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Youssef Atoini, Jack Harrowfield, Pierre Thuéry. Lead(II) complexes with Kemp's tricarboxylate: Can lone pair activity be discerned ?. Polyhedron, 2022, 218, pp.115760. 10.1016/j.poly.2022.115760 . cea-03596707

HAL Id: cea-03596707

https://cea.hal.science/cea-03596707

Submitted on 3 Mar 2022

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Lead(II) Complexes with Kemp's Tricarboxylate: Can Lone Pair Activity be Discerned ?

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Dedicated to Professor Peter Junk on the occasion of his 60th birthday.

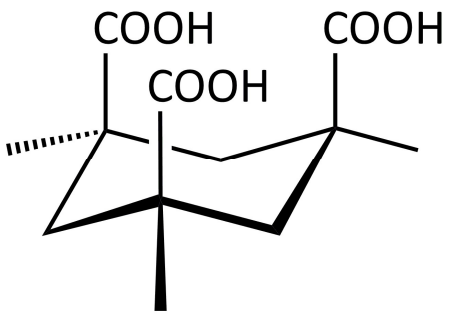
Abstract

Kemp's triacid (H_3kta; *cis,cis*-1,3,5-trimethylcyclohexane-1,3,5-tricarboxylic acid) has been used to synthesize three lead(II) complexes under solvo-hydrothermal conditions. [Pb_3(kta)Cl_3] (**1**) and [Pb_3(H_3kta)(kta)$_2$] (**2**) are both diperiodic coordination polymers displaying hydrophobic surfaces with protruding methyl groups, complex **2** being isomorphous with an Sr^{II} complex previously reported. In contrast, [Pb(Hkta)(phen)] (**3**), where phen is 1,10-phenanthroline, is a monoperiodic, helical coordination polymer. In all cases, Pb^{II} cations are in seven- or eight-coordinate environments of predominantly hemidirected nature. The possible effects of the Pb^{II} valence shell lone pair are discussed in terms of coordination geometry and Pb···H weak interactions as revealed on Hirshfeld surfaces. Only in complex **1** is a short Pb···H contact at 2.84 Å possibly indicative of appreciable basicity of the metal ion. All three complexes show similar weak luminescence, apparently independent of the nature of the ligands.

Keywords: Carboxylic acids, Lead(II) cation, Luminescence properties, Metal–organic networks, Structure elucidation

1. Introduction

The coordination chemistry of Pb^{II} is quite typical of that of heavy main group metal ion complexes in showing a wide range of coordination numbers associated commonly with rather irregular coordination sphere geometry [1,2]. It has, however, been widely investigated because of the specific aspect of the presumed influence, proposed long ago [3], of the valence shell lone pair formally originating from the $6s^2$ electrons of the atom. Unlike Sn^{II}, Pb^{II} provides little clear evidence of acting as a Lewis base [4], so that the presence of a lone pair has usually been discerned through its "stereochemical activity" seen largely in X-ray structure determinations on crystalline solids [5–11], though supported by theoretical calculations (*e.g.* [10,12–17]) and solution EXAFS (*e.g.* [18,19]) and ^{207}Pb NMR (*e.g.* [20,21]) studies. Thus, "holodirected" coordination spheres have been associated with structures where any lone pair influence is negligible and "hemidirected" coordination spheres with those where this influence appears to be important [10], even though the lone pair itself cannot be directly imaged. In extending the known [22] coordination chemistry of Pb^{II} with Kemp's tricarboxylic acid (H_3kta; *cis,cis*-1,3,5-trimethylcyclohexane-1,3,5-tricarboxylic acid, Scheme 1), we have structurally characterized three new species, for all of which there is some justification for the claim that they display coordination sphere distortions due to the presence of a valence shell lone pair. Comparison of one of these structures with that of the isostructural Sr^{II} species [23], however, raises some doubt as to the straightforwardness of such structural analyses.



Scheme 1. Kemp's tricarboxylic acid.

2. Results and discussion

2.1. Crystal structures

The tripodal form of Kemp's tricarboxylate in which all three carboxylate groups are axial bears some resemblance to 1,3-diketonate ligands such as acetylacetonate which are well known to form complexes with two or more such ligands in which a metal-oxido core is enclosed within an apolar sheath formed by the O-donor substituents, rendering the entire complex lipophilic [24]. Such a property may explain the utility of Kemp's triacid as a reagent for the removal of metal-ion-containing deposits on surfaces [25] and indeed the known structure of $[Pb_3(kta)_2(dmf)_3]$ [22] shows that a diperiodic polymer is present in a sheet form, where trimethylcyclohexyl faces of tri(carboxylato)-axial kta^{3-} units provide a lipophilic cover (incorporating dmf N-methyl groups) to each side of the sheet, a usual trend in complexes with this ligand [23,26]. The two inequivalent ligand units of this structure, both with threefold rotation symmetry, do not, however, have the same conformation, one having the tripodal form with three axial carboxylate substituents and the other having the discoidal form with all three equatorial. Pairs of the tripodal ligands garlanded by six Pb^{II}, each with one bound dmf, form capsular entities which are linked together in a trigonal manner by the discoidal ligands, which, in alternation, also project their axial methyl substituents towards the faces of the sheets. The structure of complex **1**, $[Pb_3(kta)Cl_3]$, though of much lower crystallographic

symmetry, so that the unique tripodal kta^{3-} ligand unit has no symmetry at all, is nonethless similar in that a diperiodic coordination polymer is present and lies in sheets parallel to (10$\bar{1}$), with “upper” and “lower” lipophilic surfaces formed by trimethylcyclohexyl units (Fig. 1).

