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References and Notes

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Communications to the Editor

Synthesis, Structure, and Stereochemical Implications of the $[\text{Pt}_{19}(\text{CO})_{12}(\mu_2\text{-CO})_{10}]^{4-}$ Tetraanion: A Bicapped Triple-Decker All-Metal Sandwich of Idealized Fivefold (D_{5h}) Geometry

Sir:

We report here the preparation and structure of a 19-metal-atom cluster, the $[\text{Pt}_{19}(\text{CO})_{22}]^{4-}$ tetraanion. This remarkable polynuclear metal species was prepared by Ceriotti, Longoni, and Chini. The metal framework together with the 10 bridging and 2 axial carbonyl ligands were established by Washecheck and Dahl and later substantiated by Manassero and Sansoni from X-ray structural determinations of the $[n\text{-Bu}_4\text{N}]^+$ salt. The complete structure was determined for the $[\text{Ph}_4\text{P}]^+$ salt by Washecheck and Dahl. The salient structural feature is that the entire platinum carbonyl cluster contains a pseudofivefold principal axis, which is without precedent in discrete transition metal clusters but which has been found for small metallic crystallites on heterogeneous surfaces. In addition, this complex provides the first example of a metal carbonyl cluster with (1) 19 homonuclear metal atoms—the largest discrete metal aggregate reported to date; (2) two completely encapsulated metal atoms; and (3) a CO-to-(total metal) ratio of $22:19 = 1.16$, which is considerably less than the previously known lowest value of ~ 1.7 for other metal carbonyl species. The CO-to-(surface metal) ratio of $22:17 = 1.29$ is closest to the situation observed for the chemisorption of carbon monoxide either on platinum single crystal surfaces or on small platinum particles of the type used

in supported metal catalysts, for which the maximum CO-to-(surface metal) ratio is ~ 0.75 .¹ These characteristics indicate that its as yet unknown physicochemical properties may provide a better model for the properties of small metal aggregates² than those of any other previously reported discrete metal cluster.

This work is an outgrowth of systematic studies by Chini, Longoni, and co-workers³ who have prepared a large number of nickel and platinum carbonyl cluster anions. Those isolated and structurally characterized include the $[\text{M}_3(\text{CO})_3(\mu_2\text{-CO})_3]_n^{2-}$ dianions ($n = 2, 3$ for $\text{M} = \text{Ni}$; $n = 2-5$ for $\text{M} = \text{Pt}$),^{3a-d,f} the $[\text{Ni}_5(\text{CO})_9(\mu_2\text{-CO})_3]^{2-}$ dianion,^{3c,f} and the $[\text{Ni}_{12}(\text{CO})_{21}\text{H}_{4-n}]^{n-}$ anions ($n = 2-4$).^{3i,j}

In the synthesis of the $[\text{Pt}_3(\text{CO})_3(\mu_2\text{-CO})_3]_n^{2-}$ oligomers,^{3a,f} brown side products were obtained. Refluxing of the triangular platinum clusters in acetonitrile solution was found to produce these brown ionic compounds in good yields. In addition, other brown compounds were detected from infrared carbonyl spectral measurements of the reactions of these brown compounds with either acid or oxidizing agents. The isolation of the $[\text{Pt}_{19}(\text{CO})_{22}]^{4-}$ tetraanion in crystalline form for structural analysis has required extensive work involving the use of nine different cations. In this communication the results of three X-ray diffraction determinations of this Pt-19 tetraanion are presented.

