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Structural Features Suggesting Relativistic Effects in a Dimeric Gold Complex

Here we present the crystal structure of $[Au(CH_2)_2PPh_2]_2Br_4$, which contains a trigonal-bipyramidal-like geometry of the Au^{III} centers, an unprecedented result for cofacial d^8 dimers. This result constitutes evidence that relativistic effects can cause pronounced structural differences to be observed between dimers of Au^{III} and dimers of other d^8 metal centers.

The importance of relativistic effects in chemistry has gained attention recently.[1] Among transition metals, the magnitude of relativistic stabilization of outer-shell s electrons reaches a maximum for gold: for example, the stability of the auride ion and the yellow color of metallic gold. Due to the relativistic expansion of the 5d and contraction of the 6s orbitals, there is considerable interaction between formally nonbonded gold atoms held at distances larger than the 2.88-Å distance found in the metal. A small positive Au–Au overlap population of 0.0435 has been calculated[2] for an Au_2^{2+} unit at an Au–Au separation of 3.04 Å. Also, aggregates of LAu^IX neutral molecules with short (3.07–3.72 Å) Au–Au intermolecular separations have been observed.[3] The commonness of 2-coordinate linear Au^I species is attributed to the spin–orbit coupling, which gives a large separation between the $p_{1/2}$ and $p_{3/2}$ functions. It has been proposed[4] that a role of gold in the antiarthritic drugs is to promote the quenching of singlet oxygen (through intersystem crossing by spin–orbit coupling).

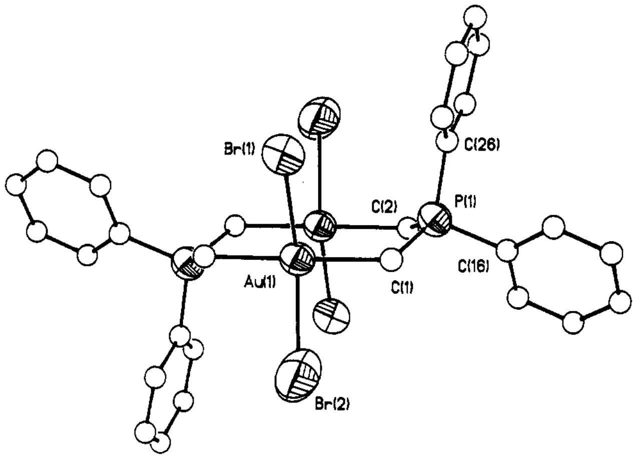

Figure 1. Structure of *trans,trans*-$[Au(CH_2)_2PPh_2]_2Br_4$ (**1**). Thermal ellipsoids are drawn at the 50% probability level. Carbon atoms are given arbitrary radii. Important distances (Å) and angles (deg): Au···Au = 3.069 (2), Au–Br(1) = 2.535 (4), Au–Br(2) = 2.576 (4), Au–C(1) = 2.10 (2), Au–C(2) = 2.15 (3); Br(1)–Au–Br(2) = 149.5 (2), C(1)–Au–C(2) = 178.2 (10), Br(1)–Au–C(1) = 92.5 (6), Br(1)–Au–C(2) = 87.1 (7), Br(2)–Au–C(1) = 89.3 (6), Br(2)–Au–C(2) = 91.9 (7).

