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Molecular CHEVREL-like Clusters $[(RhPPh_3)_6(\mu_3\text{-}Se)_8]$ and $[Pd_6(\mu_3\text{-}Te)_8]^{4-}$

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Supporting Information

ABSTRACT: $[(RhPPh_3)_6(\mu_3\text{-}Se)_8]\cdot 0.5en$ (**1**; en = ethane-1,2-diamine), obtained by the reaction of $[Pb_2Se_3]^{2-}$ anions with $[Rh(PPh_3)_3Cl]$ in en, represents the first compound comprising a molecular $[Rh_6]$ octahedron with all faces capped by Se atoms. Analogous treatment of $[Pb_2Te_3]^{2-}$ with $[Pd(PPh_3)_2Cl_2]$ yielded $[Li_4(en)_{10}][Pd_6(\mu_3\text{-}Te)_8]$ (**2**), the first compound exhibiting a molecular, chalcogen-capped $[Pd_6]$ aggregate. Besides syntheses and structures of the title compounds, we report quantum-chemical calculations to understand the electronic properties of these molecular CHEVREL-like complexes.

For many years, rhodium and palladium compounds have attracted great interest in inorganic, organometallic, and organic chemistry because of their properties in various catalytic reactions, such as Grubbs et al.'s $[RuCl_2(=CHR')(PR_3)_2]$ for alkene metathesis[1] and Wilkinson et al.'s $[Rh(PPh_3)_3Cl]$ for hydrogenation of olefins and acetylenes.[2]

Polynuclear rhodium complexes incorporating a $[Rh_6]$ octrahedron, such as the hexadecacarbonylhexarhodium $[Rh_6(CO)_{16}]$,[3] with its unique properties as a redox catalyst,[4] have been extensively investigated, as well. A large diversity of Rh clusters with terminal, bridging, and/or capping carbonyl groups are known, including condensed clusters with up to 33 Rh atoms,[5] amine- and phosphine-ligated derivatives,[6] as well as the corresponding hydride clusters, such as $[Rh_6H_{12}(PCy_3)_6][B(C_8H_3F_6)_4]_2$[7] or $[Rh_6H_{12}(P^iPr_3)_6]$,[8] and a "pure" $[Rh_6]$ octahedron[9] with potential in syngas conversion.[10] Compounds that contain $[Pd]_6$ aggregates, in contrast, are far less represented in the literature. Apart from $[Pd_6(CO)_4(PMe_3)_7]$,[11] only higher aggregates such as the $[Pd_{33}Ni_9(CO)_{41}(PPh_3)]^{4-}$ cluster anion[12] or $[Pd_{37}(CO)_{28}\{P(p\text{-tolyl})_3\}_{12}$ were reported.[13]

Corresponding molecular $[M_6]$ octahedra with face-bridging chalcogenide ligands are only known for transition metals of groups V−VIII[14] and Co[15] to date. These represent molecular analogues of the fundamental building units of CHEVREL phases $A^{II}Mo_6Ch_8$ (A = Ca, Sr, Ba, Sn, Pb, Au, Ln; Ch = chalcogen), which have triggered large interest because of their thermoelectric and/or superconducting potentials.[16]

In the course of our investigations on the reactivity of $[Pb_2Ch_3]^{2-}$ anions[17] toward transition-metal complexes, a solution resulting from reaction of a binary Pb:Se phase (1:2) with 2.2 equiv of 18c6 and 2.1 equiv of K (18c6 = 1,4,7,10,13,16-hexaoxacyclooctadecane) in ethane-1,2-diamine (en) was treated with a stoichiometric amount of $[Rh(PPh_3)_3Cl]$ in THF, which resulted in the formation of $[(RhPPh_3)_6(\mu_3\text{-}Se)_8]\cdot 0.5en$ (**1**) upon slow removal of the solvent. In a corresponding reaction of a solution resulting from reaction of a binary Pb:Te phase (1:2) with 2.1 equiv of Li with $[Pd(PPh_3)_2Cl_2]$, we obtained the related compound $[Li_4(en)_{10}][Pd_6(\mu_3\text{-}Te)_8]$ (**2**). For synthesis and characterization details, see the Supporting Information (SI). Both product compounds, **1** and **2**, are based on octahedral $[M_6]$ aggregates. They represent the first octahedral clusters in Rh or Pd chemistry to be capped by chalcogen atoms, in the style of molecular CHEVREL-like complexes.