This compound was obtained in $\sim 50\%$ yield by a heating of the appropriate salt of the $[\text{Pt}_3(\text{CO})_3(\mu_2\text{-CO})_3]_3^{2-}$ dianion in refluxing acetonitrile. Anal. on the vacuum-dried product. Found: NBu_4 , 17.37 (calcd, 18.3); Pt, 74.02 (calcd, 70.00);

CO, 11.35 (calcd, 11.65). Analyses for other salts are in better agreement for the platinum content. An infrared spectrum of the $[n\text{-Bu}_4\text{N}]^+$ salt of the $[\text{Pt}_{19}(\text{CO})_{22}]^{4-}$ tetraanion in acetonitrile exhibited carbonyl bands at 2000 (vs), 1992 (sh), 1930 (mw), and 1795 (s) cm^{-1} . A ^{13}C NMR spectrum of an $\sim 50\%$ ^{13}C -enriched $[n\text{-Bu}_4\text{N}]^+$ salt under N_2 in a 2.3:1.0 $\text{C}_2\text{H}_5\text{CN}-\text{CD}_3\text{CN}$ solution at -50°C displayed two broad resonances at δ 167.5 and 228.0 ppm (relative to Me_4Si) in a 1:1 ratio. (The signal-to-noise ratio was not sufficiently great to ascertain a third resonance presumably due to the two equivalent axial carbonyl ligands.) Both the IR and ^{13}C NMR data are in agreement with the crystallographically determined structure of the tetraanion.

The initial structural determinations⁴ were complicated by a number of factors. More than 30 optically acceptable crystals (sealed in thin-walled glass capillaries under rigorous exclusion of air) of the tetraphenylarsonium, trimethylbenzylammonium, and tetrabutylammonium salts were examined by X-ray measurements before even a weakly diffracting crystal of the $[n\text{-Bu}_4\text{N}]^+$ salt (recrystallized by slow diffusion of diisopropyl ether into an acetonitrile solution) was uncovered. Although for the first data set the crystal was coated with epoxy resin, crystal decay due to loss of solvent molecules was encountered during data collection, and a presumed crystal disorder of the tetrabutylammonium cations (which are notorious in this respect⁵) prevented their unambiguous locations, despite extensive efforts. Nevertheless, the platinum atoms were found by a combined use of the Patterson technique and direct methods, and all of the bridging carbonyl ligands were then clearly resolved from Fourier difference maps. A second X-ray data set was subsequently collected on another crystal of the $[n\text{-Bu}_4\text{N}]^+$ salt in which crystal decay was prevented by the inclusion of some of the mother liquor in the capillary. Although these data likewise did not provide unequivocal atomic coordinates for either the cations or solvent molecules, the structure of the metal framework along with the 10 bridging and 2 axial carbonyls was completely verified. For these two data sets a disorder was observed in the region of the terminal carbonyls. In addition, the remaining 10 terminal carbonyl ligands could not be resolved or distinguished from possible imaging of the platinum atoms.

The inherent problems of the $[n\text{-Bu}_4\text{N}]^+$ structures were overcome by the synthesis and ultimate crystallization of the $[\text{Ph}_4\text{P}]^+$ salt. Crystal decay was again prevented during data collection by inclusion of mother liquor in the capillary. Convincing evidence that the actual formula is $[\text{Ph}_4\text{P}]_4\text{[Pt}_{19}(\text{CO})_{22}]\cdot 4\text{CH}_3\text{CN}$ was established by the resolution of the solvent molecules in difference Fourier maps and substantiated by a comparison of the calculated and experimental densities. The structural equivalence of the carbonyl ligands in the tetraanion of the $[n\text{-Bu}_4\text{N}]^+$ and $[\text{Ph}_4\text{P}]^+$ salts was ascertained from the virtually identical IR solution spectra in the carbonyl stretching region.

The Pt-19 framework of the tetraanion (Figure 1) consists of three five-membered rings stacked in an eclipsed conformation with the other four Pt atoms lying on the principal fivefold axis, two internally sandwiched between the rings, and two externally capping the two outer pentagons. The resulting Pt-Pt₅-Pt-Pt₅-Pt-Pt₅-Pt array is also linked together by 10 bridging carbonyls and Pt-Pt bonds between adjacent Pt atoms of the 3 eclipsed pentagonal Pt rings. Alternatively, the Pt framework may be generated from a planar Pt₇ fragment of five fused triangles composed of atoms A, B, C, D, C, B, A (Figure 2) by the operation of the pseudofivefold axis along the A-C-C-A direction. The platinum atoms of this planar Pt₇(μ_2 -CO)₂ fragment (Figure 1) may be considered as a portion of one close packed metal layer, with the central Pt₅(μ_2 -CO)₂ part (i.e., comprised of the B, C, D, C, B Pt atoms) being analogous in configuration to the corresponding

