Gold Rings That Do Not Glister. The Crystal and Molecular Structures of Two Novel Gold(II) Compounds Containing 12- and 13-Atom Gold-Sulfur Rings, [Au(CH$_2$)$_2$P(C$_6$H$_5$)$_2$]$_2$S$_8$ and [Au(CH$_2$)$_2$P(C$_6$H$_5$)$_2$]$_2$S$_9$

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Although the coordination chemistry of anionic polysulfide ligands is well established, much of the work in this area has focused on cluster compounds containing small sulfide groups frequently bridging two or more transition-metal centers.[1] There are, however, several examples of transition-metal complexes containing four- and five-atom sulfur linkages,[2] and in a limited number of instances, complexes containing nine- and eleven-atom polysulfide chains have been prepared and characterized.[3,4] Large (more than six atoms), neutral (hydrocarbon soluble) ring structures containing catenated sulfur and metal atoms appear to be rather rare, the largest heretofore described apparently being the eight-atom ring in [(MeCp)$_2$TiS$_3$]$_2$.[2] The importance of metal-sulfide chemistry in industrial, environmental, and biological systems continues to make new developments in this field of interest. Therefore we report here the synthesis and structural characterization of two hydrocarbon-soluble ring compounds containing both catenated sulfur and catenated gold. These 12- and 13-atom ring structures are the largest metal-sulfur rings formed to date.

The addition of approximately equimolar amounts of aqueous ammonium polysulfide solutions to the gold(II) ylide dimer [Au(CH$_2$)$_2$P(C$_6$H$_5$)Br]$_2$ (1) in tetrahydrofuran results in the immediate formation of a red product 2 in about 60% yield.[16] Upon crystallization from dichloromethane/diethyl ether solutions, this product has the structure shown in Figure 1. The addition of solid Na$_2$S to 1 in tetrahydrofuran, however, results in the formation of, among several things, the minor hydrated product 3, whose structure is shown in Figure 2. This same product without water can also be obtained in good yield (>70%) by reacting a dinuclear gold(II) benzoate complex, [Au(CH$_2$)$_2$P-(C$_6$H$_5$)$_2$(C$_6$H$_5$CO$_2$)]$_2$ (4), with H$_2$S in THF at room tempera-

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(16) A 90-MHz NMR spectrum of this complex was essentially featureless but did show a broad multiplet with a $w_{1/2}$ of approximately 15 Hz at 1.5 ppm. Resonances in this region are typically indicative of the presence of gold(II) species, but more detailed information was not obtainable.
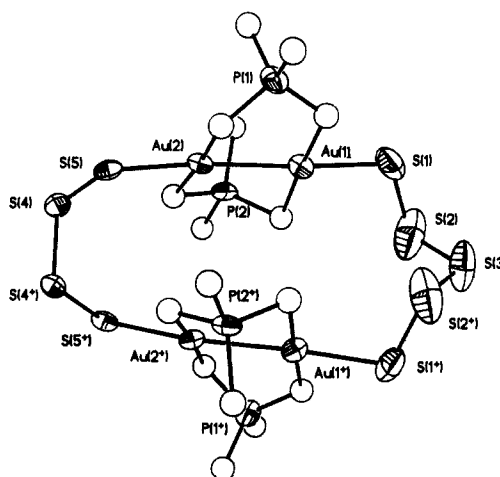
Figure 1. Perspective drawing of the dimeric gold(II) ylide adduct containing four- and five-atom polysulfide bridges. Thermal ellipsoids have been drawn at the 50% probability level; carbon atoms have been given arbitrary thermal parameters and phenyl rings have been omitted for clarity. Au1-Au2 = 2.649 (9) Å; Au1-S1 = 2.420 (25) Å; Au(2)-S(5) = 2.431 (20) Å; average S-S distance = 2.028 (40) A.
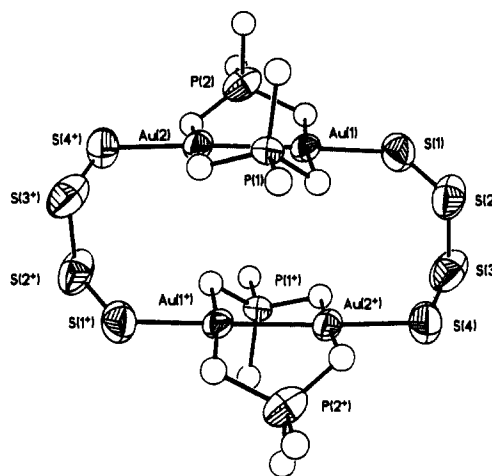

