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Electrical Conductivity in Platinum-Dimer Columns

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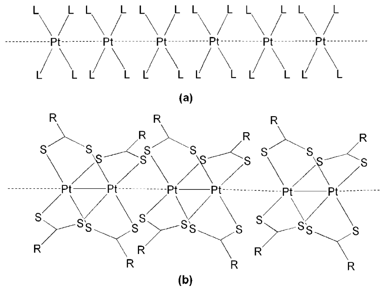
Three new compounds of formula $[Pt_2(SSCR)_4]$ (R = CH_3, $(CH_2)_4CH_3$, cyclohexyl) have been prepared and characterized by X-ray diffraction. Their crystal structures consist of one-dimensional linear chains formed by stacking of the dimetallic complexes in which the alkyl group on the dithioacetate modulates the intermetallic distances between dimetallic entities. Direct current electrical conductivity studies show that crystals of the three compounds behave as semiconductors and their conductivity values are directly connected to the intermolecular metal-to-metal distances. These experimental results are supported by density functional theory calculations.

For decades, one-dimensional materials have been widely studied because of their unusual physical properties.[1] Recently, research into this area has attracted attention because of their perspectives toward applications in nanotechnology.[2] Columnar inorganic systems formed by one-dimensional chains of coordination complexes with metal cations aligned have been reported for a long time.[3,4] Emphasis has been given to those presenting short metal-to-metal distances because of their applications as materials with electrical and magnetic properties.[5] The columnar structures are formed typically by square-planar monomer complexes. The highly conducting one-dimensional transition-metal complexes are generally based on third-row transition-metal elements stacked with collinear metal atoms. Their electrical properties arise from electron delocalization in the band formed by the overlapping of the $5d_{z^2}$ orbitals and are mainly affected by the metal-to-metal distances.

Scheme 1. Representation of the KCP Chains (a) and Chains Formed by Stacking of Dimetallic $[Pt_2(S_2CR)_4]$ Units (b)



Particularly, in the transition-metal complexes, tetracyanoplatinates, $K_2Pt(CN)_4X_{0.3}\cdot nH_2O$ (X = Cl, Br), commonly called KCP (Scheme 1a), the columnar compounds are formed by the stacking of square-planar $[Pt(CN)_4]^{2-}$ anion complexes.[6] These structures allow the overlapping of $5d_{z^2}$ orbitals, which is strongly affected by the Pt−Pt intermolecular distances. The anisotropic conductive properties of the KCPs are connected to their intrachain metal−metal distances. It has been reported that for KCPs the maximum distance showing $5d_{z^2}$ overlapping is 3.3 Å.[7] The electrical conductivity for $K_2[Pt(CN)_4]$ (5×10^{-7} $S\cdot cm^{-1}$) is substantially increased upon partial oxidation of KCPs. This is related to a shortening of the Pt−Pt distances, which become close to that found in the Pt metal (2.78 Å). KCP-based materials represent the first inorganically designed "molecular wires".

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On the other hand, discrete dinuclear complexes with metal−metal bonds (or interactions) show fascinating electronic properties.[8] Some of them have been shown to be suitable as precursors for one-dimensional metal chains. Recently, a comparative study on the electrical properties of a new metal-dimer-assembled system has been reported.[7] The one-dimensional metal-dimer structures are formed by stacking of the dimetallic units $M_2(dtp)_4$ (M = Ni, Pd, and Pt; dpt = dithiopropionate; Scheme 1b). They clearly show that platinum linear chains are the best electrical conductors with values of conductivity several orders of magnitude over the analogous complexes of palladium(II) and nickel(II) stacked systems because of the most efficient d_{z^2} overlapping. In the last years, we have focused on the study of one-dimensional coordination polymers as molecular wires.[9−12] Herein we report on the synthesis and structural and electrical characterization of three $[Pt_2(S_2CR)_4]$ [R = CH_3 (**1**), $(CH_2)_4CH_3$ (**2**), cyclohexyl (**3**)] metal-dimer chains. The series formed by the stacking of dinuclear platinum(II) complexes shows different intermetallic Pt−Pt distances, allowing, for the first time, a study of the influence of the Pt−Pt interdimer overlapping in the conductivity of well-ordered crystals of these compounds. Density functional theory (DFT) calculations confirm the experimental results.

