Inorganic Lead(IV) Compound

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$K_4[PbSe_4]\cdot en\cdot NH_3$: A Non-Oxide, Non-Halide Inorganic Lead(IV) Compound**

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Dedicated to Professor Walter Thiel on the occasion of his 65th birthday

Abstract: *The first inorganic lead(IV) compound without oxygen, nitrogen or halogen ligands attached to the lead atom was obtained as the potassium salt of the tetraselenidoplumbate(IV) anion $[Pb^{IV}Se_4]^{4-}$. It is stable under inert conditions which may enable the transfer of the chemistry of chalcogenidogermanate(IV) or chalcogenidostannate(IV) materials, to the lead homologues.*

The chemistry of lead is both very traditional, going back to the late 7th millennium B.C. and ancient metallurgy,[1] and also highly topical, for instance in the synthesis of low-valence organometallic lead compounds,[2] chalcogenide or pnictogenide clusters,[3] or the use of Zintl polyanions of lead as precursors to form intermetalloid clusters.[4]

However, most academic as well as technical developments are correlated with formal oxidation states of the Pb atoms from −I to +II. Of course, this is a well-established feature, and textbooks attribute this situation to the relativistic effect that strongly stabilizes the 6s atomic orbital (AO), thus making it fairly unavailable to chemistry; exceptions are limited to salts with extremely high electronegativity nonmetal partners provided suitable crystal lattices exist which can overcompensate the high ionization energy through the corresponding lattice energies, and to lead(IV) organic compounds, such as $PbEt_4$ that was used in petrol.

By ab initio calculations on the series R_xPbX_{4-x} (R = H, Me; X = F, Cl; x = 0–4) and R_xPbX_{4-x} (x = 0–2), the concept of stable "organic Pb^{IV}" compounds, in addition to stable "inorganic Pb^{II}" compounds has been illustrated. According to these studies, an increase of the metal charge caused by more electronegative ligands leads to the 6p AO becoming unfavorable for covalent bonding.[5a] These results are in excellent agreement with the empirically found decrease of stability in the order $R_4Pb > R_3PbX > R_2PbX_2 \gg RPbX_3 > PbX_4$.[5b]

Thus, the only known "inorganic Pb^{IV}" compounds can be listed in a few lines:[6] PbO_2, as the minerals scrutinyite and plattnerite,[7] or as the prominent anode material in car batteries as well as several binary oxides, such as Pb_2O_3 and Pb_3O_4, various oxoplumbates, as first described by Zintl and co-works,[8] $Pb(OAc)_4$, an oxidizing agent for organic syntheses,[9] Pb^{IV} salts with anions of high symmetry, such as $[HAsO_4]^{2-}$, $[HPO_4]^{2-}$, $[SeO_3]^{2-}$, plumbate anions with substituents of high group electronegativity, $(AsPh_4)_2[Pb(N_3)_6]$,[10] $K_2[Pb(OH)_6]$,[11] and the corresponding acid $Pb(OH)_4$, characterized by infrared spectroscopy in solid argon.[12] For the halides, only PbX_4 (X = F, Cl)[13] and salts of the $[PbX_6]^{2-}$ ions with X = F, Cl, (IO_6) have been crystallographically determined.[14] In conclusion, no (isolable) chalcogenides PbE_2 (E = S, Se, Te) and no tetrahedral Pb^{IV}/E aggregates are known to date.