Figure 2. View of the more symmetrical gold(II) ylide dimer containing two four-atom bridging polysulfide ligands. Carbon atoms have been given arbitrary thermal parameters and phenyl rings have been omitted for clarity. A view of the molecule of water has not been included. Au1-Au2 = 2.662 (1) Å; Au1-S1 = 2.395 (10) Å; Au2-S4 = 2.358 (9) Å; average S-S distance = 1990 (15) Å.

ture.[15] All of these products form deep red regularly shaped crystals that are readily distinguishable on the basis of external appearance. Intensely colored red solutions of these complexes are obtained upon dissolution in organic solvents.

The structures of the complexes described here were determined from intensity data collected at room temperature on a Nicolet R3m/E diffractometer. Structure solution and refinement were carried out by using the SHELXTL collection of crystallographic software.[5] Compound 2 crystallizes in the orthorhombic space group *Pncn* with Z = 4, a = 14.814 (13) Å, b = 17.211 (4) Å, c = 28.217 (14) Å, and V = 7194 (7) Å^3. Final conventional R values of R = 0.0716 and R_w = 0.0734 were obtained by using 1113 reflections with $I > 3\sigma(I)$. The more symmetrical structure, 3, obtained from Na$_2$S crystallizes in the space group *P*$\bar{1}$ with a single centrosymmetric molecule in a cell with lattice parameters a = 10.700 (3) Å, b = 13.060 (4) Å, c = 13.872 (5) Å, α = 117.76 (2)°, β = 98.47 (2)°, γ = 95.60 (2)°, and V = 1665.7 (8) Å^3. Convergence to final R values of R = 0.0660 and R_w = 0.0698 was obtained by using 2669 reflections with $I > 3\sigma(I)$.

The structures of both 2 and 3 are similar and have in common the presence of two dinuclear gold(II) ylides. They differ in the number of sulfur atoms involved in the ring structure. The coordination geometry about the gold centers in these structures is

Table I. Comparison of S–S Bond Lengths in Systems Containing S₄ Ligands

	S(1)–S(2)	S(2)–S(3)	S(3)–S(4)	ref
[Au(CH₂)₂P(C₆H₆)₂]₂S₈	1.991 (13)	1.907 (19)	2.036 (14)	this work
[Au(CH₂)₂P(C₆H₆)₂]₂S₉	2.041 (29)	2.017 (40)	2.041 (29)	this work
(Ph₃P)₂PtS₄	2.024 (8)	2.022 (10)	2.081 (10)	8
[AsPh₄][Mo₂S₁₀]⁽ᵃ⁾	2.019 (5)	1.970 (6)	2.115 (5)	9
[AsPh₄][Mo₂S₁₀]⁽ᵃ⁾	2.096 (16)	1.936 (19)	2.169 (14)	10
(Et₄N)₂MoS₄	2.107 (1)	2.012 (1)	2.166 (1)	11
(μ⁵-C₅H₅)₂MoS₄	2.081 (8)	2.018 (9)	2.085 (7)	12
(μ⁵-C₅H₅)₂WS₄	2.105 (7)	2.016 (8)	2.116 (9)	13
BaS₄·H₂Oᵃ	2.069 (4)	2.063 (4)	2.069 (4)	14
BaS₄·H₂Oᵃ	2.079 (3)	2.062 (4)	2.079 (3)	14

ᵃ Two or more crystallographically different S₄ groups per molecule.

best described as square-planar. Within each dinuclear gold(II) ylide a discrete gold–gold bond is formed. The overall configuration of the ylide units in both complexes is that of a twisted boat; other structural features of the ylide groups are unexceptional and will not be discussed further here except to note that both chair and boat configurations are typically observed in these systems.[6,7]

The geometries of the polysulfide groups in the structures described here are similar to those observed in other transition-metal–polysulfide systems. The S–S–S bond angles range from 104 (7)° to 111 (8)° and are well within the range normally observed in other transition-metal complexes containing large polysulfide ligands. The sulfur–sulfur bond distances observed in the S₄ linkages of both complexes show the alternation in length occasionally observed in other systems and range from 1.907 (19) to 2.036 (19) Å. The very short 1.907 (19) Å bond formed between S2 and S3 in **3** is an extreme example of this phenomenon and is, in fact, one of the shortest S–S bonds documented in the chemical literature (Table I).

