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## [Pb{Mn(CO)<sub>5</sub>}<sub>3</sub>][AlCl<sub>4</sub>]: a lead-manganese carbonyl with AlCl<sub>4</sub>-linked PbMn<sub>3</sub> clusters†

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[Pb{Mn(CO)<sub>5</sub>}<sub>3</sub>][AlCl<sub>4</sub>] containing a trigonal planar PbMn<sub>3</sub> cluster was obtained by the reaction of PbCl<sub>2</sub> and Mn<sub>2</sub>(CO)<sub>10</sub> in the ionic liquid [BMIm][AlCl<sub>4</sub>]. The title compound is composed of [Pb{Mn(CO)<sub>5</sub>}<sub>3</sub>]<sup>+</sup> carbonyl cations and [AlCl<sub>4</sub>]<sup>-</sup> anions that are connected to infinite zig-zag chains. The [Pb{Mn(CO)<sub>5</sub>}<sub>3</sub>]<sup>+</sup> cation exhibits a central PbMn<sub>3</sub> cluster with three equal Pb–Mn single bonds, resulting in an almost equilateral triangle of three manganese atoms with a formal Pb<sup>+1</sup> in its center. Such a cluster and compound were identified for the first time. In addition to single-crystal structure analysis, the composition, structure and properties were further characterized by density functional theory (DFT) calculations, energy dispersive X-ray spectroscopy (EDXS), and Fourier-transform infrared spectroscopy (FT-IR), as well as optical spectroscopy (UV-Vis).

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## Introduction

Due to their high redox stability, ionic liquids meanwhile have turned out to be versatile reaction media for the synthesis of metal clusters and reactive carbonyl compounds.<sup>1</sup> Prominent examples include, for instance, □<sub>24</sub>Ge<sub>136</sub> as a new modification of germanium (□ indicating non-occupied lattice sites),<sup>2</sup> [Hg<sub>4</sub>Te<sub>8</sub>(Te<sub>2</sub>)<sub>4</sub>]<sup>8-</sup> with a porphyrin-analogous structure,<sup>3</sup> or the Zintl-like cation [CuBi<sub>8</sub>]<sup>3+</sup>.<sup>4</sup> In addition to the excellent redox stability of ionic liquids, their weakly coordinating properties and the inherent stabilization of compounds *via* cation–anion interactions are further merits.<sup>5</sup>

With our studies on the reactivity of metal carbonyls, we could show that ionic liquids also represent powerful liquid media to obtain novel carbonyl compounds and clusters.<sup>1b</sup> Selected examples comprise, for instance, the adamantane-type Fe<sub>4</sub>Sn<sub>6</sub> cluster in [Fe(CO)<sub>3</sub>]<sub>4</sub>[SnI<sub>6</sub>I<sub>4</sub>]<sup>2-</sup>,<sup>6a</sup> the Ge<sub>12</sub>Fe<sub>8</sub> germanium-iron cluster in Ge<sub>12</sub>{Fe(CO)<sub>3</sub>}<sub>8</sub>(μ-I)<sub>4</sub><sup>6b</sup> or the anti-(WCl<sub>2</sub>)<sub>6</sub>-like [(Pb<sub>6</sub>I<sub>8</sub>){Mn(CO)<sub>5</sub>}<sub>6</sub>]<sup>2-</sup>.<sup>6c</sup> In particular, by the reaction of Fe(CO)<sub>5</sub> with Lewis-acidic metal iodides (*e.g.*, SnI<sub>4</sub>, GeI<sub>4</sub>), we could identify several novel carbonyl compounds that are specifically designated by the absence of alkyl and aryl ligands.<sup>6a,b,7</sup> Such organic ligands were often considered essential for electronic and steric stabilization of carbonyl compounds.<sup>8</sup> In this regard, the specific features of the ionic

liquids allow preparation and stabilization of highly reactive carbonyl compounds and metal clusters that contain additional, even more destabilizing halogenide ligands.<sup>8</sup>

Based on our experience with the Fe–Sn and Fe–Ge system, we have expanded our studies to the Pb–Mn system. In principle, Pb–Mn bonding is well-known for carbonyl clusters and was intensely studied in regard to the structural, magnetic, catalytic and optical properties of the resulting compounds.<sup>9</sup> Most often isolated Pb–Mn or Mn–Pb–Mn strings were described. Larger Pb–Mn arrangements are rare and limited to Pb{=Mn(CO)<sub>2</sub>Cp}{–Mn<sub>2</sub>(CO)<sub>4</sub>Cp<sub>2</sub>} (Cp: η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub>).<sup>10</sup> This compound is featured by a planar PbMn<sub>3</sub> unit that exhibits two Pb–Mn single bonds as well as a significantly shorter Pb=Mn double bond. In addition, a covalent Mn–Mn bond was assumed by the authors between the two Mn atoms with Pb–Mn single bonds. As discussed above,<sup>8</sup> halogenide-coordinated Pb–Mn clusters were considered as highly reactive and require alkyl-/aryl-ligands for electronic and steric stabilization, since halogenide ligands were described to cause a cleavage of the Pb–Mn bonds.<sup>11</sup> This background motivated us to evaluate the feasibility of ionic liquids for obtaining novel carbonyl clusters with Pb–Mn bonding. This results in the synthesis of [Pb{Mn(CO)<sub>5</sub>}<sub>3</sub>][AlCl<sub>4</sub>] containing a [Pb{Mn(CO)<sub>5</sub>}<sub>3</sub>]<sup>+</sup> carbonyl cation with a trigonal planar PbMn<sub>3</sub> cluster and three equal Pb–Mn single bonds.