It thus is quite unexpected to find a tetrahedral unit in the first chalcogenidoplumbate(IV), $K_4[PbSe_4]\cdot en\cdot NH_3$ (**1**, Figure 1; en = ethane-1,2-diamine), which was obtained by solvothermal extraction of a homogeneous phase with the nominal composition "K_2PbSe_2". The reaction was performed

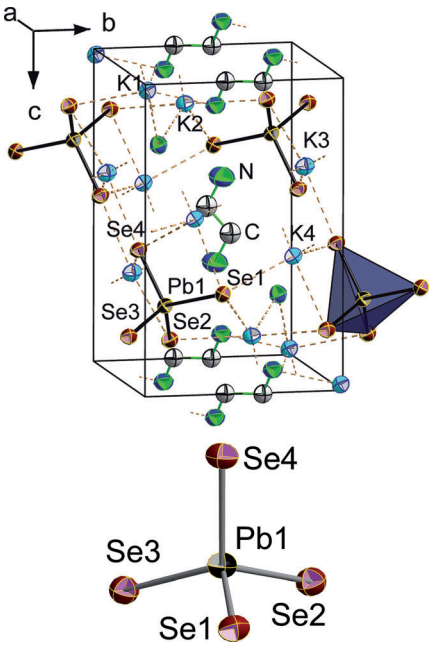

Figure 1. Fragment of the crystal structure (top) and thermal ellipsoid plot (ellipsoids set at 50% probability) of the $[Pb^{IV}Se_4]^{4-}$ ion (bottom) in **1**. Selected structure parameters: Pb-Se 2.600(2)–2.610(1) Å; Se-Pb-Se 107.71(6)-110.79(6)°.

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based on our expertise on the chemistry of chalcogenidotetrelates(IV),[15] and on the extraction of ternary phases A/T/E (A = alkali metals, T = Group 13–14 (semi-)metal, E = pnictogen, chalcogen) by means of basic solvents.[16]

The title compound was obtained as deep red crystals (Figure 2). The crystal structure (triclinic space group $P\bar{1}$) contains near tetrahedral $[PbSe_4]^{4-}$ ions that are embedded

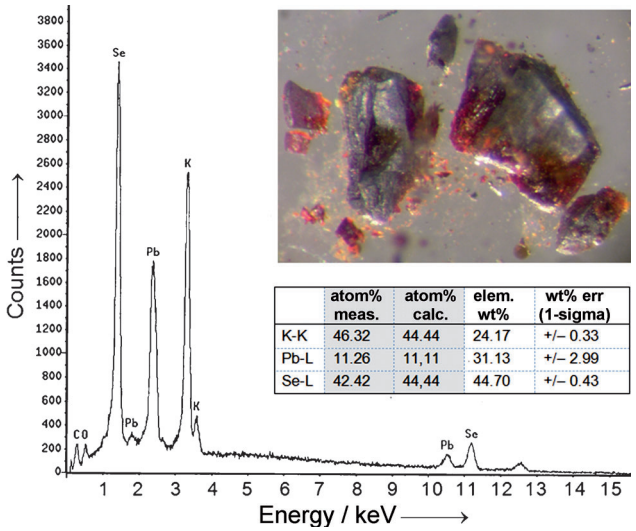

Figure 2. EDX spectrum of **1** along with the analysis data; the inset shows a photograph of partially crushed crystals of **1**, as used for the structural and elemental analyses.

between four K^+ counterions (K···Se 3.282–3.412 Å) and two solvent molecules (NH_3 and en; Se···(H)N 3.346–3.969 Å) per formula unit. The atomic K:Pb:Se ratio of **1** was confirmed by means of EDX analyses of the crystals (Figure 2). The formal +IV oxidation state at the Pb atom was rationalized by quantum chemical calculations using Møller–Plesset 2nd order perturbation theory (MP2) methods[17] implemented in the program system TURBOMOLE,[18] which show unreasonable elongations of the Pb–Se bonds for a hypothetic "$[Pb^{II}Se_4]^{6-}$" ion (Supporting Information, Table S3).

Single-crystals of the title compound are rapidly covered by a metallic film upon contact with air, but are stable under inert conditions for months. They are stable enough to be kept as a suspension in nujol oil between two quartz plates for several hours; over more than 12 h, the solid-state UV/Vis spectrum (Figure 3) remained the same. Neither room temperature, nor illumination by visible light changed the situation. Only upon exposure of the suspension to air, the sample color turned black and the absorption signal diminished, indicating decomposition of the compound. In agreement with the visible color (Figure 2), the measured optical excitation energy, given as onset of absorption, amounts to $E_{onset} = 2.0$ eV.