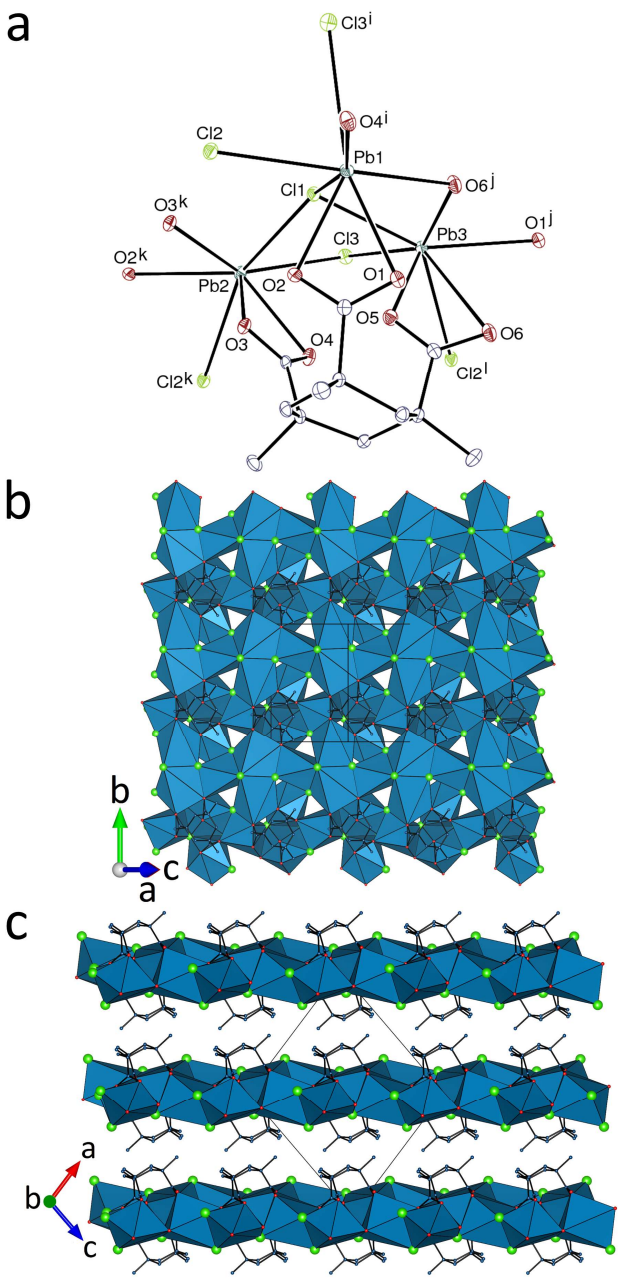


Fig. 1. (a) View of complex **1**. Displacement ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted. The longest Pb–Cl contact is not shown. Symmetry codes: i = *x* – 1/2, 1/2 – *y*, *z* – 1/2; j = 1 – *x*, 1 – *y*, 1 – *z*; k = 1 – *x*, –*y*, 1 – *z*; l = *x* + 1/2, 1/2 – *y*, *z* + 1/2. (b) View of the diperiodic polymer with lead(II) coordination polyhedra colored blue. (c) Packing with layers viewed edge-on.

Viewed perpendicular to the sheets, ligand units do not project upon another, so there is no formation of capsular units and the three inequivalent, μ_3-bridging chlorido ligands alone form a diperiodic array with the three inequivalent Pb^{II} cations. As is rather commonly the case in relation to Pb^{II} structures, assignments of the coordination number and geometry of the metal ion carry some uncertainty [4,13,27]. In $[Pb_3(kta)_2(dmf)_3]$, the unique Pb^{II} centre is said [22] to be 7-coordinate in a hemidirected environment but this is to ignore a Pb–O1 contact of 2.87(1) Å, only slightly longer than the otherwise longest Pb–O3 of 2.74(1) Å, and on the Hirshfeld surface (HS) [28] calculated with CrystalExplorer [29], it certainly appears as an interaction greater than dispersion. Its inclusion in the coordination sphere would make the hemidirected nature less obvious, though bond extension in one area of the coordination sphere may in fact be due to proximity to the lone pair [13,27]. Consideration of the HS for complex **1** indicates that Pb1 can be considered to have at least a 7- and possibly an 8-coordinate environment (O_4Cl_3 or O_4Cl_4, respectively), one of the Pb–Cl bonds being much longer than the others [3.4793(8) Å compared to 2.8901(7), 2.9148(7) and 3.1148(8) Å]. One Pb–O bond is also somewhat longer than the others [Pb1–$O6^j$ 2.806(2) Å compared to Pb1–O1 2.591(2) Å; Pb1–O2 2.443(2) Å; Pb1–$O4^i$ 2.598(2) Å]; the three shortest are adjacent, so that the coordination sphere can still be regarded as hemidirected. Both Pb2 and Pb3 have an O_4Cl_3 coordination sphere which appears to be markedly hemidirected, though with all bond lengths being shorter than 3.1 Å, with relatively small variations in the Pb–Cl bond lengths [2.8599(7)–2.9692(8) Å] but more important ones in the Pb–O bond lengths [2.316(2)–3.087(3) Å]. The Hirshfeld surface shows an additional Pb···H interaction for Pb2 (Pb2···$H2B^k$ 2.84 Å), possibly providing further evidence that the lone pair may sometimes show detectable basicity [4,27], though this is not apparent for Pb1 and much less for Pb3 (see discussion ahead). Overall, the lead(II) centres are bound to either three (Pb1) or two (Pb2 and Pb3) kta^{3-} ligands, while the

