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$[PdS_2C_2(COOMe)_2]_6^n$ ($n = 0, -1, -2, -3, -4$): Hexanuclear Homoleptic Palladium Dithiolene Complexes

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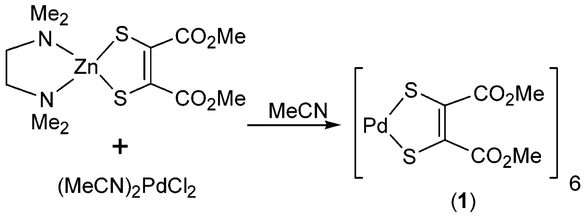
Metal-dithiolene chemistry is based on a well-developed foundation of synthesis and characterization of core molecular structures.[1] Interest in dithiolene complexes has continued in the 21st century including such areas as selective olefin coordination/separation,[2] conductive and magnetic properties,[3] optical and sensor applications,[4] and enzymatic function.[5] This diversity has encouraged investigation of new and more varied metal-dithiolene structures in the hope of finding as yet unrealized properties and applications.

Coordinatively saturated, homoleptic dithiolene-metal complexes are common structural types and are readily synthesized.[1] Metal complexes containing a mix of dithiolene and nondithiolene ligands are also well known.[5,6] However, potentially coordinatively unsaturated dithiolene-metal complexes are rare,[1,7] and 1:1 dithiolene-transition-metal complexes *with no other ligands* are, to our knowledge, unprecedented.[8] What follows is our initial findings in the syntheses of new dithiolene-palladium complexes emphasizing the synthesis, structure, and electrochemical characterization of a well-behaved hexanuclear dithiolene-palladium complex family.

The neutral complex, $[PdS_2C_2(COOMe)_2]_6$ (**1**), is homoleptic containing one dithiolene unit for each palladium atom and no other ligands. This product arises from the reaction of $(tmeda)ZnS_2C_2(COOMe)_2$[6b,9] and $(MeCN)_2PdCl_2$, which results in the transfer of a single dithiolene unit per palladium center.[10]



A single crystal of **1** grown from a toluene solution[11] was examined by X-ray diffraction analysis.[12] Figure 1A reveals that the highly symmetric, cube-octahedron core contains six palladium and 12 sulfur atoms. Four sulfur atoms provide square planar coordination for each palladium atom. The molecule possesses inversion symmetry. If an imaginary, approximate cube is superimposed on the structure, the palladium atoms are each located at the center of a cube face. Each sulfur atom occupies the midpoint of a cube edge. The sulfur positions centered around the octahedral metal core are similar to general M_6X_{12} structure types.[13,14] Figure 1B shows a second view of **1** along the axis perpendicular to the plane formed by the three corner sulfur atoms S11′, S21, and S31′. This perspective reveals that a single, noncrystallographic, six-fold inversion axis (S_6) is preserved in the structure despite the presence of the dithiolene-ester units.[15] This structure illustrates the bonding flexibility inherent in dithiolene coordination whereby each sulfur atom contained within a chelating dithiolene unit bridges to another palladium center.