Quantum chemical calculations using time-dependent DFT methods (TDDFT, singlet excitations)[19] also implemented in the program system TURBOMOLE[18] were performed to rationalize the measured excitation energy, and to compare it to the E_{onset} values of the entire $[TE_4]^{4-}$ series with T = Si–Pb and E = O–Te (Figure S1). The calculations show a con-

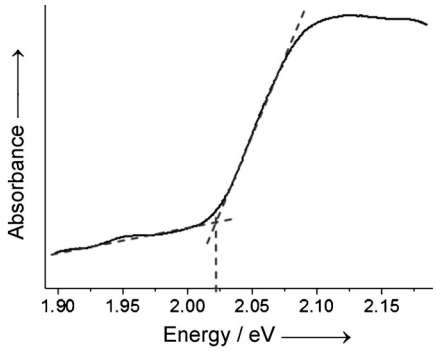

Figure 3. Solid state UV/Vis spectrum of **1**, recorded from a suspension of pulverized crystals in nujol oil.

tinuous development of E_{onset} along the tetrel family and, for a given tetrel element, along the chalcogen family.[20] As expected from the color of the deep red crystals, $[PbSe_4]^{4-}$ and $[SnTe_4]^{4-}$ [20a–c] have the same absorption energy. In both cases, the calculated values (1.9 eV) differ by only 0.1 eV from the measured ones (2.0 eV).

More detailed information about the electronic situation was gained by further MP2 calculations and consecutive inspection of the molecular orbitals (MOs) of all possible $[TE_4]^{4-}$ combinations (T = Si–Pb; E = O–Te) by means of Mulliken population analysis.[21] The highest occupied MOs (HOMO, HOMO−1, HOMO−2) and the lowest energy valence MO (HOMO−5) have distinct lone-pair character at the terminal chalcogenide ligands, whereas HOMO−3 and HOMO−4 are T–E bonding in nature. Most developments of MO energies are steady along the T or E series (Figure S2), indicating slight destabilization of the HOMO along Pb→Si, nearly no change for HOMO−1 and HOMO−2, and a slight stabilization for HOMO−3, however, the HOMO−4 energies reflect the distinct stabilization of the 6s and 6p AO at Pb. As an example, we compare the MOs for $[PbSe_4]^{4-}$ and $[SnSe_4]^{4-}$ (Figure 4) into detail.

In $[PbSe_4]^{4-}$, HOMO and HOMO−1 (t_2, t_1) are nearly the same energy, HOMO−2 (e) is lower by 0.7 eV. The higher-energy Pb–Se bonding orbital (HOMO−3, t_2) is below the "lone pairs" by another 1.2 eV. As expected, a very stable, Pb–Se bonding MO (HOMO−4, a_1) with a significant Pb 6s contribution is found another 5 eV lower, that is, 7 eV below the HOMO energy level; according to population analyses, the contributions to this MO are 23.3% Pb 6s and 23.3% Pb 6p, along with 40.8% Se 4s, and 12.6% Se 4p (all four Se atoms in total). Apart from the energetic order of the highest t_2 and t_1 MOs (t_2 is higher in energy than t_1 by 0.002 eV for $[PbSe_4]^{4-}$), both the energy differences and AO contributions found for HOMO, HOMO−1, HOMO−2, and HOMO−3 are very similar for $[PbSe_4]^{4-}$ and $[SnSe_4]^{4-}$. In contrast, the situation for HOMO−4 differs significantly: for the Sn/Se combination, not only the orbital contributions of the central atom are lower (19.0% Sn 5s and 19.0% Sn 5p along with 50.5% Se 4s and 11.5% Se 4p), but this MO is also by only 4 eV lower in energy than HOMO-3, and by only 6 eV below the HOMO level in $[SnSe_4]^{4-}$. Both the energies of the T–E bonding MOs HOMO−3 and HOMO−4, and the electron-

