol dm^{-3}, CH_3CN) = 350 ohm^{-1} cm^2 mol^{-1}.

[Pb([18]aneO_4Se_2)(BF_4)$_2$]: [18]aneO_4Se_2 (0.084 g, 0.215 mmol) and 50% aqueous $Pb(BF_4)_2$ (0.082 g, 0.215 mmol) were dissolved in MeCN (20 mL) and allowed to stir overnight. A small amount of very fine white powder precipitated. The solution was filtered and the filtrate was slowly allowed to evaporate, giving colourless crystals identified crystallographically as [Pb([18]aneO_4Se_2)(BF_4)$_2$], but analytically pure samples were not obtained even after recrystallization from MeCN. ^1H NMR (CD_3CN): δ = 2.4 (br, H_2O), 3.10 (t, [8H], $SeCH_2$), 3.84 (s, [8H], OCH_2), 4.02 (t, [8H], OCH_2). $^{19}F\{^1H\}$ NMR (CD_3CN, 293 K): −150.5. IR (Nujol): 3600vbr (νOH), 1630s (δH_2O), 1068s, 1051sh, 1038s (νBF_4), 519s (δBF_4) cm^{-1}.

[Pb([18]aneO_4Se_2)(NO_3)$_2$]: [18]aneO_4Se_2 (0.070 g, 0.018 mmol) was dissolved in MeCN (20 mL) after which 50% aqueous $Pb(NO_3)_2$ (0.059 g, 0.018 mmol) was added and the granular suspension allowed to stir overnight. Slowly a fine white powder began to form. The solid was filtered and crystals were grown from the filtrate. Yield: 0.10 g, 77%. Required for $C_{12}H_{24}N_2O_{10}PbSe_2$ (721.4): C, 20.0; H, 3.4; N, 3.9. Found: C, 19.9; H, 3.2; N, 4.1. ^1H NMR (CD_3CN): δ = 3.01 (t, [8H], $SeCH_2$), 3.74 (s, [8H], OCH_2), 3.91 (t, [8H], OCH_2). IR (Nujol): 1348, 1027, 816 (NO_3) cm^{-1}.

¶Under high resolution two very closely spaced singlets in approximate ratio 1 : 4 due to ^{10}B and ^{11}B isotopomers are seen in all the BF_4 complexes. R. K. Harris and B. E. Mann, *NMR and the Periodic Table*, Academic Press, NY. 1977. $^1J_{BF}$ couplings are very small and not resolved.

[Pb(18-crown-6)(NO_3)(PF_6)]: $Pb(NO_3)_2$ (0.100 g, 0.301 mmol) and 18-crown-6 (0.080 g, 0.301 mmol) were left to stir in deionised water (40 mL) for 30 min. To the resulting clear solution $[NH_4][PF_6]$ (0.245 g, 1.506 mmol) was added and left to stir for 12 h. A small amount of fine white solid formed was filtered off, and the remaining clear solution concentrated *in vacuo*. Large colourless crystals formed which were washed with ethanol and dried *in vacuo*. ^1H NMR ($CDCl_3$, 293 K): δ = 3.77 (s, CH_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 295 K): −143.3 (sept). IR (Nujol): 1356, 1025, 813 (NO_3), 836s (νPF_6), 560m (δPF_6) cm^{-1}.

[Pb(18-crown-6)(H_2O)$_2$(PF_6)]PF_6: A aqueous solution of $Pb(PF_6)_2$ (0.14 mmol) was added to MeCN (10 mL) resulting in an immediate white solid forming. To the stirring mixture was added 18-crown-6 (0.037 g, 0.141 mmol) and the solution began to clear and was left to react overnight. A small amount of fine white solid remained which was removed by filtration, and the filtrate concentrated *in vacuo.* X-ray quality crystals grew upon concentration. These were removed. Yield: 0.045 g. ^1H NMR ($CDCl_3$, 293 K): δ = 3.80 (s, CH_2). $^{19}F\{^1H\}$ NMR ($CDCl_3$): −72.1 (d, $^1J_{PF}$ = 710 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 295 K): −143.3 (sept. $^1J_{PF}$ = 710 Hz). IR (Nujol): 3500br, 1680br (H_2O), 837s (νPF_6), 558m (δPF_6) cm^{-1}.

[Pb([18]aneO_4S_2)(H_2O)$_2$(PF_6)]PF_6: was made similarly to the 18-crown-6 complex. ^1H NMR ($CDCl_3$, 293 K): δ = 3.10 (t, [8H], SCH_2), 3.78 (s, [8H], OCH_2), 3.89 (m, [8H], OCH_2). $^{19}F\{^1H\}$ NMR ($CDCl_3$): −72.2 (d, $^1J_{PF}$ = 710 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 295 K): −143.3 (sept). IR (Nujol): 3500br, 1680br (H_2O), 840s (νPF_6), 558m (δPF_6) cm^{-1}.