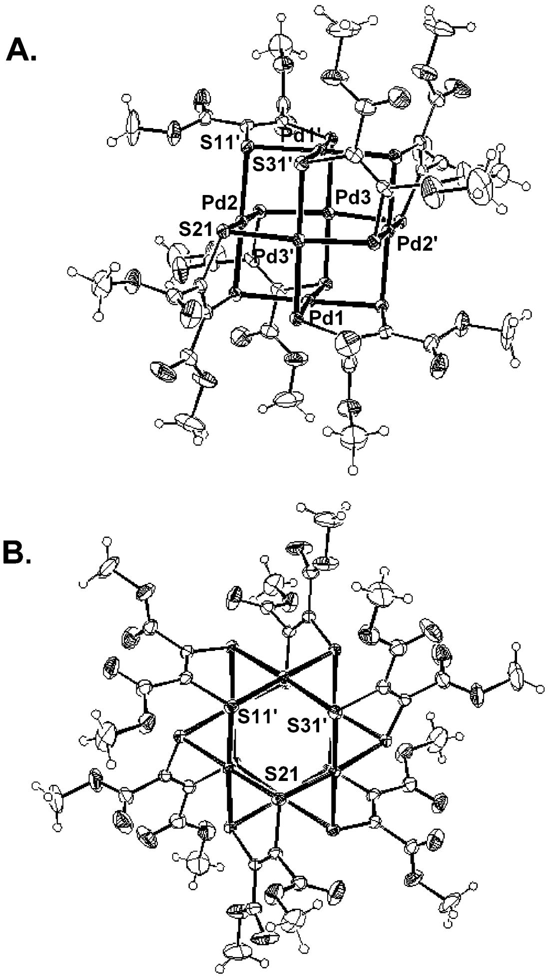


Figure 1. Molecular structure of **1** $\{[PdS_2C_2(COOMe)_2]_6\}$. Thermal ellipsoid drawings are shown at the 40% probability level, and the $MeOOC_4$-OOMe portion of the dithiolene ligands is lightly shaded to emphasize the core geometry. Toluene solvent molecules, also present in the lattice, have been excluded for clarity. (A) View indicating the distorted cube shape of the core. (B) View along the "imaginary cube diagonal" (defined by the midpoint of sulfur atoms S11′, S21, and S31′ and the point related by inversion symmetry) showing the noncrystallographic, S_6 molecular symmetry. Selected bond lengths: Pd−Pd (adjacent) = 3.232−3.434; Pd−Pd (opposite) = 4.678−4.719; Pd−S (intra) = 2.2911(7)−2.3041(7); Pd−S(inter) = 2.3582(7)−2.3882(7); S−C = 1.764(3)−1.776(3); and C=C = 1.333(4)−1.339(4) Å.

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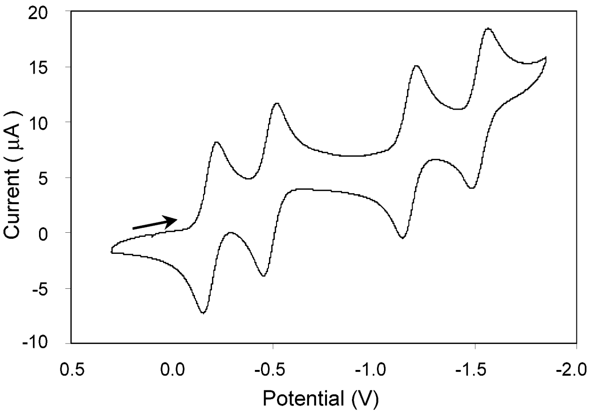

Figure 2. Cyclic voltammogram of **1** in dichloromethane containing 0.1 M n-Bu_4NPF_6 at a scan rate of 30 mV/s.

Table 1. Half-Wave Redox Potentials of **1** versus a Saturated Calomel Reference Electrode

redox couple	potential (mV)
0/−1	−186
−1/−2	−484
−2/−3	−1174
−3/−4	−1524
ferrocenium$^+$/ferrocene	+409

Despite the equivalence of the dithiolene ligand units by symmetry, two distinct ^{1}H NMR singlet signals ($\delta = 3.89$ and 3.83 ppm) and six ^{13}C NMR signals are observed in solution consistent with an asymmetry *within* each dithiolene unit. Examination of Figure 1B shows that each dithiolene ligand contains two diastereotopic ester groups: one located near an opening (top or bottom), and one in a quasi equatorial position near the plane that bisects the molecule perpendicular to the S_6 axis.[15]

Electrochemical reduction of **1** proceeds in four reversible steps. A cyclic voltammogram is shown in Figure 2, and half-wave potentials are listed in Table 1. Neither multiple potential scans nor varied sweep rates (3−2000 mV/s) indicate complex instability or the presence of significant chemical reorganization barriers.