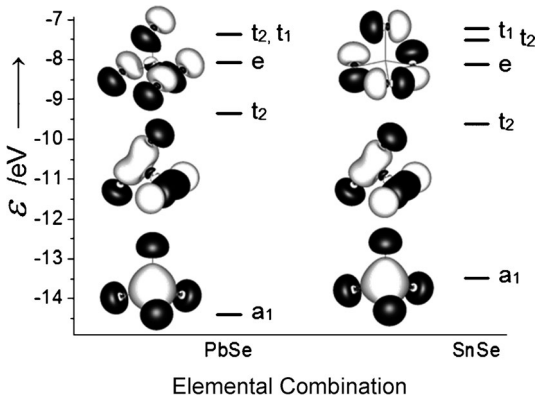

Figure 4. MO schemes along with the visualization of representative occupied orbitals in $[PbSe_4]^{4-}$ (left) and $[SnSe_4]^{4-}$ (right). MO plots from top: HOMO ($[PbSe_4]^{4-}$: t_2, $[SnSe_4]^{4-}$: t_1), HOMO−3 (t_2), HOMO−4 (a_1). Amplitudes are drawn at ±0.033 a.u.; note that only one of the degenerate MOs is shown for all examples. The lowest energy valence orbitals (HOMO−5) that represent the 5s AOs from Se atoms in both cases are not shown.

density distribution in HOMO−3 may be made responsible for the observed stability. In the particular case of $[PbSe_4]^{4-}$, although the higher energy bonding MO (t_2, HOMO−3) is slightly destabilized (with respect to the situation in $[SnSe_4]^{4-}$), the plumbate(IV) anion is not that reactive as a consequence of the high stability of the lower energy bonding MO (a_1, HOMO−4), which is indeed the lowest energy HOMO−4 in the entire $[TE_4]^{4-}$ series (Figure S2). By inspection of the relative energies, our recent observation that a preparation of $[PbTe_4]^{4-}$ is not possible using the described method can be explained, whereas the synthesis of $[PbS_4]^{4-}$ should, in general, be possible. Our efforts so far have failed because no homogenous parent phase (such as "K_2PbS_2") could be obtained. In addition to these molecular effects, we assume a considerable influence of the lattice energy of the solid **1**. This assumption is supported by the observation that **1** precipitates from the mother liquor during the solvothermal treatment and does not re-dissolve in en, which can be understood in terms of suitable molecular measures: the Pb–Se bond lengths in **1** (2.600(2)–2.610(1) Å) are right within the Sn–E bond lengths observed in *ortho*-selenidostannate (2.50–2.54 Å) and *ortho*-telluridostannate anions (2.72–2.80 Å),[15] the potassium salts (hydrates) of which are known,[20a,22] hence rationalizing the stability of the corresponding crystal lattice for **1**.

To further elucidate the stability or reactivity of *ortho*-chalcogenidotetrelate anions, including the anion in **1**, we calculated reaction energies E_r (Table 1) for all possible permutations of elements in reactions of the following type [Eq. (1)].

$$[T^1E_4]^{4-} + T^2 \rightarrow [T^2E_4]^{4-} + T^1 \qquad \Delta E = E_r \tag{1}$$

For a given chalcogen E, all reactions forming a lighter $[T^2E_4]^{4-}$ homologue are exoenergetic; for given tetrel atoms T^1 and T^2, the reactions become more exoenergetic as the chalcogen E is replaced by a lighter congener; as expected, a maximum step in E_r is observed when changing from E = S to E = O, in accordance with the extraordinary stability of oxotetrelates compared to all of their heavier homologues. In contrast, the E_r values differ only marginally between $[TE_4]^{4-}$ species comprising the heavier elemental combinations, such as $[PbSe_4]^{4-}$ versus $[SnSe_4]^{4-}$ (5.2 kJ mol^{-1}), suggesting similar stabilities and reactivities of the respective anions.

