

Crystal Structures of the Odd and Even Electron One-Dimensional Metal–Metal Bonded Chain Compounds

Mixed valency (MV) is at the heart of many interesting properties, electrical, magnetic and optical or a combination thereof, and is in many cases the source of a wide range of instabilities. The presence of MV has been the driving force in the development of highly conducting and superconducting materials, molecular magnetism and also of highly colored complexes [1]. MV was first realized in inorganic compounds and in particular, one-dimensional (1D) chain compounds of platinum. However, most 1D mixed-valent metal complexes are semiconducting except for $K_2[Pt(CN)_4]Br_{0.3} \cdot 3H_2O$ (KCP(Br)) and $K_{1.62}[Pt(C_2O_4)_2] \cdot 2H_2O$ (α -K-OP), which show metallic conduction in a limited range of temperature [2].

Our approach to construct highly conducting metal–metal bonded solids is to start with a platinum dimer having sulfur ligands, such as $[Pt^{II}_2(RCS_2)_4]$ (RCS_2^- = a dithiocarboxylato), and to partially oxidize it. Here, we used ClO_4^- as a counterion in the electrocrystallization and organic solvents. In choosing the divalent Pt–Pt dimer, we expect a decrease in the Coulomb repulsion U by sharing an unpaired electron through a Pt–Pt bond, and the presence of the delocalized sulfur orbitals should favor an increase in the charge-transfer energy t . Following the above strategy, we have succeeded in obtaining high-quality crystals of the partially oxidized 1D Pt–Pt

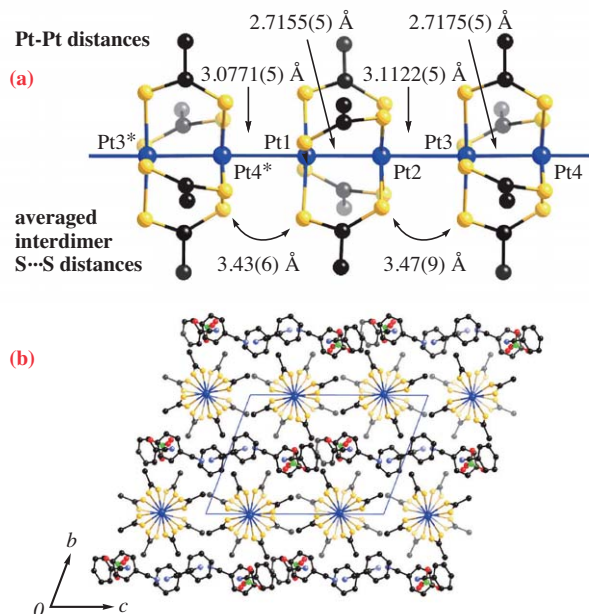


Fig. 1. (a) Repeat unit of the 1D chain $\{[Pt_2(MeCS_2)_4]_4\}_n^{n+}$ in **1** at 204 K and (b) view of the unit cell along the chain axis (a axis).

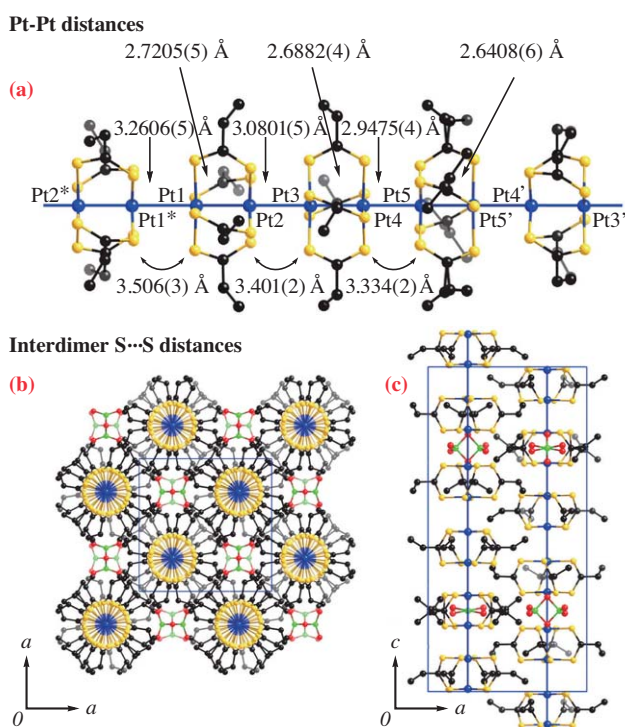


Fig. 2. (a) Repeat unit of the 1D chain $\{[Pt_2(EtCS_2)_4]_5\}_n^{2n+}$ in **2** at 298 K and a view of the packing projected down the (b) c and (c) a axes.

chain compounds, $[Pt_2(MeCS_2)_4]_4ClO_4 \cdot 5PhCN$ (**1**) and $[Pt_2(EtCS_2)_4]_5(ClO_4)_2$ (**2**) from the corresponding dimers.