The dimetallic platinum complexes **1** and **2** were synthesized following their already reported synthesis.[14] Complex **3** was prepared following a similar procedure (see the Supporting Information). The crystal structure analysis of compounds **1**−**3** revealed the presence of quasi-one-dimensional chains based on the collinear alignment of $[Pt_2(S_2CR)_4]$ dimeric entities with short intra- and interdimeric Pt−Pt distances (Figure 1).[13] The dimeric entities show a windmill-shaped arrangement in which four μ-dithiocarboxylato-κS:κS′ ligands bridge two Pt^{II} atoms with a metal···metal distance in the range 2.745−2.771 Å. The coordination environment around the metal atoms consists of four sulfur atoms defining the equatorial plane from which the platinum atoms are deviated 0.013−0.089 Å. Above and below this plane are placed the other platinum atom of the dimer and a platinum atom from the next dinuclear unit. The two PtS_4 squares of the dimeric entity are rotated by 22.32−27.25° from the eclipsed arrangement. The dimers are stacked along the *c* axis by means of S···S contacts (shortest distances: 3.434−3.501 Å) that impose short interdimer Pt−Pt distances: 3.1375(14), 3.1412(12), and 3.3389(17) Å, respectively. Adjacent PtS_4 squares belonging to different dimers are also rotated by 27.25−44.05°. These chains are held together only by weak van der Waals interactions (closest interchain S···S distance: 4.68 Å). It is noteworthy to indicate that the packing of the diplatinum entities found in some analogous compounds presents a zigzag disposition, which decreases the effective overlapping of the $5d_{z^2}$ orbitals. In particular, a previously reported polymorph of the $[Pt_2(S_2CCH_3)_4]$ complex shows a zigzag chain with significantly longer interdimeric Pt···Pt distances of 3.776(1) and 3.819(1) Å but with short interdimeric Pt···S contacts (3.28−3.52 Å). The large interdimer distance in **3** could be a compromise between the different arrangements of the dimers and the sizes of the ligands. A careful revision of the synthetic procedures of this polymorph suggests that probably the key factor in the crystallization process determining the alignment of the dimetallic complexes is the solvent. Thus, while the crystals obtained upon crystallization in toluene crystallized as zigzag chains,[14] those obtained here in CH_2Cl_2 are linear. The difference in polarity/polarizability of these solvents seems to play an important role in the disposition of the dimers. However, the full explanation to this issue and its extrapolation to other analogous compounds are still unclear.[15,16]

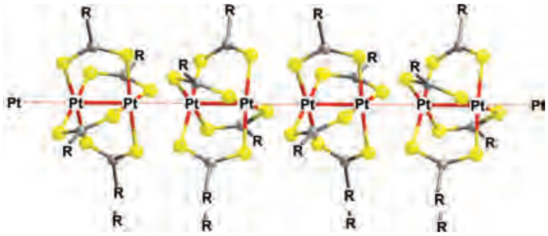

Figure 1. Representation of the chains formed by the stacking of dimetallic $[Pt_2(S_2CR)_4]$ [R = CH_3 (**1**); $(CH_2)_4CH_3$ (**2**)] complexes. Color code: sulfur, yellow; carbon, gray. The dimer entities in **3** (R = hexenyl) are eclipsed.

The analysis of the crystal structures of these compounds together with the previously published examples of platinum dithiocarboxylate polymeric complexes suggests that the steric hindrance of the substituents of the dithiocarboxylato ligands influences the interdimeric Pt···Pt distances: the bulkier the substituent is, the longer is the interdimer metal-to-metal distance. On the other hand, the elongation of the interdimer distance induces a slight compression in the intradimer metal-to-metal distances.

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(13) Crystal data for **1**: tetragonal, *P4/ncc*; $a = b = 12.7130(6)$ Å, $c = 11.8180(10)$ Å, $V = 1910.0(2)$ Å^3, $Z = 4$, fw = 754.84 g·mol^{-1}, $D_{calcd} = 2.625$ Mg·m^{-3}, $2\theta = 28.09°$, $T = 293(2)$ K, λ(Mo Kα) = 0.710 73 Å, $\mu = 15.488$ mm^{-1}, 13 505 reflections, 1167 unique reflections, 44 parameters, $R1(F_o) = 0.0480$ [$I > 2\sigma(I)$], $wR2$ (F_o^2) = 0.1408 (all data), GOF = 0.836. Crystal data for **2**: orthorhombic, *Pccn*; $a = 29.241(6)$ Å, $b = 9.2388(18)$ Å, $c = 11.773(2)$ Å, $V = 3180.5(11)$ Å^3, $Z = 4$, fw = 979.31 g·mol^{-1}, $D_{calcd} = 2.045$ Mg·m^{-3}, $2\theta = 71.00°$, $T = 293(2)$ K, λ(Cu Kα) = 1.541 78 Å, $\mu = 21.223$ mm^{-1}, 19 894 reflections, 3049 unique reflections, 157 parameters, $R1(F_o) = 0.0666$ [$I > 2\sigma(I)$], $wR2$ (F_o^2) = 0.2011 (all data), GOF = 1.049; the alkyl chains have to be refined by imposing soft restraints on the C−C distances and C−C−C angles. Crystal data for **3**: tetragonal, *I*4; $a = b = 16.927(6)$ Å, $c = 6.0850(12)$ Å, $V = 1743.5(9)$ Å^3, $Z = 2$, fw = 1027.29 g·mol^{-1}, $D_{calcd} = 1.957$ Mg·m^{-3}, $2\theta = 27.5°$, $T = 293(2)$ K, λ(Mo Kα) = 0.710 73 Å, $\mu = 8.512$ mm^{-1}, 2791 reflections, 911 unique reflections, 88 parameters, $R1(F_o) = 0.0245$ [$I > 2\sigma(I)$], $wR2(F_o^2) = 0.0377$ (all data), GOF = 0.830.