In summary, it was possible to prepare and unambiguously characterize the first non-oxide, non-halide inorganic Pb^{IV} compound. The potassium salt of the tetraselenidoplumbate(IV) anion can be kept under inert conditions (inert gas or oil) without change to date. This stability should enable the previously unexpected transfer of the chemistry of chalcogenidogermanate(IV) or chalcogenidostannate(IV) materials, which has been comprehensively investigated in recent times, to the homologues of the heaviest tetrel congener, with accordingly varied photophysical, photochemical, and redox behavior of the resulting compounds.

Experimental Section

General: All manipulations and reactions were performed under an Ar atmosphere using standard Schlenk or glove box techniques. The ternary parent phase "K_2PbSe_2" was prepared by fusion of potassium and lead in a 2:1 molar ratio, subsequent addition of granular selenium (2 equiv), and heating with an oxygen/methane burner for 15 min, which yielded an amorphous black powder upon grinding. Ethane-1,2-diamine (en) was freshly distilled and stored under Ar prior to use.

1: "K_2PbSe_2" (500 mg) and en (2 mL) were placed in a glass vial within a Teflon-lined autoclave; the autoclave was tightly closed and heated for 7 days at 150 °C. After turning off the heating, the autoclave was left for another 2 days to slowly cool down to room temperature. Compound **1** appeared as deep red crystals along with orange polyselenide by-products.

Single-crystal X-ray diffraction: Data collection was performed using a Stoe IPDSI diffractometer at 193 K with $Mo_{K\alpha}$ radiation and graphite monochromatization ($\lambda = 0.71073$). Structure solution was realized by direct methods, refinement with full-matrix-least-squares against F^2 using SHELXS-97, SHELXL-97, and Olex2 software.[24] Crystal data for $C_2H_{11}K_4N_3PbSe_4$ (**1**, $M_W = 756.6$ g mol^{-1}): $a = 8.055(2)$, $b = 8.292(2)$, $c = 12.790(3)$ Å, $\alpha = 92.64(2)$, $\beta = 103.69(2)$, $\gamma = 92.45(2)$°. CCDC 970129 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Quantum chemical methods: DFT calculations were performed with the program system TURBOMOLE[18] using the RIDFT program[25] and employing the Becke–Perdew 86 (BP86) functional[26] with def2-TZVP bases[27] and respective fitting bases[28] for the evaluation of the

Table 1: Reaction energies E_r [kJ mol^{-1}] for the reactions given in Equation (1).[a]

T^1	Pb	Pb	Pb	Pb	Pb	Pb	Pb	Pb	Pb	Pb	Pb	Pb
T^2	Si	Ge	Sn	Si	Ge	Sn	Si	Ge	Sn	Si	Ge	Sn
E	O	O	O	S	S	S	Se	Se	Se	Te	Te	Te
E_r	−32.8	−15.4	−10.2	−13.9	−8.8	−6.3	−11.3	−7.4	−5.2	−7.8	−5.5	−3.9

[a] Values for all further permutations with T^1 = Sn, Ge, or Si, respectively, or with $T^1 = T^2$ for different types of E can be calculated according to Born–Haber cycles[23] from the given numbers.

Coulomb matrix. MP2 calculations were undertaken with the program RIMP2,[29] using def2-TZVP bases[27] and the corresponding fitting bases.[30] Effective core potentials (ECPs) were used for Sn, Te, and Pb atoms (ECP-28, ECP-28, and ECP-60, respectively).[31] Counterions were modeled by application of COSMO with default parameters.[32] Mulliken population analyses[21] served to evaluate atomic orbital contributions to the molecular orbitals. MO plots were generated using the visualization tool gOpenMol.[33]

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