The dimeric Au^{III}–tetrabromide complex *trans,trans*-$[Au(CH_2)_2PPh_2]_2Br_4$ (**1**)[5] crystallizes in the monoclinic space group $P2_1/c$ with a half-molecule per asymmetric unit.[6] The other half of the molecule is generated by a center of symmetry located midway between the two gold atoms. The structure of complex **1** described here is a new conformation of an already known species. The first reported structure[7] of this material, also centrosymmetric, belongs to the space group $C2/c$ and contains an interstitial molecule of $CDCl_3$. In each of these crystallographically characterized conformations of complex **1** the eight-membered organometallic ring is in a chair conformation (C_{2h} symmetry), typical of these complexes[8] (Figure 1), with the phosphorus atoms at the tips of the chair and unexceptional bond lengths and angles. Some notable differences between the $C2/c$ and the $P2_1/c$ structures are seen in the geometries of their Au_2Br_4 portions (Figure 2). The Au_2Br_4 unit of the new $P2_1/c$ structure is planar within 0.016 Å, with an Au···Au distance of 3.069 (2) Å, and long Au–Br bonds of 2.535 (4) and 2.576 (4) Å. The shortest Br···Br distance is between two syn-Br atoms, 4.419 (7) Å. The C–Au–C unit is linear, as expected, but the "trans" Br–Au–Br angle is a remarkable 149.5 (2)°, bisected by the Au–Au axis. This geometry is halfway between an ideal 4-coordinate, square-planar Au^{III} center (Br–Au–Br = 180°) and a 5-coordinate, trigonal-bipyramidal structure (Br–Au–Br = 120°). The latter would require the existence of an Au–Au bond in the equatorial plane occupying the fifth coordination site. The observed deviation from

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(5) To 17 mg of $(\mu\text{-}CH_2)[Au(CH_2)_2PPh_2]_2Br_2$[20] in 3 mL of CH_2Cl_2 was added a 2-fold excess of Br_2, and the reaction mixture was stirred for 3 h at room temperature. The solvent and the Br_2 excess were removed under vacuum, and the yellow product, **1**, was washed twice with hexane. Yellow-orange crystals suitable for a crystallographic study were grown by slow diffusion of Et_2O into a CH_2Cl_2 solution of **1**; yield 10 mg, ca. 50%.

(6) Crystal data: monoclinic, $P2_1/c$ (No. 14), a = 8.465 (4) Å, b = 16.274 (5) Å, c = 11.500 (4) Å, β = 95.35 (3)°, V = 1577 (1) Å^3, Z = 2. A total of 2318 unique reflections ($0 < 2\theta < 45°$), 1475 of which had $F_o^2 > 3\sigma(F_o^2)$, were measured at 22 °C with a Nicolet R3m/E automated four-circle diffractometer with graphite-monochromated Mo Kα radiation using the ω–2θ technique. No symmetry-equivalent reflections were collected. The data were corrected for Lorentz and polarization effects and standard decay. An empirical absorption correction based on azimuthal scans was applied. The structure was solved by the Patterson method and refined by using SHELXTL (Version 5.1) software. Refinement of 139 parameters converged to conventional R values of R = 0.057 and R_w = 0.057 with a goodness-of-fit indicator of 1.630.

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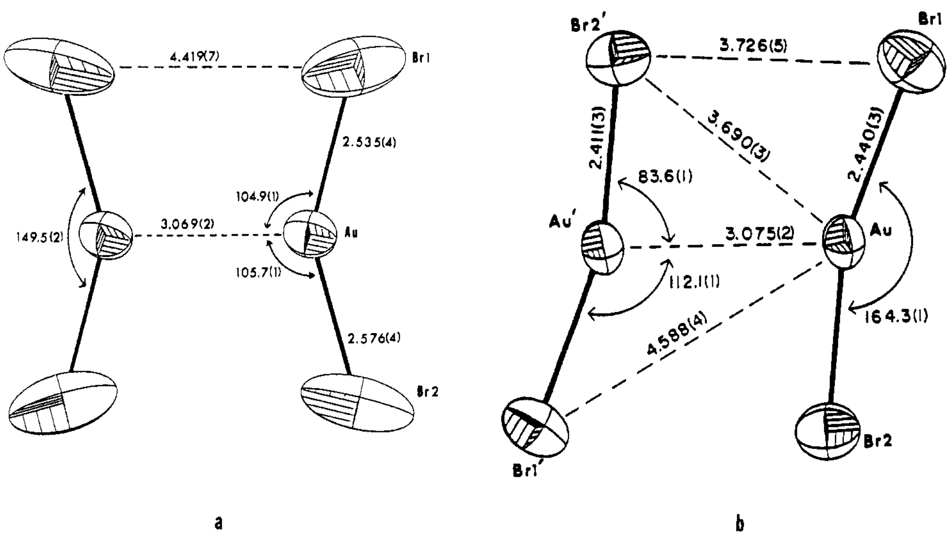

Figure 2. (a) Au_2Br_4 part of the $P2_1/c$ structure of **1**. (b) Au_2Br_4 part of the $C2/c$ structure of **1** (adapted from ref 7).

a square-planar geometry is too large to be accounted for by packing forces influencing the Br atom positions.