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Table 1. Intra- and Intermetallic Pt···Pt Distances and Electrical Conductivity at 300 K

	intradimer M−M distance (Å)	interdimer M−M distance (Å)	$\sigma_{300\ \mathrm{K}}$ (S·cm^{-1})
1	2.771(1)	3.138(1)	2×10^{-3}
2	2.745(1)	3.141(1)	92×10^{-4}
3	2.746(1)	3.339(2)	$<12 \times 10^{-6}$

Direct current (dc) electrical conductivity measurements carried out at variable temperature by the standard four-probe method show that compound **1** behaves as a typical semiconductor with a room temperature (300 K) conductivity of 2×10^{-3} S·cm^{-1} (Table 1). When the sample is cooled, the resistivity increases, following a semiconducting behavior [$\sigma = \sigma_0 \exp(E_a/kT)$] with an activation energy of 81 meV in the temperature range 300−210 K (Figure 2). Below ca. 210 K, the resistance of the sample exceeds the measuring limit of our equipment. The dc electrical conductivity of compound **2** is 9×10^{-4} S·cm^{-1} at 300 K (Table 1) and decreases in an activated manner when the temperature is lowered. Because below ca. 290 K the resistance of the samples exceeds the limit of our equipment and we could not measure meaningful data, we performed instead a warming scan up to 350 K. In the temperature range 300−350 K, the sample shows a semiconducting behavior with an activation energy of 119 meV (Figure S3 in the Supporting Information). For compound **3**, it was only possible to make room temperature measurements because the crystals were extremely fragile. These measurements show very low values, of less than 1×10^{-6} S·cm^{-1} in all cases. Hence, we report in Table 1 only an upper value of the conductivity as imposed by our instrumental resolution. The indication is anyway that the conductivity of compound **3** is negligible. Note the remarkable decrease of the conductivity by about 1 order of magnitude from compound **1** to compound **2**. Despite the very similar Pt···Pt distances in compounds **1** and **2**, there is a slight increase of the interdimer distance, which is the limiting factor for conductivity. We attribute the conductivity trends in this series of compounds to a consequence of the interdimer distance variations. Although, in principle, other geometrical factors can be relevant (such as the distances between chains determined by the different lateral groups), we believe that the one-dimensional features are dominant. This can be tested by performing band structure calculations along the different symmetry lines of the crystals. The ground-state electronic structure of the selected systems (**1**−**3**) was obtained from first principles by means of plane-wave pseudopotential DFT calculations.[17] The computational details are thoroughly reported in the Supporting Information. We simulated the MM···MM chains in the crystalline phase by using three-dimensional periodically repeated supercells. Each model system included four monomeric units arranged in two chains. The number of atoms and the cell dimensions were different in the three cases because of the different intra- and interchain distances. The atomic configurations were taken from the experimental X-ray results, and no further atomic relaxation was carried out.

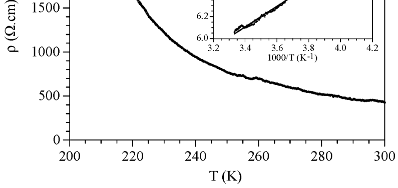

Figure 2. Thermal dependence of the electrical resistivity of compound **1**. The inset shows the Arrhenius plot with a fit to the Arrhenius law.

All of the simulated crystals have a semiconducting behavior with a DFT direct energy gap at the Γ point: $E_g = 0.44$ eV for **1** and $E_g = 0.46$ eV for **2** and **3**. The calculated band structures along the intra- and interpolymer directions are reported in the Supporting Information. The bands are flat in the interchain directions, accordingly with the lateral nonbonding interactions, while they are notably dispersive along the intrachain direction (Γ−*A* in Figure S4 in the Supporting Information). This picture is coherent with a direct (covalent) interaction among the dimetallic complexes in the single wire and the formation of fully delocalized electronic states, which derive from $5d_{z^2}$ overlapping and may sustain a charge (hole) transport along the polymers (see the Supporting Information). By using a parabolic fit near the Γ point, we calculated the effective masses for intrachain mobility for the hole carriers at the top of the valence band: $m_h^* = 0.50$, 0.52, and 0.60 for compounds **1**−**3**, respectively (in units of the free electron mass). The effective mass m_h^* decreases as the Pt−Pt distance decreases, being pretty close for **1** and **2** and larger for compound **3**. Because the charge mobility and conductivity in semiclassical crystal models are inversely proportional to the effective mass,[18] these theoretical findings support the scaling of the conductivity with the intrachain interdimer distance coherently with the experimental data.

Conclusion

The results shown in this study indicate that systems based on platinum dimetallic subunits have the potential to build up conductive wirelike materials. The conductivity of the synthesized polymeric crystals is typical of semiconducting materials and exhibits a remarkable dependence of even the tiniest metal-to-metal distances. Compared to other related systems,[19] these chains show both suitable Pt−Pt distances and Pt−Pt−Pt angles. In addition, the partial oxidation of these compounds will probably lead to a significant increase in the conductivity.

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Supporting Information Available: Details on the synthesis and characterization, electrical measurements, DFT calculations, and X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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