orbitals on CO. Since the π-orbitals on CO are C–O antibonding, population of these orbitals results in lowering of ν_{CO}. The lowering of ν_{CO} may be expressed in valence bond language by the two resonance structures.

$$\mathrm{Cp_3U{\leftarrow}\overset{-}{C}{\equiv}\overset{+}{O} \leftrightarrow Cp_3U{=}C{=}O}$$

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Supplementary Material Available: Listing of postional parameters, general temperature factors, and rms amplitudes of thermal vibration, ORTEP diagrams of the four molecules in the unit cell, tables of bond lengths and angles, crystal data and method of solution, and structure factor tables for $(Me_3SiC_5H_4)_3UCNEt$ (48 pages). Ordering information is given on any current masthead page.

Synthesis and Structure of $[Au_6(o\text{-}CH_3C_6H_4CS_2)_6]$, a Novel Gold Cluster Compound

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Gold cluster compounds have been known for two decades, but only recently has research accelerated in this area, spurred on perhaps by the potential catalytic activity of such clusters. Beyond the relatively common dinuclear compounds containing two univalent linearly coordinated gold species, there is a growing number of compounds containing the Au_n^{x+} species with Au–Au bonds and an average oxidation state <1, where n = 4, 5, 6, 8, 9, 11, 13 (and at least one compound with n = 55) and x = 2 or 3.[1] The attached ligands are organophosphines and occasionally halide. Very recently[2] a tetranuclear dithioacetate (dta) complex, $[Au_4(dta)_4]$, was prepared and its X-ray structure showed it to contain four nearly equivalent Au–Au distances (averaging 3.013 Å) with the four gold(I) atoms at the vertices of a rhombus. An analogous dithiobenzoate (dtb) complex, Au(dtb), was also prepared,[2] but its structure could not be obtained.

Previously known compounds containing an Au_6 cluster have been either octahedra, as in $Au_6[P(p\text{-}CH_3C_6H_4)_3]_6^{2+}$,[3] or edge-sharing bitetrahedra, as in $\{Au_6[P(C_6H_5)_3]_6\}(NO_3)_2$,[4] and molecular orbital calculations have been completed[5] for such clusters where the metal atoms are situated on the surface of a regular polyhedron.

We now report the synthesis and crystal structure[6] of an entirely new type of gold cluster in which the six gold atoms in the (o-methyldithiobenzoato)gold(I) complex, $[Au_6(o\text{-}CH_3C_6H_4CS_2)_6]$, lie nearly in a plane with the bidentate ligands each attached to neighboring gold atoms and lying alternately above and below the plane.

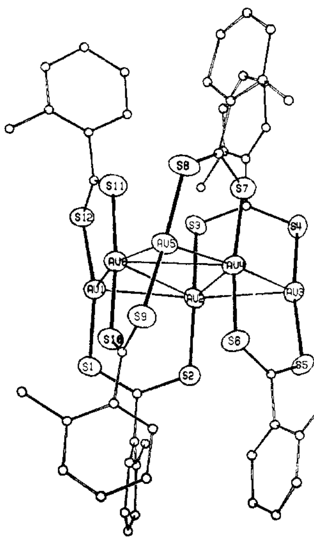

Figure 1. Gold hexamer, giving numbering scheme for Au and S. C atoms are arbitrarily small, and H atoms are omitted.

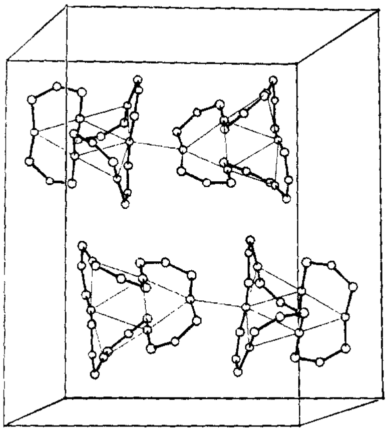

Figure 2. Unit cell, illustrating chains of hexamers along *c* axis, horizontal. Only S–C–C portions of ligands are shown.

The new gold compound was prepared by addition of $NaAuCl_4{\cdot}2H_2O$ to the $(n\text{-}Pr)_4N^+$ salt of the ligand, each dissolved in DMF, in a 2:1 ligand-to-metal molar ratio. A reddish orange solid separated after the warmed, stirred solution stood overnight. Dark red needles of the hexamer were formed by slow evaporation of a CS_2 solution.

The gold hexamer is illustrated in Figure 1. The six gold atoms of the central cluster are coplanar to within 0.14 Å. The odd-numbered Au atoms lie at the vertices of a triangle which is approximately equilateral with side 5.94 Å. The even-numbered Au atoms lie slightly outside the lines connecting these vertices, such that Au–Au distances around the periphery average 2.987 Å and alternate angles average 169.3° and 69.5°. The even-numbered Au atoms thus form a central triangle with edges Au2–Au4 3.240 (1), Au2–Au6 3.547 (1), and Au4–Au6 3.421 (1) Å. Each Au(I) forms two bonds in near linear fashion (S–Au–S angles range 160.7 (2)–174.6 (2)° and average 167.3°) to bridging ligands alternately above and below the cluster plane. Au–S distances range 2.283 (5)–2.305 (5) Å and average 2.296 Å. This ligand bridging pattern is analogous to that found in the tetramer $Au_4(dta)_4$, in which Au–Au distances average 3.013 Å, Au–S distances average 2.296 Å, and S–Au–S angles average 167.7°.[2]

The ligands are distinctly nonplanar. Aromatic rings are rotated with respect to dithiocarboxylate planes by angles ranging 60.4–87.1°, presumably as a result of the steric effects of 2-methyl substitution.