## Results and discussion

[Pb{Mn(CO)<sub>5</sub>}<sub>3</sub>][AlCl<sub>4</sub>] was obtained by reacting PbCl<sub>2</sub> and Mn<sub>2</sub>(CO)<sub>10</sub> in a mixture of [BMIm]Cl and AlCl<sub>3</sub> (1:1). Although, in principle, large quantities were obtained, the title

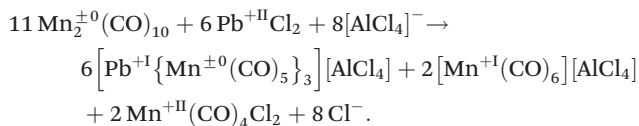
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compound formed only very small dark red, almost black crystals that were found on the surface of large blue, rod-shaped crystals of  $[\text{Mn}(\text{CO})_6][\text{AlCl}_4]$  as a side phase.  $[\text{Mn}(\text{CO})_6][\text{AlCl}_4]$  was described already,<sup>12</sup> and its composition was confirmed here as well by single-crystal structure analysis. Taken together, the formation of the title compound can be rationalized by a redox reaction with reduction of  $\text{Pb}^{\text{II}}$  to  $\text{Pb}^{\text{I}}$  and oxidation of  $\text{Mn}^0$  to  $\text{Mn}^{\text{I/II}}$  according to the following equation:



From the obtained products,  $\text{Mn}(\text{CO})_4\text{Cl}_2$  completely remained in solution, whereas  $[\text{Mn}(\text{CO})_6][\text{AlCl}_4]$  shows partial crystallization. Due to its solubility and being driven by Ostwald ripening, only a few bluish crystals appear that grow to millimeter-sized individuals. The title compound  $[\text{Pb}\{\text{Mn}(\text{CO})_5\}_3][\text{AlCl}_4]$  is most insoluble in the system, and thus, formed small crystals on the surface of the large seed crystals of the co-product. Since the reactivity of  $[\text{Pb}\{\text{Mn}(\text{CO})_5\}_3][\text{AlCl}_4]$  (title compound) and  $[\text{Mn}(\text{CO})_6][\text{AlCl}_4]$  (co-product) is very similar, separation is difficult and was here performed by manual separation of crystals. According to single-crystal structure determination,  $[\text{Pb}\{\text{Mn}(\text{CO})_5\}_3][\text{AlCl}_4]$  crystallizes monoclinically with the space group  $P2_1/c$  (Table 1, Fig. 1).

The title compound consists of  $[\text{Pb}\{\text{Mn}(\text{CO})_5\}_3]^+$  cations and  $[\text{AlCl}_4]^-$  anions. The  $[\text{Pb}\{\text{Mn}(\text{CO})_5\}_3]^+$  cation is composed of a central Pb atom, which is connected to three  $\text{Mn}(\text{CO})_5$  fragments (Fig. 2). Herein, Pb–Mn distances of 275.0(1) (Pb–

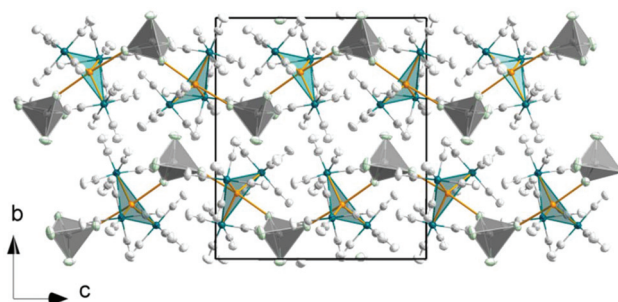


Fig. 1 Unit cell of  $[\text{Pb}\{\text{Mn}(\text{CO})_5\}_3][\text{AlCl}_4]$ :  $\text{PbMn}_3$  units in yellow-green,  $[\text{AlCl}_4]^-$  tetrahedra in grey, and C atoms and O atoms of CO ligands in light grey.