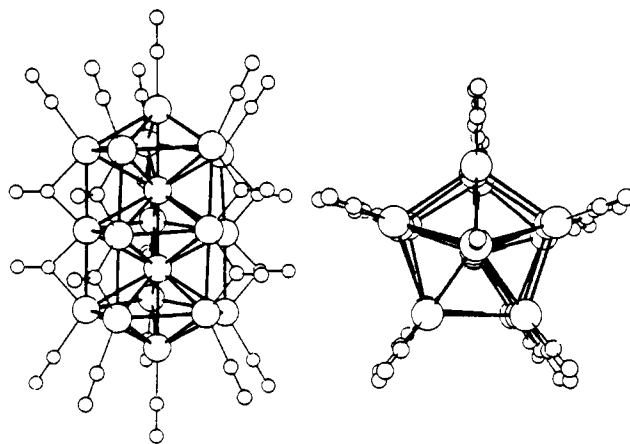


Figure 1. The $[\text{Pt}_{19}(\text{CO})_{12}(\mu_2\text{-CO})_{10}]^{4-}$ tetraanion of idealized D_{5h} geometry. The Pt_{19} core, surrounded by only 12 terminal and 10 bridging carbonyl ligands, may be envisioned as arising from a head-to-tail fusion of three eclipsed pentagonal-bipyramidal platinum units at two common axial platinum atoms.

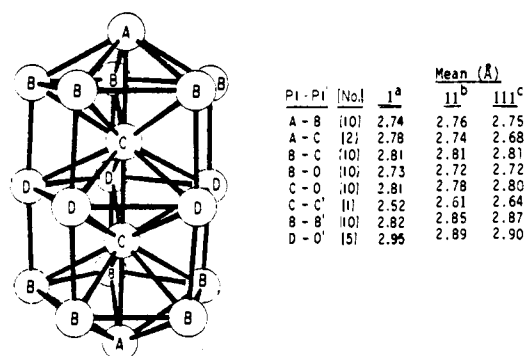


Figure 2. The Pt_{19} core with the four types of platinum atoms labeled under assumed D_{5h} symmetry. The means of the eight resulting kinds of Pt-Pt distances are listed along with the number of equivalent distances enclosed in square brackets. The esd's for the individual distances are 0.02–0.03 \AA for I and II and 0.004–0.006 \AA for III. The cluster has crystallographic C_{2v} site symmetry for I and II, whereas no symmetry constraints are imposed for III. (a) First $[n\text{-Bu}_4\text{N}]^+$ data set; (b) second $[n\text{-Bu}_4\text{N}]^+$ data set; and (c) $[\text{Ph}_4\text{P}]^+$ data set.

$\text{Ni}_5(\mu_2\text{-CO})_2$ part of the central $\text{Ni}_6(\text{CO})_3(\mu_2\text{-CO})_6$ fragment found in the $[\text{Ni}_{12}(\text{CO})_{21}\text{H}_{4-n}]^{n-}$ anions. The entire $[\text{Pt}_{19}(\text{CO})_{12}(\mu_2\text{-CO})_{10}]^{4-}$ tetraanion approximately conforms to D_{5h} symmetry.⁶ The σ_h mirror plane, one of the five σ_v mirror planes, and one horizontal C_2 axis are rigorously required by the crystallographic C_{2v} site symmetry in the $[n\text{-Bu}_4\text{N}]^+$ salt, while no symmetry constraints are imposed on the tetraanion in the $[\text{Ph}_4\text{P}]^+$ salt.

