Isolation of the Hexathioorthooxalate $[C_2S_6]^{6-}$ Ligand in the Complexes α- and β-$[Pd_6(C_2S_6)(S_3)_6]^{6-}$ and $[Pd_6(C_2S_6)(S_3)_4(S_4)_2]^{6-}$

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Recently, the revival of the hydrothermal, or more generally, solvothermal, technique has led to some remarkable new compounds normally inaccessible by other techniques.[1] In the field of chalcogenides the solvothermal approach is now playing a major role. Particularly noteworthy are the new solid state compounds $Cs_4Sn_5S_{12}{\cdot}2H_2O$,[2] $RbSb_3Se_5$,[2] $K_2Ag_{12}Se_7$,[3] K_2PdSe_{10},[4] $[N(C_3H_7)_4]Sb_3S_5$,[5] $(N_2C_4H_8)Sb_4S_7$,[5] $Cs_6Sb_{10}S_{18}{\cdot}1.2H_2O$,[6] and $(Me_4N)_2RbBiAs_6S_{12}$,[7] in addition to the discrete molecular examples of $(Me_4N)_2MoSe_{13}$,[8] $K_{12}Mo_{12}Se_{56}$,[9] and $K_8Mo_9Se_{40}{\cdot}4H_2O$.[10] $K_2[PdSe_{10}]$ is distinguished among these examples by virtue of its two different and uniquely interpenetrating $[Pd(Se_x)_2]^{2-}$ ($x = 4$, 6) three-dimensional frameworks. This compound stimulated our interest in the corresponding Pd/Se_x^{2-} chemistry. Although the considerable effort expended to prepare $K_2[PdS_{10}]$ has yet to be successful, we did come across an unexpected but most certainly exciting discovery. The analogous methanothermal approach leads to several soluble compounds containing novel discrete clusters where the unprecedented hexathioorthooxalate ligand, $[C_2S_6]^{6-}$, plays a central stabilizing role.

$Na_3\{(CH_3)N(CH_2CH_2)_3N\}_3[Pd_6(C_2S_6)(S_3)_6]{\cdot}3CH_3OH$ (**I**) formed from the methanothermal reaction of Na_2PdCl_4, Na_2S_4, and $\{(CH_3)N(CH_2CH_2)_3N(CH_3)\}I_2$ in a 1:3:1 molar ratio at 110 °C, while $Na_2\{(CH_3)N(CH_2CH_2)_3N\}_4[Pd_6(C_2S_6)(S_3)_4(S_4)_2]{\cdot}CH_3OH$ (**III**) formed from a similar reaction at 80 °C but using $PdCl_2$ instead of Na_2PdCl_4. The reddish black hexagonal rod crystals (30% yield) of **I** are soluble in water and ethylenediamine, whereas the reddish black rectangular rod crystals (30% yield) of **III** are sparingly soluble in water and most organic solvents, except ethylenediamine. Compound **I** is considered to be thermodynamically more stable than **III** because it is the major product if the reaction is carried out at 110 °C. $K_4\{(CH_3)_3N(CH_2CH_2)N(CH_3)_2\}_2[Pd_6(C_2S_6)(S_3)_6]{\cdot}2CH_3OH$ (**II**) was prepared from the methanothermal reaction of K_2PdCl_4, K_2S_4, and $\{(CH_3)_3N(CH_2CH_2)N(CH_3)_3\}I_2$ in a 1:3:1 molar ratio at 80 °C. The reddish black hexagonal rod crystals (35% yield) of **II** are soluble in water. The structures of these compounds were established with single-crystal X-ray diffraction studies.[11]

Figure 1 shows two views of a α-$[Pd_6(C_2S_6)(S_3)_6]^{6-}$ cluster found in **I**. There are two crystallographically independent α-$[Pd_6(C_2S_6)(S_3)_6]^{6-}$ clusters in the unit cell of **I**. α-$[Pd_6(C_2S_6)(S_3)_6]^{6-}$ is a large hexanuclear cluster composed of a $[C_2S_6]^{6-}$ ligand and six S_3^{2-} ligands connecting six Pd^{2+} metal clusters. The remarkable $[C_2S_6]^{6-}$ ligand has an ethane-like geometry in a staggered conformation. Each S atom of the $[C_2S_6]^{6-}$ ligand coordinates to two different square-planar Pd metal atoms. The $[C_2S_6]^{6-}$ ligand is situated on a crystallographic 3-fold axis passing through the C−C bond and has a center of symmetry at the midpoint of the C−C bond. Being crystallographically equivalent, all six Pd metal atoms in the cluster lie in the same plane. The idealized point group symmetry of α-$[Pd_6(C_2S_6)(S_3)_6]^{6-}$ is D_{3d}.