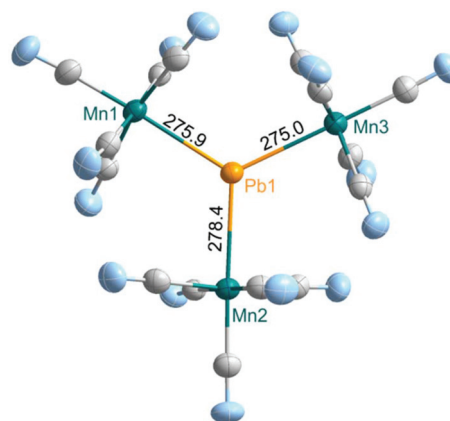


Fig. 2 Structure of the  $[\text{Pb}\{\text{Mn}(\text{CO})_5\}_3]^+$  cation (Pb–Mn distances in pm; ellipsoids comprise 50% of the probability density of the atoms).

Table 1 Crystallographic data and refinement details of  $[\text{Pb}\{\text{Mn}(\text{CO})_5\}_3][\text{AlCl}_4]$

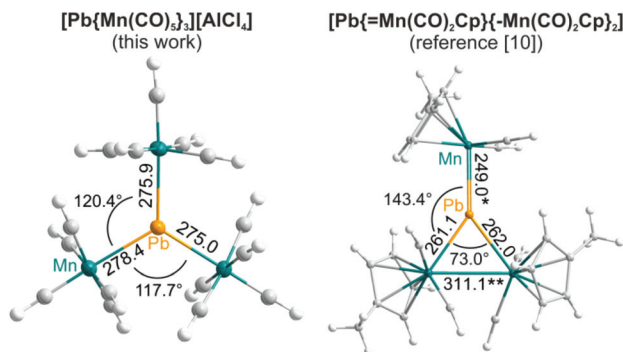
Data	$[\text{Pb}\{\text{Mn}(\text{CO})_5\}_3][\text{AlCl}_4]$
Sum formula	$\text{C}_{15}\text{O}_{15}\text{AlCl}_4\text{Mn}_3\text{Pb}$
Molar mass	$960.95 \text{ g mol}^{-1}$
Crystal system	Monoclinic
Space group	$P2_1/c$ (no. 14)
Lattice parameters	$a = 1020.8(2) \text{ pm}$ $b = 1762.0(3) \text{ pm}$ $c = 1791.5(5) \text{ pm}$ $\beta = 120.9(1)^\circ$
Cell volume	$V = 2763.8 \times 10^6 \text{ pm}^3$
Formula units per cell	$Z = 4$
Calculated density	$\rho = 2.309 \text{ g cm}^{-3}$
Measurement limits	$-13 \leq h \leq 12$ , $-18 \leq k \leq 23$ , $-9 \leq l \leq 23$
Theta range for data collection	$3.32$ to $64.34^\circ$
Measurement conditions	Stoe Stadivari diffractometer (Stoe) $\lambda(\text{Ga-K}\alpha) = 134 \text{ pm}$ , $T = 150 \text{ K}$ $\mu = 17.89 \text{ mm}^{-1}$
Linear absorption coefficient	
Number of reflections	17 417 (independent 14 261)
Refinement method	Full-matrix least-squares on $F^2$
Merging	$R_{\text{int}} = 0.0233$
Number of parameters	352
Residual electron density	$3.23$ to $-0.82 \text{ e}^- 10^{-6} \text{ pm}^{-3}$
Figures of merit	$R_1 (I \geq 4\sigma_1) = 0.0325$ $R_1 (\text{all data}) = 0.0344$ $wR_2 (\text{all data}) = 0.0889$ Goof = 0.998

Table 2 Selected distances of  $[\text{Pb}\{\text{Mn}(\text{CO})_5\}_3][\text{AlCl}_4]$  in comparison with literature data

Compound	Pb–Mn (pm)	Pb–Cl (pm)
$[\text{Pb}\{\text{Mn}(\text{CO})_5\}_3][\text{AlCl}_4]$ (this work)	275.0(1)–278.5(1)	313.9(2), 334.4(2)
$\text{Pb}\{\text{Mn}(\text{CO})_2\text{Cp}\}_3$ [10]	261.1–262.0 (single bond) 249.0 (double bond)	—
$[(\text{Pb}_6\text{I}_8)\{\text{Mn}(\text{CO})_5\}_6]^{2-}$ [6c]	279.9–281.2	—
$\text{PbCl}_2$ [18]	—	284.7, 308.4

$\text{Mn3}$ ) to 278.5(1) pm (Pb–Mn2) are observed (Table 2). Based on this equidistant connectivity and Mn–Pb–Mn angles of 117.7(1) (Mn2–Pb–Mn3) to 121.9(1) $^\circ$  (Mn1–Pb–Mn3), an almost ideal trigonal planar  $\text{PbMn}_3$  arrangement is formed (Fig. 2). The Pb–Mn distances clearly point to three covalent single bonds and fit well with  $\text{Pb}^{\text{I}}\text{–Mn}$  single bonds (279.9–281.2 pm) in  $[(\text{Pb}_6\text{I}_8)\{\text{Mn}(\text{CO})_5\}_6]^{2-}$ .<sup>6c</sup> Electron counting with three Pb–Mn electron-pair bonds results in three Pb-allocated electrons, and thus, a formal oxidation state of  $\text{Pb}^{\text{I}}$  for the group 14 element Pb. Naturally, the Pb–Mn distances in the title compound are significantly longer than the  $\text{Pb}^0\text{=Mn}$  double bond (249.0 pm) in  $\text{Pb}\{\text{Mn}(\text{CO})_2\text{Cp}\}_3$  (Fig. 3).<sup>10</sup> Certain