Table 1 Crystal data and structure refinement details[a]

Compound	[Pb([15]aneO_3S_2)$_2$][BF_4]$_2$·nCH_2Cl_2 (n = 1.22)	[Pb([18]aneO_4S_2)(OH_2)$_2$(BF_4)]BF_4	[{Pb(18-crown-6)(H_2O)(BF_4)}$_2$][BF_4]$_2$	[Pb(15-crown-5)(NO_3)$_2$]
Formula	$C_{21.22}H_{42.44}B_2Cl_{2.44}F_8O_6PbS_4$	$C_{12}H_{28}B_2F_8O_6PbS_2$	$C_{24}H_{52}B_4F_{16}O_{14}Pb_2$	$C_{10}H_{20}N_2O_{11}Pb$
M	989.18	713.27	1326.28	551.47
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic
Space group (no.)	*Pccn* (56)	*Pbca* (61)	$P2_1/c$ (14)	$P2_1/c$ (14)
a/Å	18.747(3)	16.5374(15)	12.818(4)	15.307(4)
b/Å	28.254(10)	15.5893(15)	10.661(3)	8.303(2)
c/Å	13.263(2)	17.703(6)	15.298(5)	13.152(4)
α/°	90	90	90	90
β/°	90	90	94.66(2)	92.815(4)
γ/°	90	90	90	90
U/Å^3	7025(3)	4564.1(17)	2083.6(10)	1669.5(8)
Z	8	8	2	4
μ(Mo-K$_\alpha$)/mm^{-1}	5.304	7.667	8.199	10.165
F(000)	3898	2752	1272	1056
Total number reflns	17 991	11 444	11 962	9241
R_{int}	0.040	0.020	0.083	0.076
Unique reflns	7968	5184	4753	3811
No. of params, restraints	394, 16	293, 4	277, 11	217, 0
R_1, wR_2 [$I > 2\sigma(I)$][b]	0.046, 0.096	0.021, 0.047	0.049, 0.077	0.031, 0.071
R_1, wR_2 (all data)	0.071, 0.107	0.030, 0.050	0.082, 0.085	0.034, 0.073

Compound	[Pb([18]aneO_4Se_2)(BF_4)$_2$]	[Pb([18]aneO_4Se_2)(NO_3)$_2$]	[Pb(18-crown-6)(NO_3)(PF_6)]PF_6	[Pb(18-crown-6)(H_2O)$_{1.6}$(PF_6)][PF_6]·0.6H_2O	[Pb([18]aneO_4Se_2)$_2$(PF_6)$_2$]
Formula	$C_{12}H_{24}B_2F_8O_4PbSe_2$	$C_{12}H_{24}N_2O_{10}PbSe_2$	$C_{12}H_{24}F_6NO_9PPb$	$C_{12}H_{28.4}F_{12}O_{8.20}P_2Pb$	$C_{12}H_{24}F_{12}O_4P_2PbSe_2$
M	771.04	721.44	678.48	801.08	887.36
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group (no.)	$C2/c$ (15)	$C2/c$ (15)	$Pmn2_1$ (31)	$P2_1/m$ (11)	$C2/c$ (15)
a/Å	10.953(5)	10.969(4)	12.958(5)	8.754(3)	11.012(4)
b/Å	12.060(5)	11.735(5)	8.475(3)	15.230(4)	12.949(5)
c/Å	15.530(7)	15.385(6)	9.296(3)	9.254(3)	16.105(6)
α/°	90	90	90	90	90
β/°	90.693(6)	90.382(6)	90	91.453(6)	95.402(7)
γ/°	90	90	90	90	90
U/Å^3	2051.2(14)	1980.4(14)	1020.8(5)	1233.4(7)	2286.3(14)
Z	4	4	2	2	4
μ(Mo-K$_\alpha$)/mm^{-1}	11.862	12.248	8.441	7.096	10.819
F(000)	1440	1360	652	772	1664
Total number reflns	6169	9116	6653	5846	9667
R_{int}	0.057	0.109	0.079	0.030	0.054
Unique reflns	2340	2271	2334	2908	2599
No. of parameters, restraints	132, 7	141, 4	148, 1	178, 2	150, 0
R_1, wR_2 [$I > 2\sigma(I)$][b]	0.039, 0.070	0.060, 0.119	0.049, 0.097	0.063, 0.141	0.031, 0.076
R_1, wR_2 (all data)	0.056, 0.075	0.085, 0.134	0.058, 0.097	0.076, 0.150	0.033, 0.077

[a] Common items: temperature = 100 K; wavelength (Mo-K$_{(\alpha)}$) = 0.71073 Å; θ(max) = 27.5°. [b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$.

