Comment on the preparation of the ionic liquid 1-ethyl-3-methylimidazolium ethanoate: a unique monomeric, homoleptic pentacoordinate lead ethanoate complex

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Atomic absorption spectroscopy of the ionic liquid 1-ethyl-3-methylimidazolium ethanoate ([emim]$_2$[O$_2$CMe]), prepared according to International Patent WO 96/18459, showed it to contain large amounts of lead impurity: (*ca.* 0.5 M): [emim]$_2$[Pb(O$_2$CMe)$_4$] was isolated and shown crystallographically to contain the first known example of a monomeric, homoleptic pentacoordinate lead(II) carboxylate complex, with a stereochemically active lone-pair.

Ionic liquids are well-established media for clean synthesis,[1,2] and consequently an essential requirement is their purity. In particular, heavy metal and halide impurities pose problems with regard to human and environmental health, catalysis and corrosion. Thus it is important to develop routes that yield pure products. A number of methods for the synthesis of ionic liquids have been cited in the literature.[2,3] As part of our general work in this area, we have examined a BP Chemicals patent that describes the use of lead(II) salts in the synthesis of ionic liquids.[4] It is claimed that the ionic liquid 1-ethyl-3-methylimidazolium ethanoate ([emim][O$_2$CMe]) could be synthesised *via* the metathesis of lead(II) ethanoate and [emim]Cl or [emim]Br. Analysis by atomic absorption spectroscopy of the ionic liquid thus obtained showed that large amounts of lead remained in the product (*ca.* 0.5 M). Crystals of the dissolved lead complex were obtained from the [emim][O$_2$CMe] produced *via* a modification of this method that precludes the addition of water.†

A review of BIDS[5] and the Cambridge Structural Database[6] for lead(II) carboxylate complexes identified a total of 25 structures: 18 were polymeric with the carboxylate moiety acting as a bridging ligand; three others that, although monomeric, contained either the sterically demanding [edta]$^{2-}$ ligand or bulky crown ethers; and one containing hexanuclear units.[7] The remaining three compounds, Pb(C$_8$H$_{11}$N$_4$S)(O$_2$CMe),[8] [Pb(C$_{16}$H$_{36}$N$_4$)(O$_2$CMe)][O$_2$CMe]·2H$_2$O[9] and Pb(C$_{12}$H$_{10}$N$_3$SO)(O$_2$CMe),[10] are compared and contrasted with [emim]$_2$[Pb(O$_2$CMe)$_4$] below.

The data for [emim]$_2$[Pb(O$_2$CMe)$_4$] were collected using our usual methodology.‡ The asymmetric unit consists of one [Pb(O$_2$CMe)$_4$]$^{2-}$ unit and two [emim]$^+$ cations. The four ethanoate anions are involved in two different bonding modes: three are bonded *via* one oxygen atom, and one is chelating, Fig. 1. The three non-coordinated oxygen atoms are involved in C–H···O hydrogen bonds with the cations, and extend towards the void associated with the lead(II) centre, Fig. 2. Two [emim]$^+$ cations lie either side of this void and act as spacers between the [Pb(O$_2$CMe)$_4$]$^{2-}$ units. The large void in the coordination sphere around the lead(II) centre is indicative of a stereochemically active lone-pair, the existence of which is usually attributed to the '*inert-pair effect*'. The [Pb(O$_2$CMe)$_4$]$^{2-}$ units in [emim]$_2$[Pb(O$_2$CMe)$_4$] are hydrogen bonded to four cations forming an infinite chain *via* C–H···O interactions in the < 0 0 1 > plane, Fig. 2.

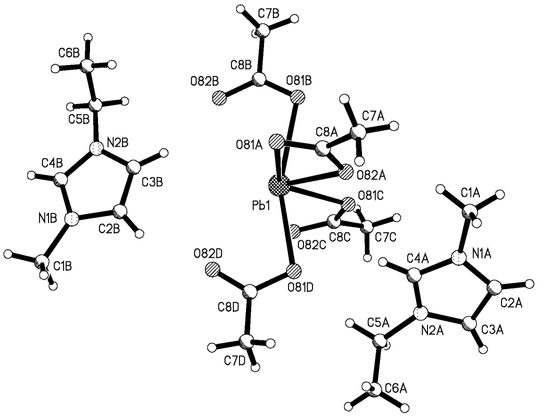

Fig. 1 Atomic numbering scheme for [emim]$_2$[Pb(O$_2$CMe)$_4$] emphasising the void created by the stereochemically active lone-pair on the lead(II) centre.