ligand itself connects seven metal cations with the three carboxylate groups bound in the μ_3-κ^2O,O':κ^1O:κ^1O' (O1/O2 and O3/O4) or μ_3-κ^2O,O':κ^1O:κ^1O (O5/O6) coordination modes, O1–O4 being bound to two metal cations each, while O5 is bound to only one and O6 to three. With a Kitaigorodski packing index (KPI), calculated with PLATON [30], of 0.78, the packing is very compact and does not display significant free space.

Complex **2**, $[Pb_3(H_3kta)(kta)_2]$, with the simplest composition of the present series, is isomorphous with its Sr^{II} analogue [23]. Its structure, shown in Fig. 2, shows some similarities to that of $[Pb_3(kta)_2(dmf)_3]$ but also some marked differences. All three inequivalent ligand units in **2** have threefold rotational symmetry and the tripodal (tricarboxylato axial) chair conformation. While two identical units can be regarded as forming centrosymmetric Pb-bridged $Pb_6(kta)_2$ capsules similar to those in the dmf solvate, these capsules are now linked through chiral $Pb_3(kta)(H_3kta)$ capsules formed from the other two inequivalent units rather than through discoidal ligand units. In the latter capsules, the two ligands, neutral and trianionic, are held together by three symmetry-related OH···O hydrogen bonds [O···O, 2.532(4) Å; O–H···O, 158(8)°], the proton being located on the only uncoordinated oxygen atom (O6). A diperiodic coordination polymer, in sheets parallel to (001), remains the overall assembly, with polyhedra sharing triangular faces arranged into hexanuclear rings and external surfaces lipophilic in the same way as in $[Pb_3(kta)_2(dmf)_3]$. The chiral capsules alternate in chirality from one to the next, so that every sheet is overall achiral. The unique lead atom has an unsymmetrical O_8 environment, with Pb–O bond lengths varying between 2.390(3) and 3.011(3) Å, but which is not obviously hemidirected, although one face can be identified where the three longest bonds are adjacent. This Pb^{II} environment is closely similar to that of Sr^{II} in $[Sr_3(H_3kta)(kta)_2]$ (Fig. 3) and although the range of Sr–O bond lengths [2.4541(16)–2.8734(15) Å] is smaller than that of Pb–O, the three longer bonds to each metal