The β-$[Pd_6(C_2S_6)(S_3)_6]^{6-}$ in **II**, shown in Figure 2, is also a large hexanuclear cluster with a $[C_2S_6]^{6-}$ ligand in its center. The metal-binding mode of the $[C_2S_6]^{6-}$ ligand is quite different in this case from that found in the isomer α-$[Pd_6(C_2S_6)(S_3)_6]^{6-}$. In the β form, the $[C_2S_6]^{6-}$ anion brings together two identical $\{Pd_3S_3(S_3)_3\}$ trinuclear fragments. The $[Pd_6(C_2S_6)(S_3)_4(S_4)_2]^{6-}$ cluster found in **III** is isostructural to β-$[Pd_6(C_2S_6)(S_3)_6]^{6-}$ except that two S_4^{2-} ligands replace two S_3^{2-} ligands.

Both starting cations $\{(CH_3)N(CH_2CH_2)_3N(CH_3)\}^{2+}$ and $\{(CH_3)_3N(CH_2CH_2)N(CH_3)_3\}^{2+}$ lost a methyl group and became singly charged during the reaction. The $[C_2S_6]^{6-}$ ligand is believed to have originated either from such liberated methyl groups or from CH_2CH_2 groups.[12] When monocations, instead of dications, were used in the above reactions, we could not isolate these Pd complexes. Although the mechanism is not known, it is suspected that Pd metal is responsible for the formation of this ligand and the process somehow involves a Pd-mediated CH-dehydrogenation pathway.[13] The addition of CS_2 or CS_3^{2-} reagents in the reaction did not help to improve the yields of the products; instead, it hindered their formation in most cases.[14]

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(11) (a) Crystal data for $Na_3\{(CH_3)N(CH_2CH_2)_3N\}_3[Pd_6(C_2S_6)(S_3)_6]{\cdot}3CH_3OH$ (**I**): trigonal $R\bar{3}$ (No. 148), $Z = 6$, $a = b = 22.320(3)$ Å, $c = 20.701(7)$ Å, and $V = 8935(4)$ Å^3 at 23 °C. $2\theta_{max} = 50°$. Number of unique data with $F_o^2 > 3\sigma(F_o^2)$: 1938. Number of variables: 203. $\mu = 26.2$ cm^{-1}. $d_{calc} = 2.206$ g/cm^3. Final $R/R_w = 0.047/0.055$. GOF = 1.77. There are two independent α-$[Pd_6(C_2S_6)(S_3)_6]^{6-}$ molecules in the unit cell. Semiquantitative analysis of the crystal using the SEM/EDS technique showed the Pd:S atomic ratio as 1.0:3.9. (b) Crystal data for $K_4\{(CH_3)_3NCH_2CH_2N(CH_3)_2\}_2[Pd_6(C_2S_6)(S_3)_6]{\cdot}2CH_3OH$ (**II**): triclinic $P\bar{1}$ (No. 2), $Z = 1$, $a = 12.542(3)$ Å, $b = 13.166(3)$ Å, $c = 10.341(3)$ Å, $\alpha = 112.88(2)°$, $\beta = 112.41(2)°$, $\gamma = 86.32(2)°$, and $V = 1447(2)$ Å^3 at 23 °C. $2\theta_{max} = 50°$. Number of unique data with $F_o^2 > 3\sigma(F_o^2)$: 3195. Number of variables: 217. $\mu = 29.5$ cm^{-1}. $d_{calc} = 2.197$ g/cm^3. Final $R/R_w = 0.074/0.088$. GOF = 2.88. Semiquantitative analysis of the crystal using the SEM/EDS technique showed the K:Pd:S atomic ratio as 0.60:1.0:4.2. (c) Crystal data for $Na_2\{(CH_3)N(CH_2CH_2)_3N\}_4[Pd_6(C_2S_6)(S_3)_4(S_4)_2]{\cdot}CH_3OH$ (**III**): triclinic $P\bar{1}$ (No. 2), $Z = 1$, $a = 12.967(6)$ Å, $b = 13.414(3)$ Å, $c = 11.262(3)$ Å, $\alpha = 110.41(2)°$, $\beta = 95.65(3)°$, $\gamma = 113.17(2)°$, and $V = 1623(2)$ Å^3 at −100 °C. $2\theta_{max} = 45°$. Number of unique data with $F_o^2 > 3\sigma(F_o^2)$: 2486. Number of variables: 255. $\mu = 24.6$ cm^{-1}. $d_{calc} = 2.130$ g/cm^3. Final $R/R_w = 0.051/0.062$. GOF = 1.78. Semiquantitative analysis of the crystal using the SEM/EDS technique showed the Pd:S atomic ratio as 1.0:4.1. Single-crystal X-ray data for all three compounds were collected on a Rigaku AFC6S diffractometer using Mo radiation. The structures were solved with SHELXS-86 and refined with the TEXSAN package[11d] of crystallographic programs. An empirical absorption correction (based on ψ scans) was applied to the data, followed by a DIFABS[11e] correction to the isotropically refined structure. All equivalent reflections were averaged after absorption correction. The homogeneity of all products was confirmed by comparison of observed X-ray powder diffraction patterns to those calculated from the single-crystal data. (d) TEXSAN: Single Crystal Structure Analysis Software, Version 5.0, Molecular Structure Corporation, The Woodlands, Texas. (e) DIFABS: Walker, N.; Stuart, D. An Empirical Method for Correcting Diffractometer Data for Absorption Effects. *Acta Crystallogr.* **1983**, *A39*, 158−166.