Compound **1** crystallizes in the triclinic space group $P\bar{1}$ with one formula unit of the C_i-symmetric cluster and one additional, heavily disordered solvent molecule of en in the unit cell. All deltahedral faces are μ_3-capped by Se atoms, and each of the Rh atoms is additionally coordinated by one PPh_3 ligand (Figure 1).

Different from the carbonyl complex $[Rh_6(CO)_{16}]$,[3] the electronic structure of compound **1** cannot be depicted by using

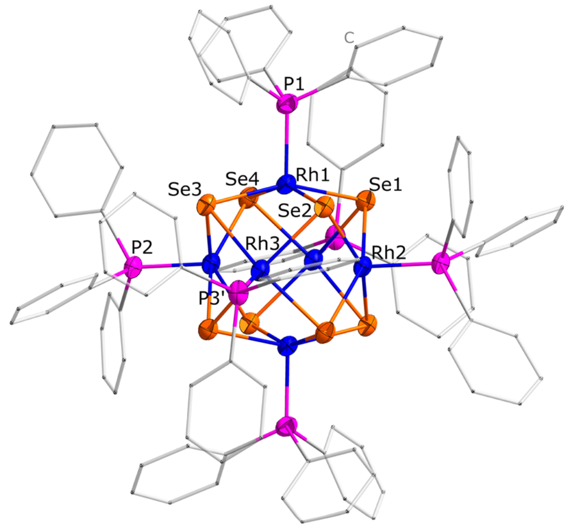

Figure 1. Molecular structure of the cluster in compound **1**. Ellipsoids are drawn at 50% probability, C atoms are drawn as wires, and H atoms and split positions of disordered Ph rings are omitted for clarity. Selected structural parameters [pm, deg]: Rh···Rh 310.69(6)−313.26(7), Se−Rh 243.63(7)−249.90(7), Rh−P 220.44(15)−221.18(16), Se···Se 339.64(9)−343.83(10); Rh···Rh···Rh(mer) 89.768(16)−90.230(16), R···Rh···Rh(fac) 59.639(14)−60.445(14), Se−Rh−Se(mer) 156.20(3)−157.24(2), Se−Rh−Se(fac) 87.01(2)−88.28(2), Se−Rh−P 90.17(4)−112.58(4), Rh−Se−Rh 77.45(2)−79.60(2).

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electron counting rules according to Wade and Mingos.[19] The $[Rh_6]$ cluster core is comprised of 98 valence electrons, with the μ_3-Se ligands counted as four electron donors and the phosphine ligands as two electron donors, much more than the number of 86 e$^-$ expected for an octahedral *closo* cluster. This is well reflected by the different Rh···Rh distances [310.69(6)−313.26(7) pm], which are much longer than those in $[Rh_6(CO)_{16}]$ (277.6 pm),[3] $[Rh_6(CO)_{10}(dpm)_3]$ [dpm = bis(diphenylphosphino)methane; 278.3 pm],[18] $[Rh_6H_{12}(P^iPr_3)_6]$ (271.8−305.9 pm),[8] or $[(Cp^*Rh)_3(\mu_3\text{-}Se)_2]$-$[PF_6]_2$ [288.0(1) and 288.79(8) pm][20a] but similar to the values observed in $[NMe_4][Rh_3(\mu_3\text{-}Se)_2(CO)_6]$ [308.6(1) and 315.9(1) pm].[20b] Still, there is a slight electron deficit (each of the Rh atoms possesses $16^{1}/_{3}$ e$^-$ without metal−metal bonding). Although an 18 e$^-$ situation for the Rh atoms is not urgently expected because the cluster is not an organometallic compound, we explored whether the Rh atoms would gain the missing $1^{2}/_{3}$ e$^-$ each from Rh···Rh interactions or not.

Quantum-chemical calculations applying density functional theory (DFT) methods,[21] with a subsequent population analysis of the DFT wave function based on occupation numbers (PABOON),[22] suggest a very weak interaction of the Rh atoms. A total shared electron number (SEN) of 1.7 e$^-$ was calculated for 12 two-center and 8 three-center Rh···Rh interactions [which can be summarized as eight Rh_3 interactions of 0.2 e$^-$]. Compared with a total of 11.1 e$^-$ for 24 Rh−μ_3-Se interactions [which can be summarized as eight Rh_3−μ_3-Se interactions of 1.4 e$^-$], the Rh···Rh interactions amount to about 14% of the strength of the Rh−Se covalent bonds that are mainly responsible for tethering of the atoms within the complex. Inspection of the molecular orbitals (MOs) and localized MOs (LMOs) confirms the absence of significant Rh···Rh bonding interactions (see Figures S5 and S6 in the SI) but indeed reveals an LMO that indicates some interaction of the Rh atoms (Figure 2, left) and is based on the highest-energy MOs.