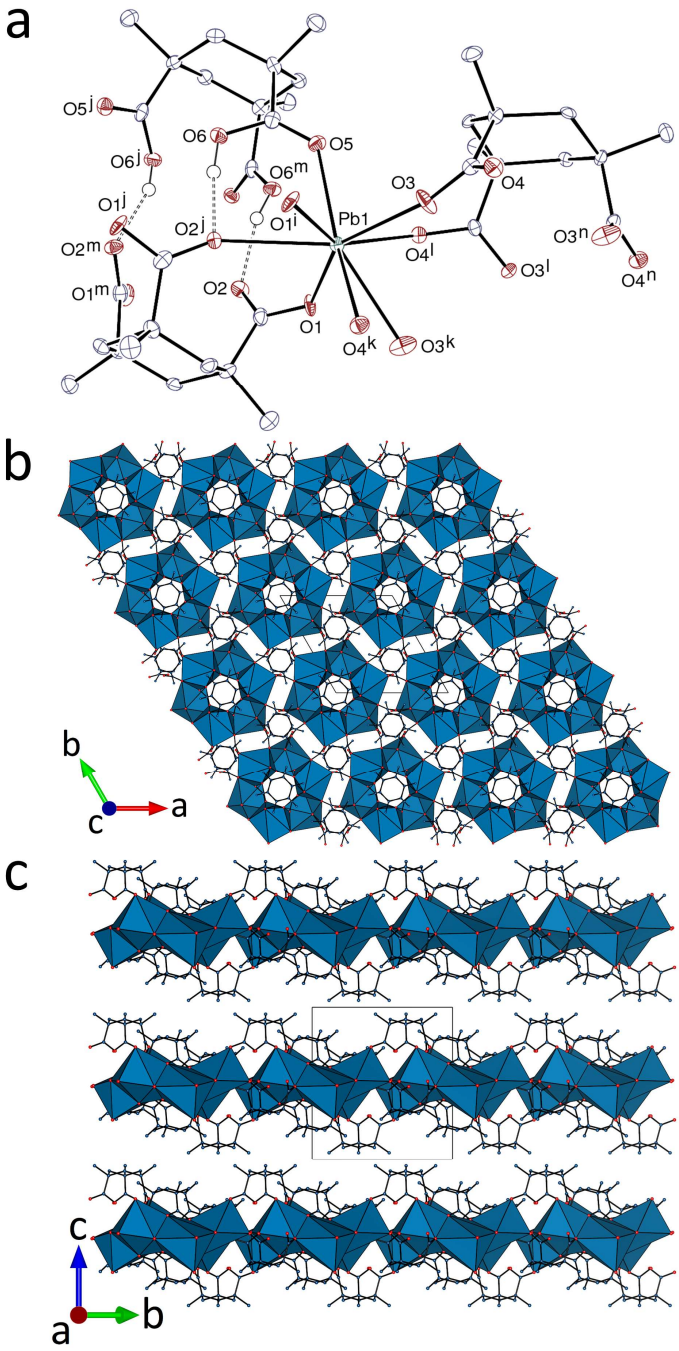


Fig. 2. (a) View of complex **2**. Displacement ellipsoids are drawn at the 50% probability level and carbon-bound hydrogen atoms are omitted. Hydrogen bonds are shown as dashed lines. Symmetry codes: i = *y*, *y* – *x* + 1, 1 – *z*; j = 1 – *y*, *x* – *y*, *z*; k = *x* – *y* + 1, *x*, 1 – *z*; l = 2 – *y*, *x* – *y* + 1, *z*; m = *y* – *x* + 1, 1 – *x*, *z*; n = *y* – *x* + 1, 2 – *x*, *z*. (b) View of the diperiodic polymer. (c) Packing with layers viewed edge-on.

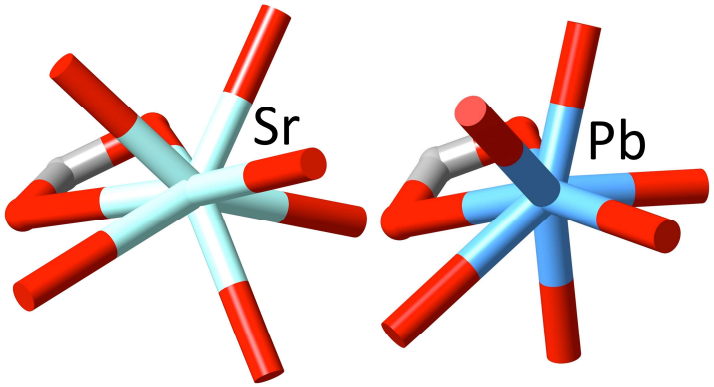


Fig. 3. Comparison, in similar orientations, of the donor atom arrays in (left) $[Sr_3(H_3kta)(kta)_2]$ and (right) $[Pb_3(H_3kta)(kta)_2]$ (stick representations, with the carbon atom of the chelating carboxylate also shown).

are adjacent in both and could be said to encircle a region which might be occupied by a lone pair. However, Sr^{II}, of course, does not have a valence shell lone pair, so the unsymmetrical form of its coordination sphere must be seen as a consequence of bonding restrictions and secondary interactions outside that primary coordination sphere. Such restrictions and interactions must also apply in the Pb^{II} complex structure, so that if there is any influence of a lone pair, it is not obvious that it must significantly perturb the effects of these other factors. Overall, the Pb^{II} cation is bound to five ligands while the kta^{3-} ligands are bound to six metal cations in the tris(μ_3-κ^2O,O':κ^1O:κ^1O') (defining three 4- and three 8-membered chelate rings) and tris(μ_3-κ^1O:κ^1O:κ^1O') coordination modes, and the H_3kta ligand to three metal ions in the monodentate tris(κ^1O) mode. With a KPI of 0.75, the packing is quite compact.

The structure of the complex [Pb(Hkta)(phen)] (**3**) (phen = 1,10-phenanthroline), involves the incompletely deprotonated ligand $Hkta^{2-}$ in tripodal form as part of a monoperiodic coordination polymer parallel to [010] (Fig. 4). Two of the carboxylate groups on the unique ligand unit act as κ^2O,O' chelates, while the third, to which the residual proton is attached on the coordinated atom O5, is bound in κ^1O mode. An intramolecular hydrogen bond is formed between O5 and O4 [O···O, 2.457(3) Å; O–H···O, 172(6)°]. Calculation of short

