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Infinite Molecular $\{[Pt_{3n}(CO)_{6n}]^{2-}\}_\infty$ Conductor Wires by Self-Assembly of $[Pt_{3n}(CO)_{6n}]^{2-}$ (n = 5–8) Cluster Dianions Formally Resembling CO-Sheathed Three-Platinum Cables

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Dedicated to Prof. Larry F. Dahl

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Miscellaneous tetrasubstituted ammonium salts of $[Pt_{3n}(CO)_{6n}]^{2-}$ (n = 5–8) clusters, obtained by the stoichiometric oxidation of the corresponding $[Pt_9(CO)_{18}]^{2-}$ salts with tropylium tetrafluoroborate, self-assemble into infinite semicontinuous or continuous $\{[Pt_{3n}(CO)_{3n}(\mu\text{-}CO)_{3n}]^{2-}\}_\infty$ conductor wires upon crystallization. Pellets of these salts exhibit conductor behavior that roughly depends on the interdianion gap along the wires.

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One dimensional molecular metal wires[1,2] and one- and two-dimensional superclusters that are assembled through M–M bonds[3,4] are interesting as low-dimensional molecular materials, and they may find applications in molecular electronics and nanolithography.[5–7] According to EHMO calculations, the LUMO of a $Pt_3(CO)_3(\mu\text{-}CO)_3$ triangular moiety involves the combination of cyclopropenyl-like in-phase Pt p_z atomic orbitals.[8,9] For an infinite stack of neutral $Pt_3(CO)_3(\mu\text{-}CO)_3$ or dianionic $[Pt_3(CO)_3(\mu\text{-}CO)_3]^{2-}$ moieties, the σMO band, which is generated along the C_3 axis by the cyclopropenyl-like MOs, should be empty or completely filled, respectively. Therefore, such a stack should not be stable. However, in the case where the stack is generated by the assembly of $[Pt_{3n}(CO)_{6n}]^{2-}$ ($n > 1$) cluster dianions, the above MO band would only be $1/n$ filled; therefore, the stack could be feasible and may behave as a conducting molecular wire.

The first hint of a possible strategy that might favor self-assembly of $[Pt_{3n}(CO)_{6n}]^{2-}$ clusters was suggested by the recent structural characterization of the $[NBu_4]_2[Pt_{12}(CO)_{24}]$ and $[NBu_4]_2[Pt_{24}(CO)_{48}]$ salts.[10,11] In fact, the $[NBu_4]_2[Pt_{12}(CO)_{24}]$ salt is based on zero-dimensional packing of separated $[NBu_4]^+$ and $[Pt_{12}(CO)_{24}]^{2-}$ ions, as it was for the previously characterized $[Pt_{3n}(CO)_{6n}]^{2-}$ (n = 2, 3, 5) dianions in their $[PPh_4]^+$ or $[AsPh_4]^+$ salts.[12] Conversely, the $[NBu_4]_2[Pt_{24}(CO)_{48}]$ salt displays a 2D packing motif based on layers of parallel 1D infinite stacks of $Pt_3(CO)_6$ units intercalated by layers of $[NBu_4]^+$ cations. It was shown by Pauling that the r^-/r^+ ratio (r = ionic radius) directs the choice of the ionic lattice of salts of monoatomic ions. In view of the cylindrical shape of the $[Pt_{3n}(CO)_{6n}]^{2-}$ dianions, it appeared more appropriate to substitute r^- with the length of the dianion (L), and consequently, to replace r^+ by the diameter of the cation (D), and to use the L/D ratio as a rough guideline to achieve self-assembly of the dianions. In particular, it was speculated that a high L/D ratio would imply a great difference between the sizes of the dianion and the cation and a decreased repulsion between the dianions; the constant 2– charge would be delocalized over an increasing number of $Pt_3(CO)_6$ units. Furthermore, in the case of self-assembly of continuous $[Pt_{3n}(CO)_{6n}]^{2-}$ stacks, L would also determine the amount of filling of the σMO band that develops along the C_3 axis.

We have, therefore, reinvestigated the synthesis and structures of miscellaneous $[NR_4]_2[Pt_{3n}(CO)_{6n}]$ salts to assess the effect of the L/D ratio on self-assembly. We report here some significant structural results, as well as preliminary resistivity measurements of the above salts, which point out that stacking of $[Pt_{3n}(CO)_{6n}]^{2-}$ dianions leads to conducting molecular wires.