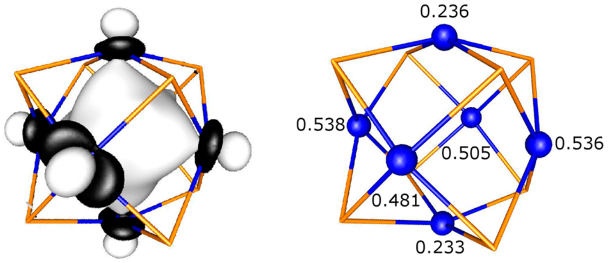

Figure 2. Left: Representation of the LMO representing (very) weak Rh···Rh interactions in **1**. Further LMOs and the valence MOs are given in the SI. Phenyl rings are omitted for clarity. Amplitudes are drawn at ±0.05 au. Right: Charges at the Rh atoms (blue) according to a Mulliken analysis of the DFT wave function calculated for the complex structure in **1** as determined by X-ray crystallography. Se atoms (orange wires) possess Mulliken charges of −0.493 to −0.587. PPh_3 fragments are omitted for clarity. Note that the charges do not reflect formal oxidations states but are a measure for them.

Formally, the Rh atoms exhibit different oxidation states, $Rh^{II}_2Rh^{III}_4$. Actually, it is not possible to clearly assign such charges based on the crystal structure because the Rh_6Se_8 core deviates only very slightly from octahedral symmetry [Rh_{ap}−Rh_{eq} 311.53(6)−313.26(7) pm, Rh_{eq}−Rh_{eq} 310.69(6)−312.83(5) pm, Rh_{ap}−Se 245.77(7)−247.98(6) pm, and Rh_{eq}−Se 243.63(7)−249.90(7) pm]. It is possible to discriminate the metal atoms by Mulliken population analysis[23] of the DFT wave function if the calculations are based on the crystal structure geometry (Figure 2, right). However, simultaneous optimization of the geometric and electronic structures leads to equalization of both the cluster core symmetry and the atomic charges. Thus, we conclude that (a) the slight deviations from octahedral symmetry may be due to packing effects and (b) the respective electrons are delocalized over all Rh atoms.

The mixed-valence character of **1** might be made responsible for failure of straightforward syntheses via the reaction of $[K(18c6)]_2Se$ with $[Rh(PPh_3)_3Cl]$; we assume that the Pb atoms in $[Pb_2Se_3]^{2-}$ most likely acted as oxidizing agents, such as observed in our earlier work on chalcogenidostannate salts, besides their role as chalcogen sources.[24] The uncommon reaction pathway also rationalizes the relatively low yield of **1**; however, the use of $[K(18c6)]_2Se$ along with alternative oxidants is not easily feasible because Se^{2-} is sensitive to oxidation itself, yielding polyselenides as highly favorable reaction products.

Compound **2** crystallizes in monoclinic space group $P2_1/n$, and the cluster possesses crystallographic C_i symmetry. The Pd···Pd distances within the $[Pd_6]$ aggregate (>320 pm) are even longer than the Rh···Rh distances in **1**. All faces are μ_3-capped by Te atoms (Figure 3). In contrast to the complex in **1**, no phosphine groups are attached to the Pd−Te core, which remains anionic. Instead, the complexes are embedded in an extended $\{[Li_4(en)_{10}]^{4+}\}_n$ network that forms sheets of double layers parallel to the $(10\bar{1})$ plane (Figure 4).

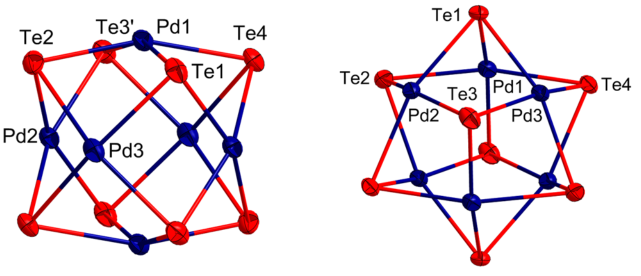

Figure 3. Molecular structure of the anion in compound **2**. Ellipsoids are drawn at 50% probability. Selected structural parameters [pm, deg]: Pd···Pd 320.64(16)−324.90(16), Pd−Te 260.43(13)−264.21(16). Te···Te 357.20(14)−408.05(13) pm; Pd···Pd···Pd(mer) 89.79(4)−90.21(4), Pd···Pd···Pd(fac) 59.34(3)−61.10(4), Te−Pd−Te(mer) 157.97(6)−161.37(6), Te−Pd−Te(fac) 86.05(5)−90.31(5), Pd−Te−Pd 74.84(4)−78.03(4).