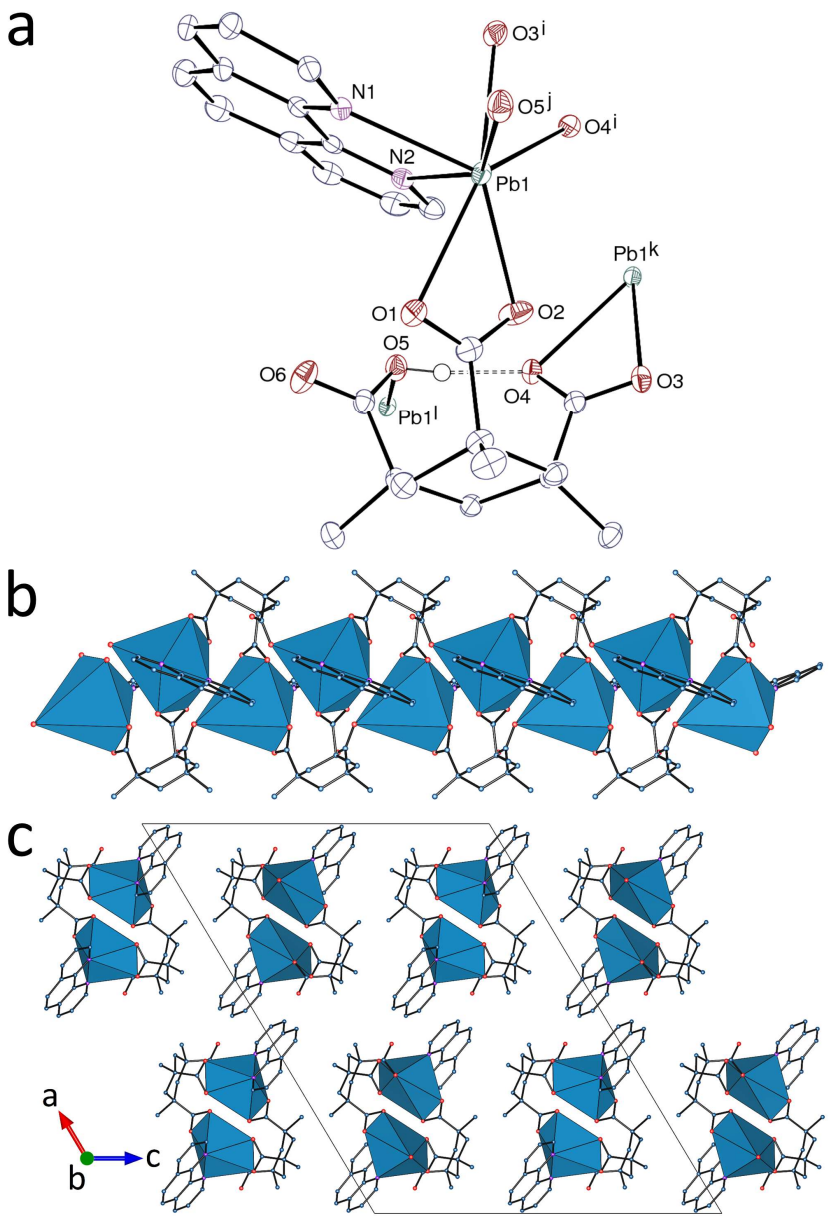


Fig. 4. (a) View of complex **3**. Displacement ellipsoids are drawn at the 50% probability level and carbon-bound hydrogen atoms are omitted. The hydrogen bond is shown as a dashed line. Symmetry codes: i = 1/2 – *x*, *y* + 1/2, 1/2 – *z*; j = *x*, *y* + 1, *z*; k = 1/2 – *x*, *y* – 1/2, 1/2 – *z*; l = *x*, *y* – 1, *z*. (b) View of the monoperiodic helical polymer. (c) Packing with chains viewed end-on.

contacts with PLATON shows that two parallel-displaced π-stacking interactions may exist between two phen ligands pertaining to different chains [centroid···centroid distances, 3.521(2) and 3.744(2) Å; dihedral angles, 0 and 1.85(18)°; slippages, 1.13 and 1.67 Å], and

examination of the HS shows that these interactions exceed dispersion. The unique Pb centre has an N_2O_5 coordination sphere of a clearly hemidirected nature, with one Pb–O bond [Pb–$O5^j$ 3.054(2) Å] considerably longer than the other four [2.543(2)–2.625(2) Å], and the Pb–N bonds [2.434(3) and 2.525(2) Å] being the shortest of all. In this case, the metal centre is bound to three $Hkta^{2-}$ ligands, and the carboxylate ligand to only three cations, with no bridging carboxylate group, the presence of the terminal phen ligand limiting the available coordination sites on the cation. The monoperiodic polymer is helical in shape, so that the chains are somewhat tubelike, although with an insignificant internal space, and the packing is compact (KPI, 0.72).