(12) The loss of methyl groups from the original dications may mislead one to believe that they are the source of carbon. However, the participation of ethylene groups cannot be ruled out since cannibalization of the entire dication can also take place. Use of $[CH_3CH_2N(CH_2CH_2)_3NCH_2CH_3]^{2+}$ gave the β-$[Pd_6(C_2S_6)(S_3)_6]^{6-}$ and the ethylpiperidinium $[CH_3CH_2NH(CH_2CH_2)_2NH]^+$ as the counterion. This suggest that ethyl groups can be carbon sources but does prove that they are the only sources. ^{13}C isotopic labeling experiments will be useful in sorting out the origin of carbon for the $[C_2S_6]^{6-}$ anion. Kim, K.-W.; Kanatzidis, M. G. Work in progress.

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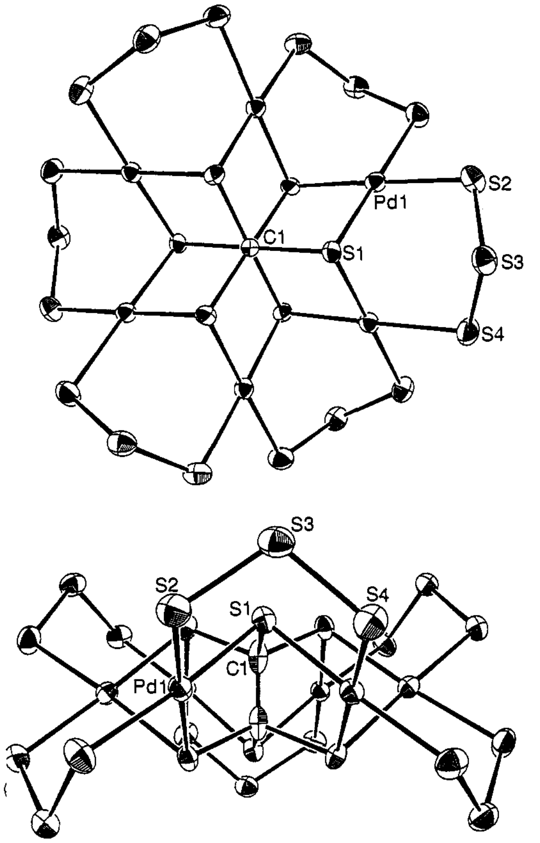

Figure 1. ORTEP representation and labeling scheme of α-$[Pd_6(C_2S_6)(S_3)_6]^{6-}$ in two views. Selected bond distances (Å) and angles (deg): Pd1−S1, 2.337(3); Pd1−S1′, 2.343(4); Pd1−S2, 2.327(4); Pd1−S4, 2.332(3); S2−S3, 2.071(6); S3−S4, 2.058(6); S1−Pd1−S1′, 86.8(2); S1−Pd1−S2, 94.6(1); S1−Pd1−S4, 175.7(1); S1−Pd1−S2′, 176.7(1); S1−Pd1−S4′, 95.9(1); S2−Pd1−S4, 82.8(1); Pd1−S1−Pd1′, 87.3(1); Pd1−S2−S3, 108.0(2); S2−S3−S4, 107.7(2); Pd1−S4−S3, 107.7(2); S1−C1−S1′, 108.7(7); S1−C1−C1′ 110.2(7).