Although the term '*inert-pair effect*' is the subject of some controversy, the structural consequences of the 6s^2 lone-pair are well documented. Shimoni-Livny *et al.*[11] identified some conditions in which the lone-pair is likely to be stereochemically active; namely, hard donor atoms, a low coordination number and attractive interactions between ligands. The structure of [emim]$_2$[Pb(O$_2$CMe)$_4$] fits well with these findings and the criteria are satisfied.

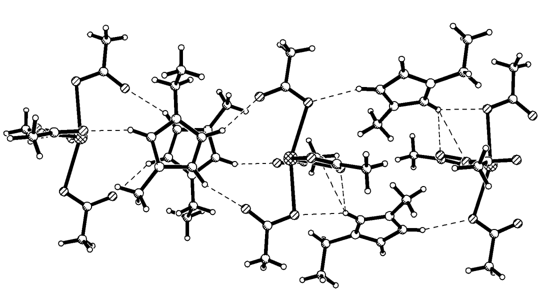

Fig. 2 A view illustrating the alternating C–H···O hydrogen bonded chains in [emim]$_2$[Pb(O$_2$CMe)$_4$] (the dashed lines represent hydrogen bonds). Hydrogen bond lengths (Å) and angles (°), (H···A), (D···A), (D–H···A): C2A–H2A···O81B′ 2.32, 3.15(3), 147; C3A–H3A···O81A″; 2.64, 3.45(3), 144; C4A–H4A···O81C 2.79, 3.22(2), 109; C4A–H4A···O81D 2.37, 3.20(2), 149; C4A–H4A···O82A 2.65, 3.38(2), 135; C2B–H2B···O82D 2.16, 3.01(3), 149; C3B–H3B···O82B 2.28, 3.14(3), 153; C4B–H4B···O82C‴ 2.03, 2.93(3), 160. Symmetry codes: $' = 1 - x, 1 - y, 1 - z$; $'' = x, 1 + y, z$; $''' = -x, -y, -z$.

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The dominant feature of the three monomeric lead complexes obtained from the CSD is the presence of a rigid organic ligand, which restricts the possible geometries available to the metal centres. In $Pb(C_8H_{11}N_4S)(O_2CMe)$[8] and $[Pb(C_{16}H_{36}N_4)(O_2CMe)][O_2CMe]\cdot 2H_2O$[9] this leads to the orientation of the inert lone-pairs associated with adjacent lead atoms towards one another with Pb···Pb contacts of 3.905 and 4.165 Å, respectively: they essentially exist as dinuclear complexes. As with $[emim]_2[Pb(O_2CMe)_4]$, the ethanoate ions are monodentate with the free oxygen atoms extending towards the void associated with the lone-pair. In $Pb(C_{12}H_{10}N_3SO)(O_2CMe)$[10] the use of a rigid ligand still influences the coordination geometry of the lead(II) centres. However, the distance between the metal centres is much longer which suggests that they are not associated with each other (Pb···Pb distance 4.822 Å). Again, the ethanoate ions are monodentate with the free oxygen atoms associated with the void. Moreover, these free oxygen atoms are also associated with the lead centre of the adjacent molecule (Pb···O distance 3.001 Å). The only common feature of these compounds and $[emim]_2[Pb(O_2CMe)_4]$ is that the monodentate ethanoate ligands are associated with the lone-pair on the metal centre. Unlike the previous complexes, the lead centres in $[emim]_2[Pb(O_2CMe)_4]$ do not show any lone-pair orientation effects and $[emim]_2[Pb(O_2CMe)_4]$ can be considered mononuclear.