The conformational flexibility and multiple degrees of deprotonation possible for Kemp's triacid promote a considerable variety in its coordination chemistry, well illustrated in the four structurally characterized complexes of Pb^{II} now known. An interesting feature of the crystal structure of the acid itself is that although hydrogen bonding is extensive, it does not involve confrontation of carboxylic acid groups in reciprocal donor-acceptor (D–A···A–D) pairs as considered typical of simple monocarboxylic acids [31]. Thus, there is no formation of a capsule where pairs of acid molecules linked by three D–A···A–D pairs might form an isolated unit of the structure. Instead, as well defined in various alkyl- and aryl-ammonium salts of the singly deprotonated acid [32], an hydrogen bonded polymer is formed. When a metal ion replaces acid protons, however, two carboxylate units can be bound to one metal ion without the two OCO units being coplanar as required in the acid dimer and the formation of a capsular entity involving two complete ligands becomes possible, as seen not only in the Pb^{II} complexes presently discussed but also in Sr^{II} and Mn^{II} species [23]. The interior volume of such capsules is very small and quite unsuited to the accommodation of guests, thus lacking the potential of known closed structures found in uranyl ion complexes of Kemp's triacid [33]. In addition, Pb^{II},

Sr^{II} and Mn^{II} all have the capacity to bind more than two carboxylate units, so that the capsules exist as part of coordination polymers formed by additional interactions of the metal ions. Given the presence of a valence shell lone pair on Pb^{II} and the possibility of Pb···Pb bonding, some unique characteristics might have been anticipated for the Pb^{II} polymers, although, as we have argued elsewhere [4], any effect of the latter may be more difficult to detect in complexes of multidentate ligands (such as Kemp's triacid or its anions) than in complexes of monoatomic ligands, where it may be prominent (along with lone pair influences) [34]. The shortest Pb···Pb separation found in the presently considered species is that of 3.9509(2) Å between Pb1 atoms of the capsular units of complex **2**, and the HS provides no evidence that this involves any interaction exceeding that of dispersion. Examination of the HSs provides some indication of the possibility of Pb···H interactions in complexes **1** (Pb2 and Pb3), **2** and **3** (Fig. 5). The associated Pb···H distances are 2.84 and 3.16 Å in **1**, 3.04 Å in **2**, and 3.21 Å in **3**,

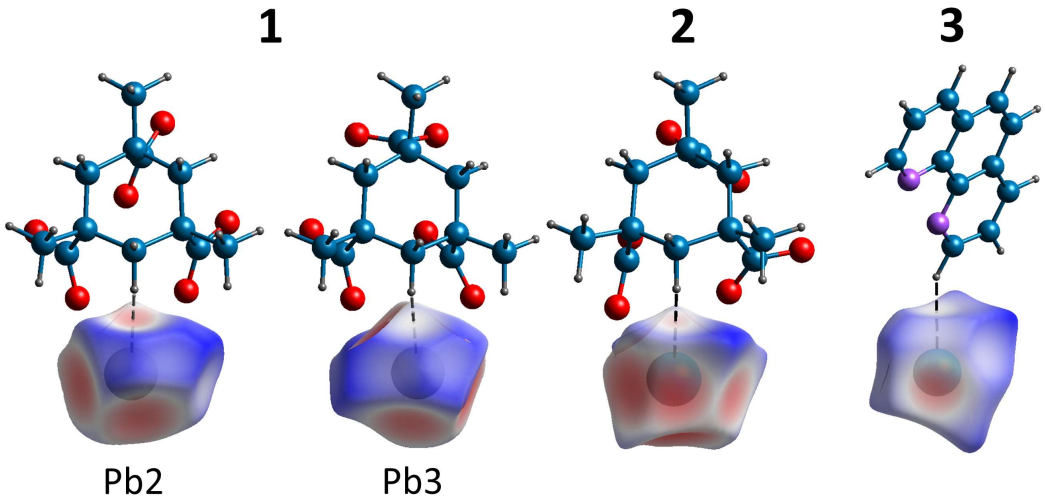


Fig. 5. HSs of the Pb^{II} cations mapped with d_{norm} showing the possible Pb···H interactions. The larger red dots on the HS correspond to the location of chlorine, oxygen or nitrogen donors.

the first two cases involving a methylenic proton from the carboxylate ligand and the third an aromatic proton from phen. The contact at 2.84 Å in **1**, which is most conspicuous on the HS,

is smaller than that measured in a hemidirected Pb^{II} complex with 1,5-naphthalenedisulfonate (3.01 Å) [4], and it may indicate the location of a lone pair. However, this is not the case generally, so that evidence for lone pair activity must be found in the Pb–(donor atom) bond lengths and the spatial distribution of the donor atoms. On these bases, as described above, it can be concluded that the Pb^{II} coordination spheres in complexes **1**–**3**, as well as in $[Pb_3(kta)_2(dmf)_3]$, are hemidirected and therefore could be indicative of stereochemical activity of a lone pair. The isomorphous nature of the structures of complex **2** and its Sr^{II} analogue, in which a Sr···H contact at 3.02 Å is found, and, in particular, the close similarities in the primary coordination spheres of the Pb^{II} and closed-shell Sr^{II} centres, however, render this conclusion uncertain for complex **2** and thus for all other cases based on these criteria.