**Fig. 3** Comparison of the  $\text{PbMn}_3$  cluster in  $[\text{Pb}\{\text{Mn}(\text{CO})_5\}_3][\text{AlCl}_4]$  and  $\text{Pb}\{\text{Mn}(\text{CO})_2\text{Cp}\}_3$  (distances in pm; \*:  $\text{Pb}=\text{Mn}$  double bond and \*\*:  $\text{Mn}-\text{Mn}$  single bond).<sup>10</sup>

increase of the  $\text{Pb}^{+1}-\text{Mn}$  distances in  $[\text{Pb}\{\text{Mn}(\text{CO})_5\}_3][\text{AlCl}_4]$  in comparison with the  $\text{Pb}^0-\text{Mn}$  single bonds (261.1–262.0 pm) in  $\text{Pb}\{\text{Mn}(\text{CO})_2\text{Cp}\}_3$  can be related to the steric hindrance of the CO ligands (Fig. 3).<sup>10</sup>

It needs to be noted that the  $\text{PbMn}_3$  cluster in  $[\text{Pb}\{\text{Mn}(\text{CO})_5\}_3][\text{AlCl}_4]$  is significantly different from the only known  $\text{PbMn}_3$  unit in  $\text{Pb}\{\text{Mn}(\text{CO})_2\text{Cp}\}_3$ .<sup>10</sup> First of all,  $[\text{Pb}\{\text{Mn}(\text{CO})_5\}_3]^+$  contains three equalized  $\text{Pb}-\text{Mn}$  distances (Table 2), so that an almost equilateral triangle of three manganese atoms is spanned with lead in its center. In difference,  $\text{Pb}\{\text{Mn}(\text{CO})_2\text{Cp}\}_3$  shows largely different distances ( $\text{Pb}=\text{Mn}$ : 249,  $\text{Pb}-\text{Mn}$ : 261–262 pm) and  $\text{Mn}-\text{Pb}-\text{Mn}$  angles (73.0, 143.4, 143.6°) significantly deviating from 120° (Fig. 3).<sup>10</sup> Moreover, the title compound contains a  $[\text{Pb}\{\text{Mn}(\text{CO})_5\}_3]^+$  cation and a positively charged  $\text{PbMn}_3$  unit with a formal  $\text{Pb}^{+1}$ , whereas the charge neutral  $\text{Pb}\{\text{Mn}(\text{CO})_2\text{Cp}\}_3$  contains lead in the formal oxidation state  $\pm 0$ .  $[\text{Pb}\{\text{Mn}(\text{CO})_5\}_3]^+$  with only six electrons (*i.e.* three  $\text{Pb}-\text{Mn}$  bonds) around the lead atom is electron deficient, for instance like  $\text{BH}_3$ , and can be considered less stable than the neutral  $\text{Pb}\{\text{Mn}(\text{CO})_2\text{Cp}\}_3$  molecule with a filled electron octet

**Table 3**  $\text{Pb}-\text{Mn}$  bond length and partial charges on Pb and Mn as obtained from Mulliken and natural population analyses (NPA) at 1c- and 2c-TPSS/dhf-TZVP-2c levels

		Pb–Mn (pm)	Mulliken		NPA	
			Pb	Mn	Pb	Mn
$[\text{Pb}\{\text{Mn}(\text{CO})_5\}_3]^+$	1c	277.7	+0.85	−0.57	+0.88	−1.13
	2c	277.7/278.1	+0.83	−0.56	+0.82	−1.12

**Table 4** Wavenumbers of the harmonic vibrational frequencies of the CO stretching modes of  $[\text{Pb}\{\text{Mn}(\text{CO})_5\}_3]^+$  as obtained at the 1c-TPSS/dhf-TZVP-2c level

Symmetry	$a_1$	$e$	$a_1$	$e$	$e$	$a_1$	$a_2$	$e$	$e$	$a_2$
$\tilde{\nu}$ ( $\text{cm}^{-1}$ )	2127	2094	2058	2054	2049	2044	2043	2032	2021	2010
Intensity (%)	0	100	0	1.4	0.3	0	76	59	0.1	0.2

at lead.<sup>10</sup> In this regard, the merit of the ionic-liquid-based synthesis and its potential to obtain highly reactive compounds are again validated. The ionic-liquid-based approach is also more straightforward since simple  $\text{PbCl}_2$  can be used as the starting material, whereas  $\text{Pb}\{\text{Mn}(\text{CO})_2\text{Cp}\}_3$  requires an elaborate heterocumulene derivative  $\text{Cp}(\text{CO})_2\text{Mn}=\text{Pb}=\text{Mn}(\text{CO})_2\text{Cp}$  as the starting material.<sup>10</sup>