Crystal structures were determined from data collected on single crystals of **1** and **2** using synchrotron radiation of beamline BL02B1 [3]. The structure of **1** (triclinic, $P\bar{1}$) consists of alternating cationic and solvated anionic layers; the former is built of stacks of Pt–Pt dimers forming chains adjacent of one another, while the latter contains ClO_4^- solvated by benzonitrile molecules (Fig. 1). One period of the linear chain has two diplatinum units, and the Pt–Pt dimers are almost equidistant from one another forming the spine with notably short interdimer S...S distances. The intradimer Pt–Pt distances are intermediate between those of $Pt^{2+}-Pt^{2+}$ and $Pt^{2+}-Pt^{3+}$. The molar ratio of $Pt_2(MeCS_2)_4$ cation to ClO_4^- is 4:1, in agreement with the results of elemental analyses. Therefore, the average formal oxidation state of the platinum atom of **1** is +2.125.

The structure of **2** (tetragonal, $P4/nnc$) is shown in Fig. 2, consisting of 1D Pt–Pt chains segregated by the ClO_4^- . The diplatinum units are stacked with a twist of the $EtCS_2^-$ ligands forming the Pt–Pt chain with a helical arrangement of the ligands. In the Pt–Pt

chain, five diplatinum units form a pentamer, and both the intra- and interdimer Pt–Pt distances are shorter at the center of the pentamer (a midpoint of Pt5–Pt5' bond). The Pt1–Pt2 distance is intermediate between those of Pt²⁺–Pt²⁺ and Pt²⁺–Pt³⁺, the Pt3–Pt4 is close to that of Pt²⁺–Pt³⁺, and the Pt5–Pt5' is intermediate between those of Pt²⁺–Pt³⁺ and Pt³⁺–Pt³⁺. The ClO₄[−] ions are incorporated simultaneously into the spaces formed partially by four 1D chains. Consequently, the interdimer Pt···Pt distance adjacent to the ClO₄[−] is lengthened by the steric hindrance. Therefore, it is considered that the periodicity of the helical arrangement of the ligands is strongly correlated with the number of ClO₄[−] ions. Since the molar ratio of Pt₂(EtCS₂)₄ to ClO₄[−] has been confirmed to be 5:2 by elemental analyses, the average oxidation number of the platinum atoms of **2** is +2.2.

1 exhibits high electrical conductivity (4.2–8.0 S cm^{−1}) at room temperature along the 1D chain and metallic behavior surviving down to 125 K in contrast to 250 K for KCP(Br). To our knowledge, it is the most stable ambient pressure metallic 1D mixed-valent metal complex known. The electrical conductivity of **2**

is 0.33–1.2 S cm^{−1} at room temperature and shows typical semiconducting behavior. The observed semiconducting behavior of **2** can be ascribed to the electronic localization due to the formation of pentamers within the chains.

The magnetic susceptibility χ_M of **1** is almost temperature independent (*ca.* 1.1 × 10^{−4} emu · mol^{−1}), which is attributed to Pauli paramagnetism, and gradually decreases with decreasing temperature to an almost spin-singlet state. On the other hand, **2** appears to be non-magnetic except for a very small Curie-like paramagnetic behavior originating from impurities and/or lattice and end-of-chain defects.

From electronic considerations as shown in Fig. 3, the one unpaired electron (odd electron) for every four dimers in **1**, i.e., twice the length of the *a* axis, is unlikely to pair, and consequently, the charge and spin degrees of freedom survive resulting in metallic conduction. On the other hand, **2** has lost the spin degree of freedom owing to the pentamer formation with electron pair formation since two unpaired electrons (even electrons) are present per unit cell, and the charge density wave (CDW) state has appeared.

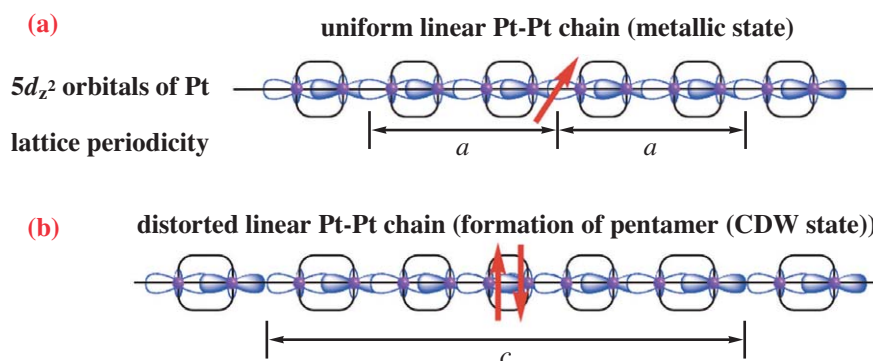


Fig. 3. Schematic representation of the spin states and lattice periodicities of the linear Pt–Pt chains for (a) **1** and (b) **2**.

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