The reduction potentials of the first two waves of **1** (−186 and −484 mV) suggested that these species could be generated in a chemically isolable form. Borohydride reduction of **1** results in the dianion $[Bu_4N]_2[(PdS_2C_2(COOMe)_2)_6]$ (**2**).[16] The compound is stable in air and is structurally similar to **1**.[16]

In addition to a unique structure and esthetically pleasing electrochemistry, **1** acts as a versatile starting material for the synthesis of Pd-based complexes containing dithiolene and non-dithiolene ligands. The details of such synthetic uses and additional chemical and electrochemical characterization will be described in a full paper.

In summary, preparation of a palladium-dithiolene complex in a 1:1 stoichiometric ratio results in a unique and stable molecular complex with remarkable electrochemical properties. This discovery comes at a time when new syntheses and enhanced properties of metal-dithiolene compounds are being discovered at a furious pace.

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Supporting Information Available: Tables of crystal data for **1** as an X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) tmeda = *N,N,N,N*-tetramethylethylenediamine.

(10) $(tmeda)ZnS_2C_2(COOMe)_2$ (800 mg, 2.1 mmol), $(MeCN)_2PdCl_2$ (540 mg, 2.1 mmol), and approximately 70 mL of acetonitrile were added to a flask. While being stirred, the mixture was gently refluxed for 1 day. After being cooled, the solution was filtered and the solid washed with acetonitrile and then diethyl ether. After residual solvent was removed under vacuum, 340 mg (0.18 mmol) of orange-brown solid was collected. Yield, 52%. Anal. Calcd: C, 23.05; H, 1.95; S, 20.45. Found: C, 22.8; H, 2.0; S, 20.3. ^{1}H NMR ($CDCl_3$): $\delta = 3.89$ (s, 3H, Me); 3.83 (s, 3H, Me). ^{13}C NMR (−20 °C): $\delta = 162.85$; 161.16; 144.69; 137.33; 53.95; 53.92. Mass spectrum (FD), m/z(%): 1872(100) ([M]$^+$).

(11) Complex **1** has limited solubility in toluene.

(12) Crystal data: triclinic; P-1; orange color; $a = 12.4637(6)$, $b = 12.6975(6)$, $c = 14.6816(7)$ Å; $\alpha = 105.8390(10)$, $\beta = 109.0640(10)$, $\gamma = 106.8990(10)°$; data collection temperature = 233(2) K; $Z = 19.50(16)$ Å^3; $R = 0.0257$; $wR^2 = 0.0593$; GOF on $F^2 = 1.030$.

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(15) It is possible to think of the structure as toroidal or "donut" shaped. The hole is defined by the Pd_6S_{12} core, and the outer ring contains the conjugated ester moieties.

(16) Synthetic procedure for **2**: Complex **1** (27 mg, 0.01_4 mmol) was dissolved in CH_2Cl_2 (~1 mL). A large excess of Bu_4NBH_4 (135 mg, 0.5 mmol) in EtOH (~3 mL) was added, and the combined mixture was stirred for 24 h. The solution was then filtered, and the solid was washed with EtOH and then Et_2O. Residual volatiles were removed under vacuum. Obtained 30 mg (0.01_3 mmol) of black powder. Yield, 88%. Anal. Calcd: C, 34.59; H, 4.62; N, 1.19. Found: C, 34.49; H, 4.54; N, 1.15 and C, 34.49; H, 4.51; N, 1.18. ^{1}H NMR (CD_3CN): $\delta = 3.86$ (s, 9H, Me); 3.75 (s, 9H, Me); 3.08 (m, 8H, CH_2); 1.61 (m, 8H, CH_2); 1.36 (m, 8H, CH_2); 0.96 (t, 12H, $J^2 = 7.36$ Hz, Me). ^{13}C NMR (25 °C, does not include quaternary carbons): $\delta = 59.96$; 31.19; 24.96; 20.96; 14.42. Mass spectrum (FD), m/z(%): 2360(10) ([M]$^+$), 1872(100).

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