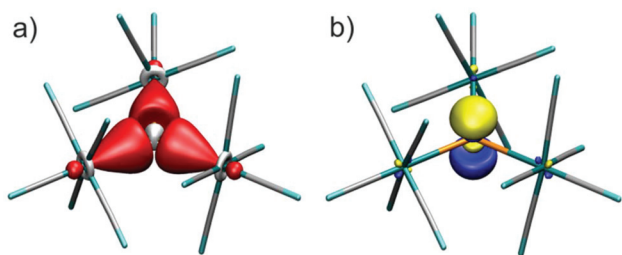
To verify the bonding situation of Pb and Mn, density functional theory (DFT) calculations were performed on a single  $[\text{Pb}\{\text{Mn}(\text{CO})_5\}_3]^+$  cation using the TPSS functional<sup>13</sup> in the dhf-TZVP-2c basis,<sup>14</sup> which includes a dhf-ECP-2c relativistic effective core potential (RECP) for Pb representing its  $\{\text{Kr}\}4d^{10}4f^{14}$  core.<sup>15</sup> The calculations were performed at the scalar-relativistic one-component (1c) and quasi-relativistic two-component (2c) levels.<sup>16</sup>

At the 1c level, scalar relativistic effects are accounted for through the spin-free part of the RECP on Pb. A geometry optimization at this level yielded a highly symmetric equilibrium structure belonging to the point group  $D_3$ , in which all three  $\text{Pb}-\text{Mn}$  distances are equal (277.7 pm, Table 3). Harmonic vibrational frequencies were computed to confirm that the optimized structure is a minimum on the potential energy surface (Table 4).

At the 2c level, also non-scalar (*i.e.*, spin-orbit) effects were accounted for through the 2c part of the RECP on Pb. An equilibrium structure belonging to the point group  $C_2$  was found at this level, with two equal  $\text{Pb}-\text{Mn}$  bonds of 277.7 pm and one slightly longer  $\text{Pb}-\text{Mn}$  bond of 278.1 pm. Thus, the distortion of the  $D_3$  structure towards  $C_2$  due to the spin-orbit interaction appears to be almost negligible. Harmonic vibrational frequencies were computed (from finite differences of analytical gradients) and confirmed that the optimized structure is a minimum.

In conclusion, spin-orbit effects play only a minor role in the  $[\text{Pb}\{\text{Mn}(\text{CO})_5\}_3]^+$  cation resulting in a similar electronic structure and bonding situation in the 1c and 2c descriptions. For example, the lowest unoccupied molecular orbital (LUMO) of the 1c calculation, which is an empty  $\text{Pb } 6p_z$  orbital, is virtually indistinguishable from the lowest unoccupied natural orbital obtained in the 2c-TPSS/dhf-TZVP-2c calculation (Fig. 4). The results obtained from a population analysis are also very similar at the 1c and 2c levels (Table 3). A Boys localization of the 1c occupied orbitals yielded three equivalent  $\text{Pb}-\text{Mn}$   $\sigma$  bonds (Fig. 4). In summary, the bonding situation in the  $[\text{Pb}\{\text{Mn}(\text{CO})_5\}_3]^+$  cation can be clearly described with a formal charge of +1 on Pb, an empty  $6p_z$  orbital, and three two-center-two-electron (2c2e)  $\sigma$  bonds. This view is in accordance with the results deduced from crystal structure analysis of





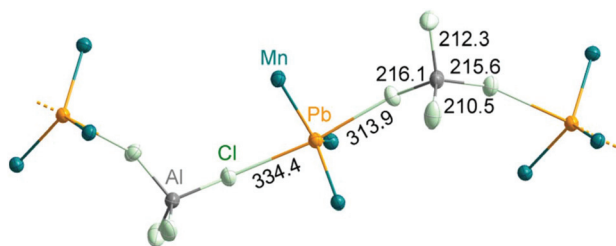
**Fig. 4** Results of the DFT calculation: (a) three localized occupied molecular orbitals describing the three Pb–Mn  $\sigma$  bonds; (b) lowest unoccupied natural orbital (isovalue surfaces shown at  $\pm 0.1 a_0^{-3/2}$ ).

the aforementioned electron-deficient character of the  $[\text{Pb}\{\text{Mn}(\text{CO})_5\}_3]^+$  cation.

The Mn–C distances in the  $[\text{Pb}\{\text{Mn}(\text{CO})_5\}_3]^+$  cation range from 182.5(5) (Mn2–C10) to 188.2(5) pm (Mn2–C9) and fit well with Mn–C distances of terminal CO ligands, such as in  $\text{Mn}_2(\text{CO})_{10}$ .<sup>17</sup> Similarly the C–O distances fit with  $\text{Mn}_2(\text{CO})_{10}$ <sup>17</sup> and range from 111.6(6) (C15–O15) to 113.6(6) pm (C5–O5).