The investigated salts are collected in Table 1. All $[Pt_{3n}(CO)_{6n}]^{2-}$ (n = 4, 5, 6, and 8) salts have been prepared by the stoichiometric oxidation of the corresponding $[Pt_6(CO)_{12}]^{2-}$ salt[13] with tropylium tetrafluoroborate and crystallized from THF/toluene or acetone/2-propanol mixtures. The formulas of miscellaneous salts were established

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by single-crystal X-ray diffraction studies, whereas the purities of the crystalline batches were ascertained by elemental analysis, ESI-MS, and IR spectroscopy.[14]

Table 1. Dependence of resistivity from crystal packing and interanionic gap.

Compound	L/D[a]	Packing	Gap[b]	Resistivity [Ωcm]	Ref.
$[NBu_4]_2[Pt_{12}(CO)_{24}]$	1.0	0D	–	$>10^8$	[10]
$[NMe_4]_2[Pt_{12}(CO)_{24}]$	2.5	0D	–	$>10^8$	
$[NEt_4]_2[Pt_{15}(CO)_{30}]$	2.0	3D	3.50	2.10^5	
$[NMe_4]_2[Pt_{18}(CO)_{36}]\cdot 2Me_2CO$	3.8	1D	3.09	6.10^2	
$[NEt_4]_2[Pt_{24}(CO)_{48}]$	3.3	2D	3.07	1.10^2	
$[NBu_4]_2[Pt_{24}(CO)_{48}]$	2.0	2D	3.21	2.10^3	[11]

[a] L = (distance between the centroids of the outer Pt_3 triangles) + [2 × (van der Waals radius of Pt)]; D = [2 × (average distance between the N and H atoms of the outer $–CH_3$ moiety)] + [2 × (van der Waals radius of H)]. [b] The gap between $[Pt_{3n}(CO)_{6n}]^{2-}$ dianions along the stack is given in Å.

The unit cell of $[NMe_4]_2[Pt_{12}(CO)_{24}]$, in spite of a L/D ratio (2.5) greater than that of $[NBu_4]_2[Pt_{24}(CO)_{48}]$ (see Table 1), contains separated $[Pt_{12}(CO)_{24}]^{2-}$ dianions and $[NMe_4]^+$ cations. As shown in Figure 1, distinct $[Pt_{12}(CO)_{24}]^{2-}$ dianions separated by $[NMe_4]^+$ cations, which hinder the formation of columnar stacks, can be clearly identified. In contrast to the previously characterized $[NBu_4]_2[Pt_{12}(CO)_{24}]$ salt,[10] the cation is also perfectly ordered. The intramolecular parameters of the $[Pt_{12}(CO)_{24}]^{2-}$ dianion are very similar in both salts.

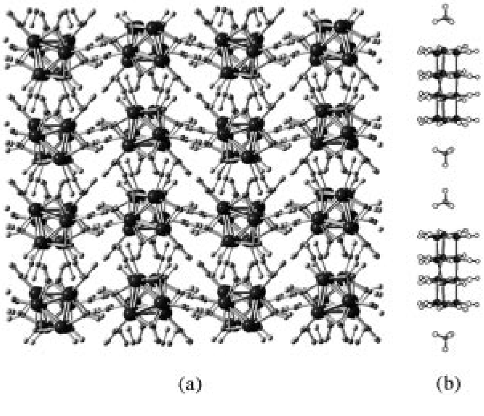

Figure 1. The packing of the $[NMe_4]_2[Pt_{12}(CO)_{24}]$ salt: (a) stacking of $[Pt_{12}(CO)_{24}]^{2-}$ dianions, (b) a portion of one stack that points out the presence of $[NMe_4]^+$ cations separating the $[Pt_{12}(CO)_{24}]^{2-}$ dianions.