2.2. Luminescence properties

The solid state emission spectra of all three complexes, obtained with excitation at 260 nm, are very similar (Fig. 6), with a broad, featureless band centred at 402 (**1**), 399 (**2**) and 397 nm (**3**), and Photoluminescence Quantum Yield (PLQY) values which vary little from 3.5 (**1**) to 2.8 (**2**) to 2.0% (**3**). Somewhat surprisingly, the presence of the aromatic 1,10-phenanthroline fluorophore [35] in **3** appears not to have a significant influence, perhaps because of the stacking interactions in the structure [36]. Lead(II) butyrate forms coordination polymers with bridging aza-aromatic ligands which show strong emission differing markedly with the ligand [37] but there are also instances where Pb^{II} complexes of aromatic anions are non-emissive [38], so that it is possible that the phen in complex **3** is completely inactive. There is evidence that in Pb^{II} coordination polymers formed from aromatic polycarboxylates the luminescence properties may reflect whether or not the lone pair is stereochemically active [36,39], and the common emission in the present cases could be attributed to the fact that all three structures

can be said to contain hemidirected Pb^{II} centres, although the absence of data for a holodirected Pb^{II} complex of Kemp's triacid engenders some uncertainty here. Assignments of the transitions responsible for emission from Pb^{II} complexes have varied [36–39] but an appealing rationalization of the present observations is that of relaxation of the MLCT transition involving a lone pair electron and a carboxylate antibonding orbital, although the evidence of some fine structure in the emissions is possibly indicative of vibronic coupling involving the tricarboxylate ligand. However, this coupling is not seen in the simple carboxylate $Pb(O_2CCH_3)_2{\cdot}3H_2O$ containing 9-coordinate Pb^{II} [40], which we have found to be essentially non-emissive, nor in lower hydrates where broad emissions which do largely resemble those seen presently have been assigned as metal-centred [41].

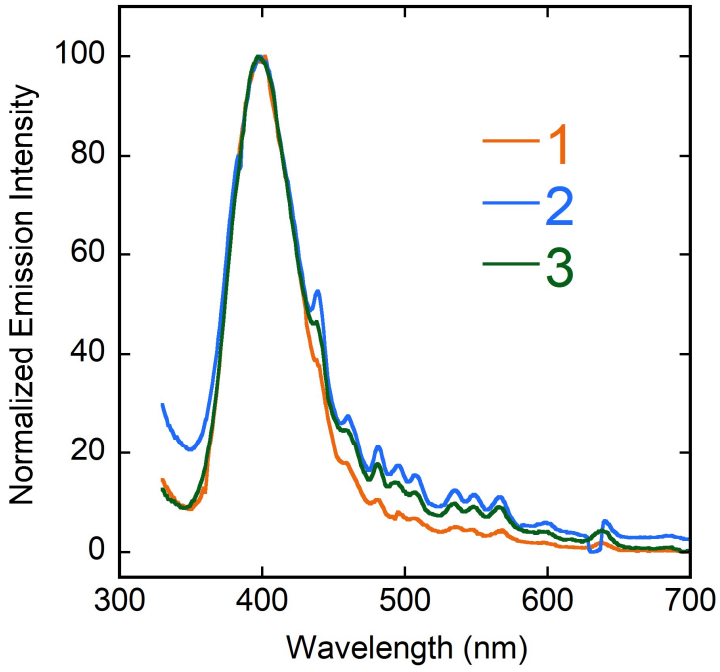


Fig. 6. Emission spectra of compounds **1**–**3** in the solid state at room temperature, under excitation at a wavelength of 260 nm.

3. Conclusions

The present structures further confirm that the preferred conformations of Kemp's triacid and its conjugate bases in metal ion complexes [23,26,33,42–47] are those where the cyclohexyl ring has a chair conformation with either all three methyl or all three carboxyl groups oriented axially. The observation of a boat conformation appears still to be limited to certain instances of uranyl ion complexes and a similarly small number of organic ammonium salts [23]. Thus, Pb^{II} appears to have no special influence in this regard and it is not clear that either of its particular attributes, the ability to form Pb···Pb bonds and to modify its coordination geometry through lone pair repulsions, has any influence within the presently known structures of Kemp's triacid derivatives. A plausible explanation of the isomorphous nature of $[M_3(H_3kta)(kta)_2]$ (M = Sr or Pb) complexes may be that in metal ion species of relatively high coordination number bound to multidentate ligands, primary coordination sphere interactions have no greater role in determining the solid state structure than those involving the ligand superstructure, an argument which has been advanced previously by others [48]. We have noted elsewhere [4] that there are other examples, admittedly few, of structures of complexes where the coordination sphere of a closed-shell metal ion closely matches that of a lone pair endowed species. Any confidence in the identification of lone pair effects on crystal structures may thus be open to question, although luminescence measurements may well be the most sensitive means of their detection.

4. Experimental part

4.1. Synthesis

General: $Pb(NO_3)_2$ was purchased from Prolabo, Kemp's triacid was from Aldrich, and 1,10-phenanthroline was from Alfa-Aesar. For all syntheses, the mixtures in demineralized

water were placed in 10 mL tightly closed glass vessels and heated at 140 °C in a sand bath, under autogenous pressure. The crystals formed directly from the pressurized and heated reaction mixtures and not as a result of subsequent cooling. The low yields of the syntheses prevented further characterization.