In accordance with the electron-deficient character of the  $[\text{Pb}\{\text{Mn}(\text{CO})_5\}_3]^+$  cation, lead is further coordinated by two chlorine atoms as electron-pair donors of two different  $[\text{AlCl}_4]^-$  anions, so that Pb – in sum – has a distorted trigonal bipyramidal coordination of three Mn and two Cl atoms (Fig. 5). Since each  $[\text{AlCl}_4]^-$  anion is well coordinated to two  $[\text{Pb}\{\text{Mn}(\text{CO})_5\}_3]^+$  cations, in sum, an infinite zig-zag chain is formed (Fig. 1 and 5). Herein, the Pb–Cl distances are not equidistant, but exhibit a shorter (Pb–Cl2: 313.9(2) pm) and a longer distance (Pb–Cl1: 334.3(2) pm) (Fig. 5). The zig-zag chains exhibit Cl–Pb–Cl angles of 173.0(1)°, and they are stacked along the crystallographic *c*-axis like a hexagonal rod-type packing (Fig. 1). Compared to  $\text{PbCl}_2$  (Pb–Cl: 284.7, 308.4 pm),<sup>18</sup> the observed Pb–Cl distances are significantly increased, which is in accordance with a formal oxidation state of  $\text{Pb}^{+1}$  and the fact that the chlorine atoms exist as  $[\text{AlCl}_4]^-$ , and thus, as part of a complex anion.

The  $[\text{AlCl}_4]^-$  anion itself is slightly distorted from an ideal tetrahedron (Cl–Al–Cl angles: 107.0(1) to 112.5(1)°). As expected, those two Cl atoms bridging to Pb exhibit slightly longer Al–Cl distances (Al–Cl1: 215.8(2), Al–Cl2: 216.1(2) pm)

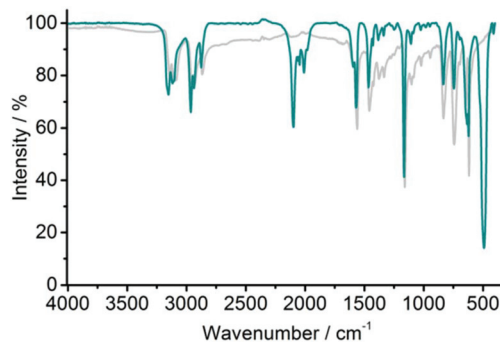


**Fig. 5** Linkage of  $\text{PbMn}_3$  units via  $[\text{AlCl}_4]^-$  to infinite chains along the crystallographic *c*-axis (distances in pm; ellipsoids comprise 50% of the probability density of the atoms).

compared to the two terminal Cl atoms (Al–Cl3: 210.3(2), Al–Cl4: 212.0(2) pm) (Fig. 5). This distortion points to the interaction of lead and chlorine and is often observed for asymmetric coordination (e.g. in  $\text{Na}[\text{AlCl}_4]$ ).<sup>19</sup>

In addition to single-crystal structure analysis, the composition, structure and properties of  $[\text{Pb}\{\text{Mn}(\text{CO})_5\}_3][\text{AlCl}_4]$  were validated by energy-dispersive X-ray spectroscopy (EDXS), Fourier-transform infrared spectroscopy (FT-IR) and optical spectroscopy (UV-Vis). Accordingly, EDXS confirms a Pb : Mn : Al : Cl ratio of 1.0 : 2.6 : 1.2 : 4.0, which fits well with the composition and the calculated values (1 : 3 : 1 : 4).

FT-IR spectroscopy shows the characteristic CO vibrations with a strong absorption at 2098  $\text{cm}^{-1}$  and three weak absorptions at 2062, 2947 and 2010  $\text{cm}^{-1}$  (Fig. 6). In comparison with  $\text{Mn}_2(\text{CO})_{10}$ ,<sup>17c</sup> the CO vibrations of the title compound are slightly shifted to higher wavenumbers (Table 5), which, on the one hand, can be ascribed to the higher electronegativity of lead (EN(Pauling): 1.8) in comparison with manganese (EN(Pauling): 1.5),<sup>20</sup> and on the other hand, to the fact that manganese carries part of the positive charge in the  $\text{PbMn}_3$  cluster. As a consequence, the observed CO vibrations are even more comparable to terminally bond carbonyl ligands in  $\text{Mn}(\text{CO})_5\text{I}$  or  $[\text{Pb}_6\text{I}_8\{\text{Mn}(\text{CO})_5\}_6]^{2-}$  (Table 5).<sup>6c,21</sup> In addition to CO vibrations, absorptions related to the ionic liquid were observed (3152–2876, 1571, 1466  $\text{cm}^{-1}$ ) and agree with reference spectra of the pure ionic liquid (Fig. 6). Finally, UV-Vis spectra of  $[\text{Pb}\{\text{Mn}(\text{CO})_5\}_3][\text{AlCl}_4]$  show a strong, continuous absorption above 450 nm as well as an absorption peak at 297 nm (Fig. 7). This finding is in accordance with the dark-red, almost black colour of single crystals (Fig. 7, inset).