The $[NEt_4]_2[Pt_{15}(CO)_{30}]$ salt exhibits incipient columnar self-assembly of $[Pt_{15}(CO)_{30}]^{2-}$ dianions, though it features a smaller L/D ratio (ca. 2) than $[NMe_4]_2[Pt_{12}(CO)_{24}]$. A similar feature was anticipated by the $[EtV^{+\cdot}]_2[EtV^{2+}][Pt_{15}(CO)_{30}]_2$ salt.[17] As shown in Figure 2a, the $[NEt_4]_2[Pt_{15}(CO)_{30}]$ salt displays a 3D packing of quasicontinuous stacks of $Pt_3(CO)_3(\mu\text{-}CO)_3$ units oriented along the four diagonals of the cubic unit cell. The infinite stacks are built from distinct $[Pt_{15}(CO)_{30}]^{2-}$ dianions that are separated by interdianion distances of 3.45–3.54 Å, which are significantly longer than the intraion–intertriangular distances, which are comprised in the 3.06 to 3.15 Å range.

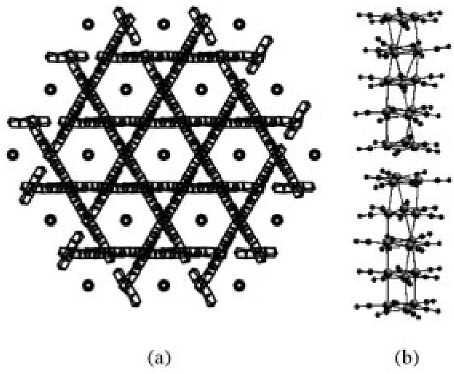

Figure 2. The packing of the $[NEt_4]_2[Pt_{15}(CO)_{30}]$ salt: (a) stacking of $[Pt_{15}(CO)_{30}]^{2-}$ dianions according to the four diagonals of the cubic unit cell (cations and carbonyl groups have been omitted for the sake of clarity), (b) a portion of the $[Pt_{15}(CO)_{30}]^{2-}$ stacks that point out the presence of a gap between the dianions.

Rewardingly, an increase in the L/D ratio beyond 3 enables the formation of continuous stacks of $Pt_3(CO)_3(\mu\text{-}CO)_3$ units, as shown by the structures of $[NMe_4]_2[Pt_{18}(CO)_{36}]\cdot 2Me_2CO$ and $[NEt_4]_2[Pt_{24}(CO)_{48}]$, respectively shown in Figures 3 and 4. They consist of 1D and 2D packing of continuous stacks of $Pt_3(CO)_3(\mu\text{-}CO)_3$ units, in which the individual $[Pt_{18}(CO)_{36}]^{2-}$ and $[Pt_{24}(CO)_{48}]^{2-}$ dianions are no longer distinguishable. Indeed, the $Pt_3(CO)_3(\mu\text{-}CO)_3$ stacks of $[NMe_4]_2[Pt_{18}(CO)_{36}]\cdot 2Me_2CO$ exhibit a constant interlayer periodicity of 3.08 Å, whereas those of $[NEt_4]_2[Pt_{24}(CO)_{48}]$ display alternating interlayer distances of 3.067 and 3.071 Å.

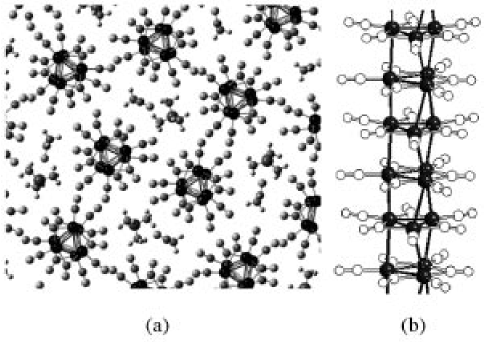

Figure 3. The packing of the $[NMe_4]_2[Pt_{18}(CO)_{36}]\cdot 2Me_2CO$ salt: (a) 1D packing of infinite columnar stacks of $[Pt_{18}(CO)_{36}]^{2-}$ dianions, (b) a portion of the stack that corresponds to a $[Pt_{18}(CO)_{36}]^{2-}$ dianion.