A recent study by Hall *et al.*[12] on lead(II) complexes containing aromatic ligands highlighted the difficulties of determining the presence or absence of a stereochemically active lone-pair. They found that in many of the materials the so-called '*lone-pair*' regions were either (a) associated with longer contacts with the oxygen atoms from anions (*e.g.* $[ClO_4]^-$, $[NO_3]^-$), leading to polynuclear motifs with consequent orientation of the lone-pairs towards each other as above, or (b) associated with inter-ring interactions between the aromatic ligands which occupied the void region. In $[emim]_2[Pb(O_2CMe)_4]$, although the cations are associated with this lone-pair region and are involved in C–H···O hydrogen bonds with the ethanoate anions, the emim cations do not occupy the void associated with the '*inert lone-pair*'.

Furthermore, the presence or absence of a stereochemically active lone-pair has implications for the design of new materials using the Group 14 elements. The use of hydrogen-bond donor cations, in conjunction with hydrogen-bond acceptors on the coordination complex anions, results in '*capping*' of the voids, which may be a useful generic strategy for the rational design of materials containing these elements. The possible application of this approach to crystal engineering is illustrated by the isolation of $[emim]_2[Pb(O_2CMe)_4]$.

In conclusion, we have isolated and structurally characterised a new and novel lead(II) homoleptic complex. Preliminary XAFS data§ show that this unusual (for lead) metal coordination environment is stable even at moderate temperature (*ca.* 373 K), which will be the subject of a further communication. This, and the previously reported $[SbCl_3][AlCl_4]$,[13] also indicates that ionic liquids may be useful media for the stabilisation and study of unusual metal coordination environments; more specifically those metals that contain stereochemically active lone-pairs.

Furthermore, the presence of this lead(II) complex, which was produced in an attempted preparation of an ionic liquid, highlights the problems inherent in the use of metathetic reactions of metal salts as a preparative methodology for ionic liquids in general. We are currently critically examining the extant methods and developing more general procedures for ionic liquid production.

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Notes and references

† *Preparation*: [emim]Cl and $Pb(O_2CMe)_2\cdot 3H_2O$ (Aldrich) were separately dissolved in solutions of methanol–water (4:1 v/v). Upon mixing the two solutions a precipitate of $PbCl_2$ was produced which was removed by filtration after cooling at −20 °C overnight. The solvent was removed from the filtrate by rotary evaporation. Analysis by ^1H NMR spectroscopy showed that this was insufficient to remove the water, and this was accomplished after heating at *ca.* 130 °C under vacuum for 24 h. The product was a viscous liquid, pale yellow in colour before drying and pale brown in colour after drying. In order to eliminate the need for drying, the above method was modified slightly to eliminate the use of water. This was achieved by placing the lead ethanoate in a Soxhlet extractor. The product obtained was a mixture of crystalline solid and viscous liquid. Single crystal X-ray analysis showed the crystalline material to be the salt $[emim]_2[Pb(O_2CMe)_4]$.

‡ *Crystallographic data* were collected on a Siemens P4 diffractometer using omega scans. A crystal was sealed into a Lindemann tube under an inert atmosphere and then mounted on to the diffractometer at room temperature. The structure was solved using direct methods using the SHELX program packages.[14] *Crystal data* for $[emim]_2[Pb(O_2CMe)_4]$: M = 665.70, triclinic, space group $P\bar{1}$, $a = 7.9761(9)$, $b = 10.4439(9)$, $c = 16.8872(15)$ Å, $\alpha = 100.222(7)$, $\beta = 99.228(9)$, $\gamma = 94.712(9)$, $U = 1357.6(2)$ Å^{-3}, $Z = 2$, $\mu = 0.117$ mm^{-1}, $R_{int} = 0.0607$. A total of 3743 reflections were measured for the angle range $4 < 2\theta < 50$ and 3455 independent reflections were used in the refinement. Final parameters were $wR_2 = 0.1815$ and $R_1 = 0.0556$ $[I > 2\sigma(I)]$.

CCDC 182/1758. See http://www.rsc.org/suppdata/cc/b0/b005095o/ for crystallographic files in .cif format.

§ *XAFS spectra* were recorded at the Synchrotron Radiation Source at Daresbury using station 9.3 on the Pb L_{II} edge using our usual method.[15]

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