The very high charge on the relatively small $[C_2S_6]^{6-}$ molecule (which lacks even an oxygen analog) may make it hard to stabilize as a simple salt, except possibly by alkylation of the terminal sulfides or coordination to divalent (or higher valent) metal ions as is the case in **I**, **II**, and **III**. The $C_2(SPh)_6$ is the closest relative of $[C_2S_6]^{6-}$ in the literature.[15] Among possible $[C_2S_x]^{y-}$ ligands with a C−C bond, only the tetrathiooxalate $[C_2S_4]^{2-}$ and the ethene-like $[C_2S_4]^{4-}$ ligands are known.[16,17] These species have been prepared by reductive head-to-head coupling of CS_2 either electrochemically or by transition-metal-activated C−C bond formation. The C−C bond formation has been proposed to occur through a free radical type mechanism.[18]

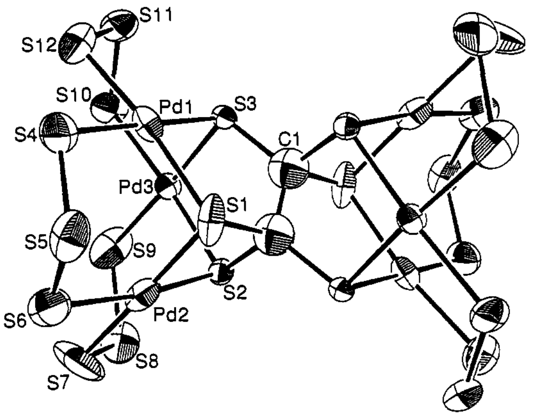

Figure 2. ORTEP representation and labeling scheme of β-$[Pd_6(C_2S_6)(S_3)_6]^{6-}$ found in **III**. Selected bond distances (Å) and angles (deg): Pd1−S1, 2.329(5); Pd1−S3, 2.316(5); Pd1−S4, 2.330(5); Pd1−S12, 2.338(6); Pd2−S1, 2.309(6); Pd2−S2, 2.326(4); Pd2−S6, 2.334(5); Pd2−S7, 2.375(8); Pd3−S2, 2.341(4); Pd3−S3, 2.330(4); Pd3−S9, 2.337(6); Pd3−S10, 2.343(5); S4−S5, 2.063(8); S5−S6, 2.043(9); S7−S8, 2.10(1); S8−S9, 2.20(1); S10−S11, 2.077(8); S11−S12, 2.080(8); S1−C1−S2, 103(1); S1−C1−S3 109(1); S2−C1−S3, 112(1); S1−C1−C1′, 96(2); S2−C1−C1′, 116(2); S3−C1−C1′, 117(2).

Several new questions are raised from this work. For example, is Pd vitally important (i.e., catalytic role) in the formation of $[C_2S_6]^{6-}$, or can this anion be formed without Pd or with different metal ions? What is the formation mechanism? Equally interesting is then whether the $[C_2S_6]^{6-}$ can be isolated as a simple ionic salt. Such ionic salts would be highly desirable as starting materials for solution chemistry with $[C_2S_6]^{6-}$. Although the $[C_2S_6]^{6-}$ anion is isostructural and isoelectronic to $[P_2S_6]^{2-}$,[19] a closer analog in terms of charge may be found in the pyrosilicate $[Si_2O_7]^{6-}$ anion, which has a linear Si−O−Si bond and similar geometry and size.[20] In conclusion, the discovery of $[C_2S_6]^{6-}$ in **I**, **II**, and **III** raises hopes for the development of fundamentally new metal−thiocarbonate chemistry.

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Supplementary Material Available: Tables of atomic coordinates and anisotropic thermal parameters of all atoms, bond distances and angles, and calculated and observed powder patterns for **I**, **II**, and **III** (17 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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