From the above results, it seems reasonable to conclude that L/D ratios > 3 favor self-assembly of $[Pt_{3n}(CO)_{6n}]^{2-}$ ($n \geq 6$) dianions into infinite continuous wires because squeezing these elongated dianions together does not trigger repulsive forces that are too high. Because repulsive forces are expected to increase rapidly for $n \leq 6$, L/D ratios comprised in the 2 to 3 range are less discriminating and may lead to zero-dimensional packing or quasicontinuous wires that are dependent on the length of the dianion. Notably, the formation of infinite $[Pt_{3n}(CO)_{6n}]^{2-}$ continuous wires should be disfavored by Peierls distortions.[18,19] Their effectiveness in

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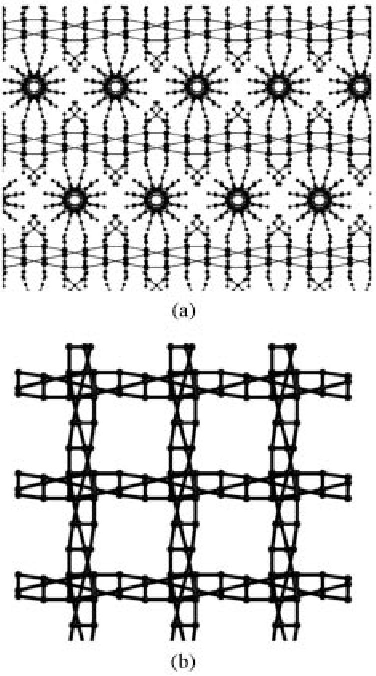

Figure 4. Two different views of the packing of the $[NEt_4]_2$-$[Pt_{24}(CO)_{48}]$ salt: (a) 2D packing of infinite columnar stacks of $[Pt_{24}(CO)_{48}]^{2-}$ dianions according to two directions of the Cartesian axes, which gives rise to two orthogonal layers of parallel stacks, (b) continuity of the stack of $[Pt_{24}(CO)_{48}]^{2-}$ dianions (in this view carbonyl groups and cations are omitted for clarity).

partitioning the stack might be contrasted by the loss of density at the highest L/D ratios.

As shown in Table 1, the resemblance of the infinite $Pt_3(CO)_3(\mu\text{-}CO)_3$ stacks found in $[NMe_4]_2[Pt_{18}(CO)_{36}]\cdot 2Me_2CO$ and $[NEt_4]_2[Pt_{24}(CO)_{48}]$ to CO-insulated platinum cables is not only morphological but also functional. Resistivity measurements were carried out under a nitrogen atmosphere at room temperature with a four-point probe on pressed pellets (ca. 13 × 1 mm) of powdered samples. Whereas the zero-dimensional salts expectedly display the resistivity of an insulator material ($>10^8\ \Omega$cm), the salts that are based on quasicontinuous or continuous stacks exhibit resistivity in the 10^5 to $10^2\ \Omega$cm range. Perhaps, it is significant that the lowest resistivity values are shown by those salts containing continuous columnar stacks of $Pt_3(CO)_3(\mu\text{-}CO)_3$ moieties. Although the resistivity of the above samples was measured on pellets of polycrystalline materials, the lowest observed values are already comparable to those exhibited by single crystals of other mixed-valence molecular chains featuring much shorter M–M bonds, such as $K_2[Pt(CN)_4]Cl_{0.32}\cdot 2.62H_2O$ and $[Rh(MeCN)_4\text{-}(BF_4)_{1.5}]_x$.[20,21] It seems, therefore, of interest to carry out further physical characterizations (particularly variable temperature resistivity on single-crystals, solid-state ^{195}Pt NMR spectroscopic analysis, and magnetic measurements) to better assess the nature of these conductor molecular materials.

A clear effect of the support on self-assembly was observed by STM imaging of HOPG impregnated with water/2-propanol solutions of $[Pt_{3n}(CO)_{6n}]^{2-}$ (n = 4–6) dianions, which pointed out the preferential formation of nanowires over other morphologies.[22] As inferred from TEM images, well-defined Pt morphologies, including Pt nanowires, were also obtained by preparing $[Pt_{3n}(CO)_{6n}]^{2-}$ (n = 2–4) dianions in the micropores of zeolites, followed by thermal decomposition.[23]

The present work demonstrates that self-assembly of $[Pt_{3n}(CO)_{6n}]^{2-}$ (n = 6, 8) into infinite wires readily occurs by crystallization from solution and affords macroscopic crystals that, in favorable cases,[24] enable full elucidation of the wire structure by single-crystal X-ray diffraction studies. In view of the above observations, salts of the $[Pt_{3n}(CO)_{6n}]^{2-}$ (n = 6, 8) dianion with L/D > 3 seem the most promising materials for patterning surfaces with conductor molecular CO-sheathed Pt nano- and microcables, as well as Pt metal nanowires by suitable treatment of the former.