The means of the eight kinds of 58 Pt-Pt distances averaged under D_{5h} symmetry are given in Figure 2. For the $[\text{Ph}_4\text{P}]^+$ salt the shortest Pt-Pt bond of 2.641 (5) \AA is between the two encapsulated Pt(C) atoms. The second shortest set consists of two bonds of 2.686 (5) and 2.675 (5) \AA from the apex atoms, Pt(A), to the encapsulated atoms, Pt(C). Next follows the two sets which comprise the longitudinal surface bonds—viz., Pt(A)-Pt(B) with mean 2.75 (3) and range 2.708 (4)–2.814 (4) \AA , and Pt(B)-Pt(D) with mean 2.72 (2) and range 2.689 (5)–2.745 (5) \AA . The next two sets are the remaining internal bonds which extend from the encapsulated atoms to the ring atoms—viz., Pt(C)-Pt(B) with mean 2.81 (9) and range 2.694 (4)–2.933 (4) \AA , and Pt(C)-Pt(D) with mean 2.80 (6) and range 2.714 (4)–2.891 (4) \AA . The last two sets consist of the surface intraring bonds—viz., Pt(B)-Pt(B) with mean 2.87 (3) and range 2.828 (4)–2.919 (4) \AA , and Pt(D)-Pt(D) with mean 2.90 (3) and range 2.877 (4)–2.961 (4) \AA . The overall

dimensions of this cylindrically shaped Pt₁₉ core are 11.1 Å in length and 7.8 Å in diameter. The diameter is similar to that reported⁷ for catalytic platinum crystallites on alumina support.

The pseudofivefold rotational symmetry exhibited by the [Pt₁₉(CO)₁₂(μ₂-CO)₁₀]⁴⁻ tetraanion is of prime importance in that such noncrystallographically allowed symmetry has been experimentally found in a number of microcrystalline materials^{2a,8a} (e.g., vapor-grown metal whiskers of Ni, Fe, and Pt,^{8b} electrodeposited copper dendrites,^{8c} nickel grains from thermally decomposed nickel tetracarbonyl,^{8d} vapor-deposited Au on various substrates,^{8e} and synthetic diamonds^{8f}). Bagley⁹ has proposed two contact-sphere modifications for the fivefold pseudosymmetric Melmed-Hayward cork-ball structure^{8b,10} which involves the continued packing of hard spheres in concentric pentagons about a central pentagonal bipyramidal nucleus. Not only does a fragment of this Melmed-Hayward structure geometrically correspond to the Pt₁₉ core but also the dimensions of the two outer crystallographically identical pentagonal bipyramids in the Pt₁₉ core are consistent with those of the second Bagley model^{9b} based on maximum density (minimum volume) in that the Pt(A)-Pt(C)/Pt(B)-Pt(B) ratio of 2.68 Å/2.87 Å = 0.934 is close to his calculated ratio of 1.000/1.018 = 0.982.

We are currently pursuing structural characterizations of the other brown platinum carbonyl compounds in that we expect the tetraanion to have important stereochemical implications in the modeling of heterogenous metal catalysts, especially small metal aggregates dispersed on various supports.

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- (4) (a) [NBu]₄[Pt₁₉(CO)₁₂(μ₂-CO)₁₀]₄·8CH₃CN: fw, 5341.1; orthorhombic; *a* = 17.380 (9), *b* = 21.201 (4), *c* = 16.728 (8) Å; *d*_{calcd} = 2.88 g cm⁻³ for *Z* = 2; *F*(000) = 4764; *μ* = 217.45 cm⁻¹ for Mo K α radiation. Systematic absences of *h**h**k*0 with *h* + *k* = 2*n* + 1 indicate *P2₁mn*, *Pm2₁n*, and *Pmnn* as probable space groups. The latter centrosymmetric group, which was ultimately selected on the basis of least squares of trial models, conformity of intensities to hypercentric statistics, and analyses by direct methods under all three symmetries, imposes *C_{2v}* crystallographic site symmetry on two tetraanions. The bridging carbonyl peaks were all found from Fourier and difference Fourier maps. Anisotropic least-squares refinement of the Pt atoms with fixed carbonyl contributions gave *R*₁(*F*) = 16.9 and *R*₂(*F*) = 17.5% for 803 independent reflections (with *I* > 2σ(*I*)) which were corrected for absorption. A second data set was collected for the [n-Bu₄N]⁺ salt in which solvent was included in the capillary to prevent decay. The systematic absences and crystal system are the same with *a* = 16.800