[Pb([18]aneO$_4$Se$_2$)(PF$_6$)$_2$]: was made similarly to the 18-crown-6 complex. ^{1}H NMR (CDCl$_3$, 293 K): δ = 3.06 (t, [8H], SCH$_2$), 3.79 (s, [8H], OCH$_2$), 3.96 (t, [8H], OCH$_2$). ^{19}F{^{1}H} NMR (CDCl$_3$): −72.2 (d, $^1J_{PF}$ = 710 Hz). ^{31}P{^{1}H} NMR (CDCl$_3$, 295 K): −143.3 (sept. $^1J_{PF}$ = 710 Hz). IR (Nujol): 844s (νPF$_6$), 560m (δPF$_6$) cm^{-1}.

X-ray crystallography

Details of the crystallographic data collection and refinement parameters are given in Table 1. Crystals suitable for single crystal X-ray analysis were obtained as described above. Data collections used a Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn724+ detector mounted at the window of an FR-E+ SuperBright molybdenum (λ = 0.71073 Å) rotating anode generator with VHF Varimax optics (100 µm focus) with the crystal held at 100 K (N$_2$ cryostream). Structure solution and refinement were straightforward,[41,42] except as detailed below, with H atoms bonded to C being placed in calculated positions using the default C–H distance. For [Pb([15]-aneO$_3$S$_2$)$_2$][BF$_4$]$_2$·nCH$_2$Cl$_2$ (n = 1.22) the [BF$_4$]$^-$ (B2 centred) anion was modelled as two conformations, with F6–F8 were split into A and B sites, and DFIX constraints were applied to the B–F and F···F distances of the A and B positions and retaining isotropic adp's. The proportions of A and B were allowed to vary through FVAR2. The discrete CH$_2$Cl$_2$ solvent identified in the difference map also showed disorder, which was modelled satisfactorily. For the partially occupied (0.22) CH$_2$Cl$_2$ molecule Cl3 (A and B) were included in the model based on the Cl3A···Cl3A′ and Cl3B···Cl3B′ distances, but the C atom was not identified (sof for Cl3A = 0.26 and for Cl3B = 0.17). For [Pb(15-crown-5)$_2$][H$_3$O][BF$_4$]$_3$ the positions of the Pb, the [BF$_4$]$^-$ anions and O atoms of the [H$_3$O]$^+$ were readily located, and the 15-crown-5 ligands are clearly coordinated to form [Pb(15-crown-5)$_2$]$^{2+}$. However, the C and O atoms of the crowns were badly disordered, and resisted a satisfactory disorder model. Similar disorder has been noted in other crown ether complexes.[6,43] Hence, the data reported simply serve to confirm the gross structure and the absence of any significant [BF$_4$]$^-$ interactions with the Pb ion.

The crystals for [Pb([18]aneO$_4$Se$_2$)(NO$_3$)$_2$] are isostructural with [Pb([18]aneO$_4$Se$_2$)(BF$_4$)$_2$], and the data were solved in space group $C2/c$, leading to a molecule with two-fold symmetry and disordered nitrate groups (but all other atoms refined well). These were modelled using split O atom occupancies for O4 and O5 with sofs of 0.5 (see Fig. 6). The alternative, non-centrosymmetric Cc refinement was also attempted, (in which the molecule has no crystallographic symmetry). In this model the two independent nitrate anions (N1, N2, O5–O10) are **not** related by an approximate 2-fold axis – the two plane normals are approximately perpendicular to each other (*ca.* 85°). Closer examination shows that the [18]aneO$_4$Se$_2$ has to a good approximation 2-fold symmetry, N1, N2, O7 and O10 are again approximately related by a two-fold axis, and it is only O5, O6, O8 and O9 that introduce the disorder seen in $C2/c$. Least squares refinement in the Cc model had severe correlations, a number of npd C atoms, and even using a DAMP instruction did not lead to satisfactory convergence (R_1 = 0.067). Hence we report the $C2/c$ refinement in Table 1, recognising that there remains a space group uncertainty. For [Pb-(18-crown-6)(NO$_3$)(PF$_6$)] the data clearly supported the orthorhombic space group $Pmn2_1$ (or less likely $Pnmm$), but the use of the usual structure solution software failed to produce a trial model that developed. A trial structure did arise in the monoclinic space group $P2_1$ with the same cell (β = 90°) which refined to R_1 = 0.052, but inspection of the cell packing diagram showed a convincing mirror plane and comments in 'checkcif' supported the additional symmetry. Transformation of the coordinate system to suit the orthorhombic cell and positioning the monoclinic (pseudo) mirror on the genuine mirror by shifting the atomic coordinates finally yielded the reported structure.

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