It can be argued that the square-planar → trigonal-bipyramidal deformation observed here in the $P2_1/c$ structure might be caused by intramolecular Br–Br repulsions. This argument is dismissed for two reasons. (a) The distance between the syn-Br atoms, 4.419 (7) Å, is considerably longer than the sum of van der Waals radii[9] for these atoms, 3.70 Å. A much shorter distance, 3.726 (5) Å, was measured in the $C2/c$ structure[7] for these atoms. (b) In structures of similar compounds with bulky ligands, such as in *trans,trans*-$[Au(CH_2)_2PPh_2]_2(CCl_3)Cl_3$[10] and *trans,trans*-$[Au(CH_2)_2PPh_2]_2(CHCl_2)Br_2Cl$,[11] the organometallic ring relieves the steric crowding of the eclipsed conformation by adopting a twist-chair configuration and retaining the square-planar geometry about the gold atoms. A comparison of the Au–Br bond lengths in the two structures of **1** shows an average lengthening of these bonds by 0.130 (5) Å for the $P2_1/c$ structure. With no other apparent reason for this observation, the longer Au–Br bonds of the $P2_1/c$ structure are attributed to an increase of the coordination number of the metal. However, a statistically significant shortening of the Au–Au distance, consistent with the hypothesis of 5-coordination, is not observed.

The large thermal ellipsoids of the bromine atoms indicate substantial vibrations in the Au_2Br_4 plane. When corrected for libration,[12] the Au–Br bond lengths are 2.638 and 2.711 Å for Br(1) and Br(2), respectively.

The isostructural $P2_1/c$ *trans,trans*-$[Au(CH_2)_2PPh_2]_2Cl_4$ complex[13] shows the same trigonal-bipyramidal distortion with a Cl–Au–Cl angle of 154°, long Au–Cl bonds of 2.36 Å, and a Au⋯Au distance of 3.06 Å.

Five-coordinate species are known in Au^{III} chemistry.[14] They all have geometries best described as square-pyramidal, with rigid bidentate ligands, such as 1,10-phen,[15] occupying one axial and one equatorial site. However, as the Au–axial ligand distance is much longer than the bonds to the equatorial ligands, the occupation of the axial site can be thought of as a sterically forced interaction rather than coordination. Some of these 5-coordinate species show a fluxional behavior (axial–equatorial interchange of the bidentate ligand), which is evident by a trigonal-bipyramidal distortion in the solid-state geometry.[16] No trigonal-bipyramidal Au^{III} complexes with monodentate ligands are known.

The trigonal-bipyramidal geometry of complex **1** has interesting implications for the bonding of dimeric gold complexes. A qualitative valence-bond description is useful here. For an Au^{III} atom to change its coordination from square planar, utilizing a dsp^2 manifold, to trigonal bipyramidal, the participation in the bonding scheme of one more metal orbital is required. In a d^8 Au atom, this additional orbital can be a filled 5d orbital. Therefore, one more bonding–antibonding pair of orbitals, both filled, is added to the bonding scheme of the digold system, which is now utilizing d^2sp^2 orbital manifolds. The HOMO, which in this scheme is antibonding with respect to the Au⋯Au axis, may be stabilized by interaction with the remaining (empty) 6p orbitals on the Au^{III} centers. The $dsp^2 \rightarrow d^2sp^2$ transformation also relieves the repulsion of the $5d_{z^2}$ orbitals of the d^8 Au^{III} centers. As the coordination number increases, the bonding of the ligands is affected. This results in the unusually long Au–Br bonds found in the $P2_1/c$ structure of complex **1**. The trigonal-bipyramidal geometry of the cofacial Au^{III} dimer **1** sets it apart from the isoelectronic Pt^{II} cofacial dimers and stacked monomers, all of which have square geometry.[17] The Pt–Pt interactions in these systems are assisted by d–p orbital mixing along the direction of the Pt–Pt axis. In the case of gold, it is possible that due to its more pronounced relativistic effects,[1] the 6p functions are significantly separated in energy, resulting in facile mixing of 5d orbitals with two of the three 6p orbitals (d^2sp^2), leaving the third available for mixing with the HOMO along the Au⋯Au axis.