The coordination behavior of the polysulfide ligands in both of these complexes is quite unusual. Only in a limited number of instances have polysulfide ligands been observed to bridge two or more transition-metal centers. Because of the large number of atoms involved in forming these heterocyclic ring systems, these adducts are the largest closed-ring metal–sulfide structures reported to date.

Of interest structurally in these complexes are the nonbonding inter- and intramolecular contacts. In the product containing four- and five-atom sulfur bridges, the intradimer metal distances measure 4.493 (8) and 4.633 (8) Å for Au1–Au1′ and Au2–Au2′, respectively. In the smaller adduct containing two four-atom sulfur bridges, the crystallographically imposed inversion center makes the corresponding distances equal at 4.457 Å. In the crystal lattice of **3** we find no particularly unusual nonbonding contacts. However, in the orthorhombic lattice of **2** we find S2 of one molecule to be only 3.2303 (3) Å away from S5 in an adjacent molecule; a distance 0.37 Å less than the sum of their van der Waal's radii.

It is interesting that the less symmetrical 13-atom complex **2** is obtained in good yield (>50%) as the principal (almost sole) product obtained by using an aqueous solution containing an equilibrium distribution of anions. In contrast, the reaction involving solid Na₂S results in several as yet uncharacterized products but includes, in small yield (<5%), **3**. The reaction of H₂S with the gold(II) benzoate dimer, however, does produce **3** in nearly quantititiave yield, and hydrogen has been identified in a GC analysis of the reaction. The linear S–Au–Au–S geometry in these adducts plays a role in determining the most stable ring size; however, the reasons behind the preferential formation of the 13-atom product remain unclear at this point. Because of the unusual nature of these complexes and their reactivity with H₂S, both their physical properties and chemical reactivities are currently being examined.

Supplementary Material Available: Lists of fractional atomic positional parameters, thermal parameters, bond length and angle data, hydrogen atom parameters, details of the crystallographic experimental procedures, and tables of observed and calculated structure factors amplitudes (42 pages). Ordering information is given on any current masthead page.

On the Rate-Determining Step in the Epoxidation of Olefins by Monooxygenase Models

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Received September 23, 1985

Currently, synthetic metalloporphyrins are receiving considerable interest as models of the cytochrome P-450 class of enzymes.[1] With single oxygen donors, e.g., iodosylbenzene,[1a] amine oxides,[1b] and hypochlorite,[2] these compounds form high-valent oxometal complexes (e.g., **2**), which, like the monooxygenases, are capable of oxygenating hydrocarbons. Recently, kinetic studies have appeared that deal with the mechanism of hydrocarbon oxidation by cytochrome P-450 models.[3–6] In some of these studies it was proposed that the rate-limiting step in the reaction is the formation of the high-valent oxometal complex.[3,5] In other studies, however, it was suggested that the rate-determining process is the transfer of oxygen from the oxometal complex to the substrate.[4] We wish to point out here that (i), in certain cytochrome P-450 model systems, dimerization of the active metalloporphyrin may occur and (ii) that this dimerization reaction has consequences for the kinetic analysis of the systems.[7] We will illustrate this point for the epoxidation of olefins by the monooxygenase model manganese(III) porphyrin with sodium hypochlorite as oxidant in the two-phase system water–dichloromethane (Meunier system[2]). With regard to the rate-determining step in this model, conflicting opinions exist.[4,5]

Previously, we reported that the epoxidation of cyclohexene by Mnᴵᴵᴵ(TPP)OAc and NaOCl is zero order in substrate.[5,8] Depending on the concentration of oxidant, the reaction order in hypochlorite varies between zero and one. We proposed that the rate-determining step in the catalytic process is the conversion of manganese(III) hypochlorite species **1** into the oxomanganese complex **2**.[5] This step is catalyzed by pyridine. Collman et al. recently measured the rate of epoxidation by Mnᴵᴵᴵ(TPP)Cl and LiOCl for various olefins and likewise reported that the order in

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(8) Abbreviations: TPP = *meso*-tetraphenylporphyrinato; TPP = *meso*-tetra-p-tolylporphyrinato; TMP = *meso*-tetramesitylporphyrinato; TTMeOPP = *meso*-tetrakis(2,4,6-trimethoxyphenyl)porphyrinato; TMeOPP = *meso*-tetrakis(4-methoxyphenyl)porphyrinato; TFPP = *meso*-tetrakis(4-fluorophenyl)porphyrinato.