In contrast to the situation in **1**, the $[Pd_6Te_8]^{4-}$ anion comprises formal Pd^{II} throughout, which is consistent with the corresponding Mulliken charges in the range of 0.170−0.172. The charges at the Te atoms are in the range of −0.703 to −0.546, thus indicating a slightly higher accumulation of electron density at the Te atoms in comparison with the situation at the Se atoms in **1** in agreement with the lower formal oxidation state on average. Considering only Pd−μ_3-Te bonds, the Pd atoms possess 16 e$^-$ each if the total charge of the anion is equally smeared over all atoms. Thus, the cluster can be viewed as an aggregate of six "$[Pd^{II}Te_4]^{6-}$" complexes that are linked by the sharing of μ_3-Te^{2-} ligands to reduce the overall charge. The absence of Pd···Pd interactions is clearly shown by negligible SEN values (<0.1 for both two-center and three-center bonds) and the analyses of canonical as well as LMOs and LMOs that show no notable Pd···Pd bonding interactions (Figures S7 and S8 in the SI).

In conclusion, two transition-metal chalcogenide complexes with CHEVREL-like topologies were obtained by the reaction of

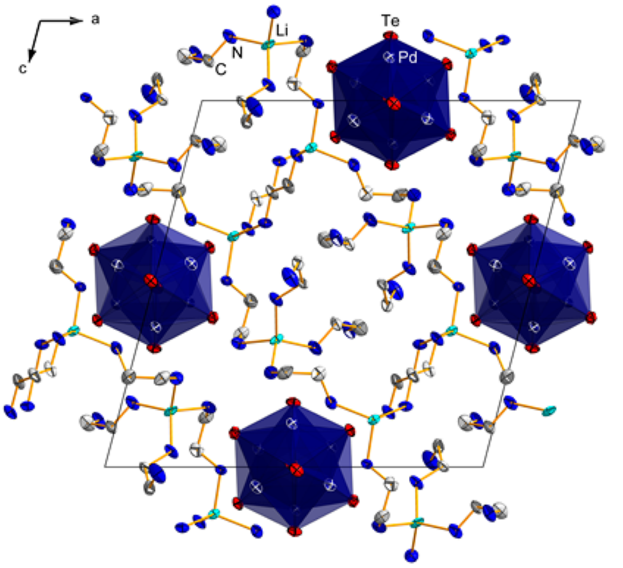

Figure 4. View of the $[Li_4(en)_{10}]^{4+}$ network in **2** that embeds the CHEVREL-like $[Pd_6Te_8]^{4-}$ clusters, viewed along the crystallographic *b* axis. The anions are highlighted by a polyhedral representation. Ellipsoids are drawn at 50% probability, and H atoms are omitted for clarity. Selected structural parameters [pm]: Li···N 203(3)−214(3), Te···N 268.24(14), Pd···N 370.26(14)−391.37(14).

$[Pb_2Ch_3]^{2-}$ anions with $[Rh(PPh_3)_3Cl]$ (Ch = Se) or $[Pd(PPh_3)_2Cl_2]$ (Ch = Te). In both cases, the $[Pb_2Ch_2]^{2-}$ anion acted as a chalcogen source; in the first case, it was also active as an oxidant to produce a mixed-valence Rh^{II}/Rh^{III} complex, as confirmed by quantum chemistry. The second compound can be viewed as six μ_3-Te-sharing, square-planar "$[Pd^{II}Te_4]^{6-}$" complexes that aggregate to reduce the overall charge. While both compounds differ in the fact that the Rh−Se cluster possesses a PPh_3 ligand shell and the Pd−Te cluster is a binary anion, both compounds comprise the first molecular $[M_6Ch_8]$ aggregates with the respective elemental combinations.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format, crystal structure refinement details, energy-dispersive X-ray analysis results, cyclovoltammetric measurement results, and experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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