(4) Å, *b* = 21.727 (6) Å, and *c* = 17.386 (6) Å for which a least-squares refinement gave *R*₁(*F*) = 13.1 and *R*₂(*F*) 17.5% for 1111 independent absorption-corrected reflections with *I* > 2σ_{*i*}. This model contains only the Pt atoms and did indicate a disorder of the axial carbonyls. (b) [(C₆H₅)₄P]₄[Pt₁₉(CO)₁₂(μ₂-CO)₁₀]₄·4CH₃CN: fw, 5844.8; triclinic; *a* = 17.234 (3), *b* = 25.480 (5), *c* = 17.171 (3) Å; *α* = 91.69 (2), *β* = 118.10 (1), *γ* = 74.60 (1)°; *V* = 6372 (2) Å³; *d*_{obsd} = 3.038 (4) vs. *d*_{calcd} = 3.046 g cm⁻³ for *Z* = 2; *F*(000) = 2594; *μ* = 201.1 cm⁻¹ for Mo K α radiation. ω-Scan data were collected for the shell with 3° ≤ 2θ ≤ 40° in which 12 443 measured reflections yielded 7540 maxima with *I* ≥ 2σ_{*i*}. In addition, another 17 828 data were examined in the shell with 40° ≤ 2θ ≤ 55°; however, if a fast prescan did not indicate sufficient intensity for the reflection to be statistically meaningful, the reflection was not examined further. This procedure resulted in the intensity measurement of 1711 data, of which 1654 maxima possessed *I* > 2σ_{*i*}. A merging of the absorption-corrected data (vide infra) gave 13 515 independent data with 8596 having *I* > 2σ_{*i*}. Approximately 20% of the observed data were from the 40–55° shell. Thirty psiscan reflections, spaced approximately every 2 degrees in 2θ, were used for an empirical absorption correction. Of the 634 reflections for which a Friedel mate was collected, there were none which had intensities of the pairs differing by more than 5σ_{*i*} after the absorption correction was applied. Full-matrix least-squares refinement was employed with anisotropic thermal coefficients for the Pt and P atoms and isotropic temperature factors for the carbonyl atoms; the C₆H₅ rings were each refined as a rigid body in accord with their well-known *D_{6h}* geometry with individual isotropic temperature factors being varied for the carbon atoms and with the isotropic temperature factor for each hydrogen atom fixed at a *B* value of 2.0 greater than that of its attached carbon atom. The acetonitrile molecules were fixed. Owing to the size of the matrix and a computer limited to 265k words, all of the parameters could not be varied at one time, but instead the cluster was varied with the remainder fixed and then the cations were varied (phenyls as rigid groups). One complete cycle (both anion and cation) required ~14 computer hours when only the observed data were used. (The departmental computer is a Harris/7 with a 600-ns cycle time.) Final refinement of the 8596 independent data, with 576 parameters being varied in two blocks of full-matrix least squares, converged at *R*₁(*F*) = 9.1%, *R*₂(*F*) = 8.0% with an error of fit of 1.23 for 576 parameters.

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Generation of the Onocerin System by Lanosterol 2,3-Oxidosqualene Cyclase—Implications for the Cyclization Process

Sir:

Despite considerable structural differences between epoxides **1a**, **1b**, and **2** on the one hand and the natural substrate on the other, the enzyme lanosterol 2,3-oxidosqualene cyclase still serves to convert these substances into members of the lano-