**Fig. 6** FT-IR spectrum of  $[\text{Pb}\{\text{Mn}(\text{CO})_5\}_3][\text{AlCl}_4]$  (green) with the ionic liquid  $[\text{BMIm}][\text{Cl}]$  shown as a reference (grey).

**Table 5** Carbonyl vibrations of  $[\text{Pb}\{\text{Mn}(\text{CO})_5\}_3][\text{AlCl}_4]$  in comparison with literature data (strong vibrations: bold)

Compound	Vibration ( $\text{cm}^{-1}$ )
$[\text{Pb}\{\text{Mn}(\text{CO})_5\}_3][\text{AlCl}_4]$ (this work)	<b>2098</b> , 2062, 2047, 2010
$\text{Mn}_2(\text{CO})_{10}$ [17c]	<b>2045</b> , <b>2014</b> , <b>1983</b>
$\text{Mn}(\text{CO})_5\text{I}$ [21]	2131, <b>2035</b> , <b>2008</b> , 1969
$[(\text{Pb}_6\text{I}_8)\{\text{Mn}(\text{CO})_5\}_6]^{2-}$ [6c]	<b>2063</b> , 2008, <b>1964</b>



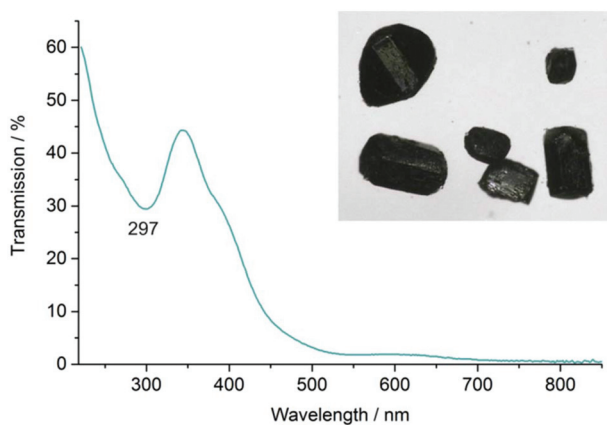


Fig. 7 UV-Vis spectrum of  $[\text{Pb}\{\text{Mn}(\text{CO})_5\}_3][\text{AlCl}_4]$  with a photo of deep red, almost black single crystals (inset).

## Conclusions

The novel carbonyl cluster compound  $[\text{Pb}\{\text{Mn}(\text{CO})_5\}_3][\text{AlCl}_4]$  is presented. The title compound was prepared by the redox reaction of  $\text{PbCl}_2$  and  $\text{Mn}_2(\text{CO})_{10}$  in the ionic liquid  $[\text{BMIm}][\text{AlCl}_4]$  upon reduction of  $\text{Pb}^{\text{II}}$  to  $\text{Pb}^{\text{I}}$  and oxidation of  $\text{Mn}^0$  to  $\text{Mn}^{+\text{I}/+\text{II}}$ . The  $[\text{Pb}\{\text{Mn}(\text{CO})_5\}_3]^+$  carbonyl cation contains a central  $\text{PbMn}_3$  cluster with three  $\text{Pb-Mn}$  single bonds (275.0 to 278.4 pm), resulting in an almost equilateral triangle ( $\text{Mn-Pb-Mn}$  angles: 117.7(1) to 121.9(1) $^\circ$ ) of three manganese atoms with a formal  $\text{Pb}^{\text{I}}$  in its center. Based on the crystal structure and DFT calculations, the bonding situation in the  $[\text{Pb}\{\text{Mn}(\text{CO})_5\}_3]^+$  cation can be described with a formal charge of +1 on Pb, an empty  $6p_z$  orbital, and three two-center-two-electron ( $2c2e$ )  $\sigma$  bonds. Similar to  $\text{BH}_3$ , thus,  $[\text{Pb}\{\text{Mn}(\text{CO})_5\}_3]^+$  represents an electron-deficient species. Such a cluster and compound were identified for the first time.

Beside the three  $\text{Mn}(\text{CO})_5$  units, the electron-deficient Pb center is further coordinated by two Cl atoms of  $[\text{AlCl}_4]^-$  anions serving as electron-pair donors. Together with the trigonal  $\text{PbMn}_3$  cluster unit, this results in a trigonal bipyramidal coordination around Pb. Due to bidentate coordination of the  $[\text{Pb}\{\text{Mn}(\text{CO})_5\}_3]^+$  carbonyl cations as well as of the  $[\text{AlCl}_4]^-$  anions, finally, infinite zig-zag chains along the crystallographic  $c$ -axis are formed.