Acknowledgments

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[14] *Crystal data for $[NMe_4]_2[Pt_{12}(CO)_{24}]$:* Monoclinic, space group $C2/c$, a = 24.8081(10) Å, b = 13.4980(6) Å, c = 15.1794(6) Å, β = 95.797(1)°, U = 5057.0(4) Å^3, Z = 4, D_c = 4.153 g/cm^3, T = 298 K, graphite-monochromatized Mo-K_α radiation (λ = 0.71073 Å), final R value was 0.0252 and wR = 0.0485 for 4443 independent reflections having $I > 2\sigma(I)$. *Crystal data for $[NEt_4]_2[Pt_{15}(CO)_{30}]$:* Cubic, space group $P2_13$, a = 27.5990(3) Å, U = 21022.3(4) Å^3, Z = 12, D_c = 3.817 g/cm^3, T = 298 K, graphite-monochromatized Mo-K_α radiation (λ = 0.71073 Å), final R value was 0.0491 and wR = 0.0860 for 12407 independent reflections having $I > 2\sigma(I)$. *Crystal data for $[NMe_4]_2[Pt_{18}(CO)_{36}]\cdot 2Me_2CO$:* Orthorhombic, space group $Pnnm$, a = 35.191(5) Å, b = 35.570(5) Å, c = 6.1674(9) Å, U = 7720.0(19) Å^3, Z = 4, D_c = 4.129 g/cm^3, graphite-monochro-

matized Mo-K_α radiation (λ = 0.71073 Å). Owing to rapid crystal decay at room temperature because of solvent loss, the data had to be collected at 100 K. Furthermore, the structure was recognized to be pseudomerohedrally twinned and a suitable set of BASF/TWIN parameters was used in the refinement, according to the procedure described in SHELX-97: [15] twin law [010 100 00–1]. Final R value was 0.1025 and wR = 0.2521 for 6583 independent reflections having $I > 2\sigma(I)$. *Crystal data for* $[NEt_4]_2[Pt_{24}(CO)_{48}]$*:* Tetragonal, space group $I\bar{4}2d$, a = 12.2675(4) Å, c = 34.251(3) Å, U = 5154.5(5) Å^3, Z = 2, D_c = 4.051 g/cm^3, T = 298 K, graphite-monochromatized Mo-K_α radiation (λ = 0.71073 Å), final R value was 0.0197 and wR = 0.0446 for 2535 independent reflections having $I > 2\sigma(I)$. Data were corrected for Lorentz-polarization and absorption effects (empirical absorption SADABS[16]). The structures were solved by direct methods and refined with full-matrix least-squares (SHELX-97[15]). CCDC-626053 to -626056 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. IR and ESI-MS are unambiguously diagnostic of the purity of the $[Pt_{3n}(CO)_{6n}]^{2-}$ (n = 4, 5, 6) dianions, as a consequence of the varying ratio of number-of-charges/number-of-CO and sufficient stability of those ions in ESI conditions. Given that the $Pt_3(CO)_6$ units are constantly held together by only two electrons, species with $n > 6$ are hardly distinguishable both by IR and ESI-MS because of the leveling of the number-of-charges/number-of-CO ratio and fragmentation under ESI conditions. An almost Gaussian distribution of oligomers with $n \leq 6$ and $n \geq 6$ is observed,[10] even if the presence of oligomers with $n < 6$ in the injected solution is excluded by IR. Therefore, the purity of the $[NEt_4]_2[Pt_{24}(CO)_{48}]$ and $[NBu_4]_2[Pt_{24}(CO)_{48}]$ batches could only be assessed by a combination of IR and elemental analysis.

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[24] Notably, $[Pt_{3n}(CO)_{6n}]^{2-}$ (n = 6, 8, and 10) salts have been isolated and formulated by elemental analysis more than 30 years ago.[13a] Attempted structural determination of several salts with miscellaneous tetrasubstituted ammonium or phosphonium cations along the years systematically failed. Their unit cells were often featuring an axis of ca. 3 Å, the cations could not be located, and only unrealistic models of the dianions, on the basis of infinite stacks of perfectly eclipsed $Pt_3(CO)_3(\mu\text{-}CO)_3$ moieties, were obtained by structure solution.

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