The proposed bonding scheme for the Au^{III} atoms of complex **1** has an important implication for the chemistry of these dimers. It suggests that a (hypothetical) Au^{IV} dimer should have a trigonal-bipyramidal geometry around the metal atoms with a metal–metal bond in the equatorial plane. No Au^{IV} species are presently known, even though an Au^{V} compound has been characterized.[18] Some isoelectronic Pt^{III} singly bonded dimers with octahedrally coordinated platinum atoms are known.[19]

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(13) Crystal data for *trans,trans*-$[Au(CH_2)_2PPh_2]_2Cl_4$: monoclinic, $P2_1/c$, $a = 8.29$ (1) Å, $b = 16.26$ (2) Å, $c = 11.36$ (3) Å, $\beta = 95.0$ (2)°, $V = 1526$ (5) Å^3, $Z = 2$, 1185 unique reflections ($0 < 2\theta < 30°$), 330 reflections with $F_o^2 > 3\sigma(F_o^2)$, 69 refined parameters, $R = 0.054$. Although the data available have prevented the development of an accurate full structure, we believe that the heavy-atom positions are well defined.

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Supplementary Material Available: Listings of crystallographic parameters, atomic coordinates, isotropic and anisotropic thermal parameters, bond distances and angles, and hydrogen coordinates and isotropic thermal parameters for **1** (6 pages); a listing of observed and calculated structure factors for **1** (12 pages). Ordering information is given on any current masthead page.

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Intercalation in the Linear-Chain Compound $MoO_2HPO_4{\cdot}H_2O$

The structure of hydrated molybdenyl hydrogen phosphate, $MoO_2HPO_4{\cdot}H_2O$ consists of bent MoO_2 groups coordinated by water molecules and linked into double chains by tetrahedral PO_3OH units. This one-dimensional material has been shown to undergo reversible intercalation reactions with a variety of small organic molecules, particularly alcohols, and water to form new crystalline phases in which the molybdenyl phosphate chains remain essentially unaltered. The molybdenum coordination in the host is approximately octahedral with three bonds to hydrogen phosphate groups, a trans pair delineating the chain, and the other in the $MoO_2(OH_2)$ plane connecting to the other half of the double chain.[1] Powder X-ray diffraction and infrared data demonstrate that the intercalated species are hydrogen-bonded between the inorganic chains.

$MoO_2HPO_4{\cdot}H_2O$[1] shows structural similarities to $UO_2HPO_4{\cdot}H_2O$,[2] β-$VOHPO_4{\cdot}2H_2O$,[3] $Zr(HPO_4)_2{\cdot}nH_2O$,[4] and particularly $VOHPO_4{\cdot}4H_2O$,[5] where tetrahedral (hydrogen) phosphate groups link together the approximately octahedrally coordinated transition metals. As the metal oxidation state rises in this family of compounds, the coordination environment of the metal ion becomes increasingly distorted, with one short vanadium–oxygen bond in β-$VOHPO_4{\cdot}2H_2O$ and two molybdenum–oxygen double bonds in $MoO_2HPO_4{\cdot}H_2O$. The uranium and zirconium materials together with β-$VOHPO_4{\cdot}2H_2O$ have two-dimensional layer structures, but $VOHPO_4{\cdot}4H_2O$ has a double-chain structure similar to that of molybdenyl hydrogen phosphate. Intercalation reactions with a range of small organic molecules[6–9] are well-known in this type of compound. For example, materials of composition $VOPO_4{\cdot}(1{-}2)ROH$ may be synthesized from anhydrous $VOPO_4$ via a vapor-phase reaction with ROH; the alcohol molecules in these intercalates may be displaced by water. Other vanadium compounds that undergo intercalation reactions with alcohols are vanadium organophosphonates[10,11] and layered vanadium sulfates.[12]