*4.1.1. $[Pb_3(kta)Cl_3]$ (**1**)*

H_3kta (13 mg, 0.05 mmol), $Pb(NO_3)_2$ (17 mg, 0.05 mmol), and $[Co(en)_3]Cl_3{\cdot}3H_2O$ (20 mg, 0.05 mmol) were dissolved in a mixture of water (0.6 mL) and acetonitrile (0.2 mL), giving a few colorless crystals of complex **1** within two months.

*4.1.2. $[Pb_3(H_3kta)(kta)_2]$ (**2**)*

H_3kta (13 mg, 0.05 mmol), $Pb(NO_3)_2$ (17 mg, 0.05 mmol), and $C(NH_2)_3NO_3$ (12 mg, 0.10 mmol) were dissolved in a mixture of water (0.6 mL) and acetonitrile (0.2 mL), giving a few colorless crystals of complex **2** within one week.

*4.1.3. [Pb(Hkta)(phen)] (**3**)*

H_3kta (13 mg, 0.05 mmol), $Pb(NO_3)_2$ (17 mg, 0.05 mmol), and 1,10-phenanthroline (9 mg, 0.05 mmol) were dissolved in a mixture of water (0.6 mL) and dmf (0.2 mL), giving a few colorless crystals of complex **3** within one week.

4.2. Crystallography

The data were collected at 100(2) K on a Bruker D8 Quest diffractometer equipped with an Incoatec Microfocus Source (IμS 3.0 Mo) and a PHOTON III area detector, and operated through the APEX3 software [49]. The data were processed with SAINT [50] and absorption

effects were corrected for empirically with SADABS [51]. The structures were solved by intrinsic phasing with SHELXT [52] and refined by full-matrix least-squares on F^2 with SHELXL [53], using the ShelXle interface [54]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms bound to O6 in **2** and to O5 in **3** were found on residual electron density maps and were refined with a restraint on the bond length. The carbon-bound hydrogen atoms were introduced at calculated positions and were treated as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent atom (1.5 for CH_3, with optimized geometry). Crystal data and structure refinement parameters are given in Table 1. The molecular plots were drawn with ORTEP-3 [55] and the polyhedral representations with VESTA [56].

Table 1

Crystal data and structure refinement details.

	1	**2**	**3**
Chemical formula	$C_{12}H_{15}Cl_3O_6Pb_3$	$C_{12}H_{16}O_6Pb$	$C_{24}H_{24}N_2O_6Pb$
M_r	983.16	463.44	643.64
Crystal system	monoclinic	trigonal	monoclinic
Space group	$P2_1/n$	$P\bar{3}$	$C2/c$
a (Å)	12.0236(5)	13.2502(4)	29.0812(14)
b (Å)	11.8694(5)	13.2502(4)	7.8611(4)
c (Å)	12.6456(5)	12.4511(5)	22.2874(10)
α (°)	90	90	90
β (°)	102.5506(18)	90	120.8904(17)
γ (°)	90	120	90
V (Å^3)	1761.57(13)	1893.14(14)	4372.4(4)
Z	4	6	8
No. of reflections collected	203294	115865	83960
No. of independent reflections	5345	2399	4132
No. of observed reflections [$I > 2\sigma(I)$]	5307	2388	4058
R_{int}	0.064	0.077	0.060
No. of parameters refined	220	178	305
R_1	0.015	0.018	0.019
wR_2	0.035	0.055	0.047
S	1.220	1.223	1.149
$\Delta\rho_{min}$ (e Å^{-3})	−1.62	−0.70	−0.64
$\Delta\rho_{max}$ (e Å^{-3})	2.31	2.04	2.40
CCDC deposition number	2119994	2119995	2119996

4.3. Luminescence measurements

Emission spectra were recorded on solid samples using an Edinburgh Instruments FS5 spectrofluorimeter equipped with a 150 W CW ozone-free xenon arc lamp, dual-grating excitation and emission monochromators (2.1 nm/mm dispersion; 1200 grooves/mm) and an R928P photomultiplier detector. The powdered compounds were pressed to the wall of a quartz tube, and the measurements were performed using the right-angle mode in the SC-O5 cassette. An excitation wavelength of 260 nm was used in all cases and the emission was monitored between 330 and 700 nm. The quantum yield measurements were performed by using a Hamamatsu Quantaurus C11347 absolute photoluminescence quantum yield spectrometer and exciting the samples between 260 and 350 nm.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

CCDC 2119994–2119996 contains the supplementary crystallographic data for <yyy>. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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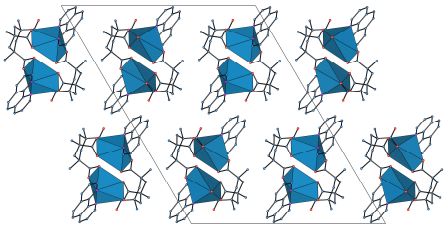
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Table of Contents Entry

Lead(II) Complexes with Kemp's Tricarboxylate: Can Lone Pair Activity be Discerned ?

Youssef Atoini, Jack Harrowfield, Pierre Thuéry



The crystal structures of mono- and diperiodic lead(II) complexes with Kemp's tricarboxylate are searched for possible effects of the lead(II) lone pair, particularly through possible Pb···H interactions.