The successful synthesis of the reactive carbonyl cluster can be considered as another example of the advantage of ionic-liquid-based synthesis and its promising features such as the weakly coordinating properties and the redox stability of the ionic liquids.

## Experimental

### Synthesis

**General aspects.** All reactions and sample handling were carried out under a dried argon atmosphere using standard Schlenk techniques or gloveboxes. Reactions were performed

in Schlenk flasks and glass ampoules that were evacuated ( $p < 10^{-3}$  mbar), heated and flashed with argon three times prior to use. The starting materials  $\text{PbCl}_2$  (99.99%, ABCR),  $\text{Mn}_2(\text{CO})_{10}$  (99%, ABCR) and  $\text{AlCl}_3$  (99.99%, Sigma-Aldrich) were used as received.  $[\text{BMIm}]\text{Cl}$  (99%, Iolitec) was dried under reduced pressure ( $10^{-3}$  mbar) at 130  $^\circ\text{C}$  for 48 h. All compounds were handled and stored in argon-filled gloveboxes ( $\text{MBraun Unilab}$ ,  $c(\text{O}_2, \text{H}_2\text{O}) < 0.1$  ppm).

**$[\text{Pb}\{\text{Mn}(\text{CO})_5\}_3][\text{AlCl}_4]$ .** 40 mg (0.144 mmol, 1 eq.) of  $\text{PbCl}_2$ , 96.5 mg (0.288 mmol, 2 eq.) of  $\text{Mn}_2(\text{CO})_{10}$ , 500 mg (2.863 mmol) of  $[\text{BMIm}]\text{Cl}$  and 381.8 mg (2.863 mmol) of  $\text{AlCl}_3$  were heated under argon in a sealed glass ampoule for 96 h at 130  $^\circ\text{C}$ . After cooling to room temperature with a rate of 1  $\text{K h}^{-1}$ , the title compound was obtained as dark red crystals together with blue needles of  $[\text{Mn}(\text{CO})_6][\text{AlCl}_4]$  as a minor phase.  $[\text{Pb}\{\text{Mn}(\text{CO})_5\}_3][\text{AlCl}_4]$  is highly sensitive to air and moisture and needs to be handled under inert conditions. Since the title compound could not be obtained phase-pure, the crystals for characterization were manually separated by crystal picking.

### Analytical equipment

**Single-crystal X-ray structure analysis.** For single crystal structure analysis, suitable crystals were selected, and covered with inert-oil (perfluoropolyalkylether, ABCR). Data collection was performed at 150 K on an Stoe Stadivari diffractometer (Stoe, Darmstadt) with Euler geometry using  $\text{Ga-K}\alpha$  radiation ( $\lambda = 134$  pm, graded multilayer mirror as the monochromator). Data reduction and multi-scan absorption correction were conducted with the X-AREA software package (version 1.75, Stoe) and STOE LANA (version 1.63.1, Stoe).<sup>22</sup> Space group determination based on systematic absences of reflections, structure solution by direct methods and refinement were performed by XPREP and SHELXTL (version 6.14, SHELX-2013).<sup>23</sup> All atoms were refined anisotropically. Detailed information on crystal data and structure refinement is listed in Table 1. DIAMOND was used for all illustrations.<sup>24</sup> Further details of the crystal structure investigation may be obtained from the joint CCDC/FIZ Karlsruhe deposition service on quoting the depository number CCDC 1890307.†

**Fourier-transform infrared (FT-IR) spectra** were recorded on a Bruker Vertex 70 FT-IR spectrometer (Bruker). The samples were measured as pellets in KBr. Thus, 300 mg of dried KBr and 0.5–1.0 mg of the sample were carefully pestled together and pressed to a thin pellet.

**Energy dispersive X-ray (EDX) analysis** was performed by using an Ametek EDAX mounted on a Zeiss SEM Supra 35 VP scanning electron microscope. Samples were prepared in a glovebox by selecting single crystals that were fixed on conductive carbon pads on aluminum sample holders. Samples were handled under inert conditions during transport and sample preparation.

**Optical spectroscopy (UV-Vis)** of powder samples was performed on a Shimadzu UV-2700 spectrometer, equipped with an integrating sphere, in a wavelength interval of 250–800 nm against  $\text{BaSO}_4$  as the reference.



## Computation

**Density functional theory (DFT) calculations** were performed using the TPSS functional<sup>13</sup> in the dhf-TZVP-2c basis,<sup>14</sup> which includes a dhf-ECP-2c relativistic effective core potential (RECP) for Pb representing its {Kr}4d<sup>10</sup>4f<sup>14</sup> core.<sup>15</sup> Version 7.4 of the TURBOMOLE program package was used.<sup>25</sup> Calculations were performed at the scalar-relativistic one-component (1c) and quasi-relativistic two-component (2c) levels.<sup>16</sup>

## Conflicts of interest

There are no conflicts to declare.

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