Table I

intercalated species	reacn time at 298 K in vapor	stoichiom of product
H_2O	3 days	$MoO_2HPO_4{\cdot}3.9(\pm0.1)H_2O$
CH_3OH	3 days	$MoO_2HPO_4{\cdot}H_2O{\cdot}2.0(\pm0.2)CH_3OH$
CH_3OH	3 days and 1 h (air)	$MoO_2HPO_4{\cdot}H_2O{\cdot}1.0(\pm0.05)CH_3OH$
CH_3CH_2OH	1 month	$MoO_2HPO_4{\cdot}H_2O{\cdot}0.6(\pm0.1)CH_3CH_2OH$
$(CH_3)_2CHOH$	3 months	$MoO_2HPO_4{\cdot}H_2O{\cdot}1.0(\pm0.1)$-$(CH_3)_2CHOH$

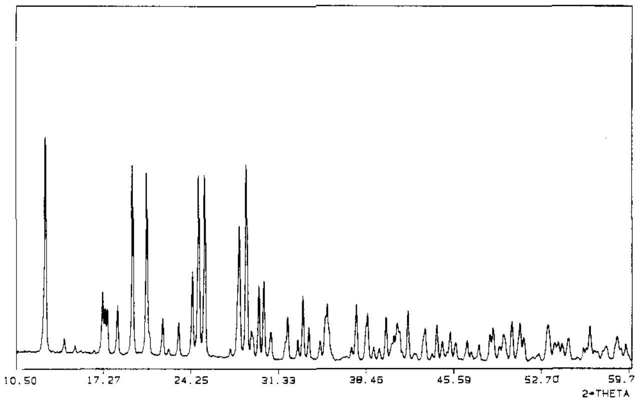

Figure 1. Powder X-ray diffraction data collected from $MoO_2HPO_4{\cdot}4H_2O$ in the 2θ range 10–60° with Cu $K\alpha_1$ radiation.

$MoO_2HPO_4{\cdot}H_2O$ was prepared by following the method described by Kierkegaard.[13] The intercalation of alcohols and additional water was achieved by equilibration of the crystalline solid with the vapor above the liquid in a closed apparatus. Reactions with water and methanol vapor were generally complete within 3 days; however, reactions with the larger species (ethanol, 2-propanol) took several weeks. Heating $MoO_2HPO_4{\cdot}H_2O$ with DMSO resulted in a different type of reaction, in which water was displaced from the solid. The progress of the reaction was most easily followed by using Raman spectroscopy. Although minor shifts (10–15 cm^{-1}) were observed in most cases, the bands are strong and sharp; particularly diagnostic in determing the extent of reaction is the disappearance of the substrate band at 885 cm^{-1} (presently unassigned), which is not observed in any of the intercalates.

Successful reactions have been achieved with a large range of alcohols and amines, but we report here our results for the better characterized water, methanol, ethanol, and 2-propanol intercalates. Table I summarizes the stoichiometry of the intercalation products as determined from weight changes during the uptake reaction, with thermogravimetric and C, H, N analyses. For methanol an initial product of approximate formula $[MoO_2HPO_4{\cdot}H_2O].2CH_3OH$ was converted to a more stable 1:1 intercalate at 30 °C after 1 h in air. In general for the alcohol intercalates the initial product seemed to undergo further slow transformations when removed from the saturated vapor.

Powder X-ray diffraction data were collected for each of the materials with use of an INEL position sensitive detector based system. The data obtained for the higher hydrate $[MoO_2HPO_4{\cdot}H_2O]{\cdot}3H_2O$ is shown in Figure 1. A feature of all the diffraction patterns, including the parent material, is a strong reflection at approximately 28.1° (*d* spacing 3.152 Å), which

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