In addition to the multitude of Au–Au interactions within the hexameric cluster, a close intermolecular contact (Au3–Au6′, 3.195 (1) Å) exists, forming chains of hexamers along the direction

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(6) $(AuC_8H_7S_2)_6$, monoclinic $P2_1/c$, a = 14.803 (2) Å, b = 22.070 (3) Å, c = 17.464 (4) Å, β = 104.45 (1)°, Z = 4, R = 0.039 for 4250 observations.

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of the *c* axis, which is the needle axis. Segments of two parallel chains are illustrated in Figure 2.

Supplementary Material Available: An experimental section plus tables of selected interatomic distances, selected bond angles, coordinates, coordinates for H atoms, and anisotropic thermal parameters (5 pages). Ordering information is given on any current masthead page.

New $[Fe_6S_6Cl_6(Mo(CO)_3)_2]^{n-}$ Clusters (n = 3, 4). Derivatives of either $[Fe_6S_6Cl_6]^{3-}$ or $[Fe_4S_4Cl_4]^{2-}$ with Possible Relevance to the Fe/Mo/S Center in Nitrogenase

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On the basis of analytical[1] and spectroscopic[2–4] data numerous structures have been proposed[5] for the unique Fe/Mo/S centers in nitrogenase[6] and the nitrogenase cofactor[7] (FeMoco). The design and synthesis of models for these centers must be directed by, and confined within, the constraints imposed by the available data. Our studies at present are directed toward the synthesis of analogue Fe/Mo/S clusters with Fe/Mo/S ratios of 6-7/1/6-8 and structures compatible with the Mössbauer,[2] EXAFS,[3] and ENDOR[4] characteristics of the heterometallic centers in nitrogenase and the nitrogenase cofactor.

Recently we reported on the synthesis and spectroscopic properties of the $[Fe_6S_6(OAr)_6(Mo(CO)_3)_2]^{3-}$ complex anion.[8] This cluster was obtained by the addition of two $Mo(CO)_3$ fragments to the $[Fe_6S_6(OAr)_6]^{3-}$ "prismane".[9b] We were unable to obtain single crystals for this compound for a structure determination. However, on the basis of elemental analysis and EPR, NMR, Mössbauer, and electronic spectroscopic data we proposed a heterometallic Pentlandite-type of structure for this compound with a $[Fe_6Mo_2S_6]^{3+}$ core.

In this paper, we report on the synthesis and spectroscopic properties of the structurally analogous $[Fe_6S_6Cl_6(Mo(CO)_3)_2]^{n-}$ anions (n = 3, 4) and the crystal structures of the Et_4N^+ and Ph_4P^+ salts of the $[Fe_6S_6Cl_6(Mo(CO)_3)_2]^{4-}$ tetraanion.

The reaction of $(CH_3CN)_3Mo(CO)_3$ with $(Et_4N)_3Fe_6S_6Cl_6$ in CH_3CN, at ca. 60 °C for 20 min, in a 2:1 molar ratio occurs readily. Upon filtering, dilution with ether, and standing, the reaction solution affords a black crystalline product. Upon recrystallization, crystals of $(Et_4N)_4[Fe_6S_6Cl_6(Mo(CO)_3)_2]$ (I) are isolated in 40% yield. The IR spectrum of I shows two CO stretching vibrations at 1896 and 1834 cm^{-1} and suggests the presence of $Mo(CO)_3$ units with C_{3v} microsymmetry. The electronic spectrum of I in CH_3CN solution shows only a shoulder at 470 nm, and no EPR signals were detected from a frozen CH_3CN solution at 9 K.

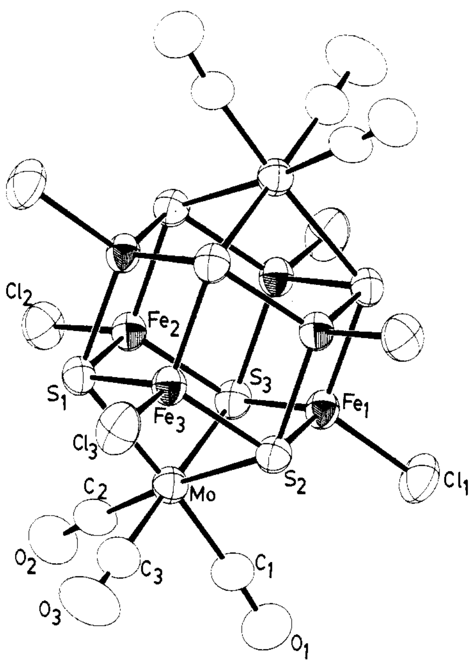

Figure 1. Structure and labeling of the anions in I and II. Thermal ellipsoids as drawn by ORTEP (Johnson, C. K., ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, TN, 1965) represent the 40% probability surfaces.

Table I. Selected Distances[a] (Å) and Angles (deg) in the $(Ph_4P)^+$ (A) and $(Et_4N)^+$ (B) Salts of the $[Fe_6S_6Cl_6[Mo(CO)_3]_2]^{4-}$ anions and the $[Fe_6S_6Cl_6]^{n-}$ Prismanes, n = 3 (C), n = 2 (D)

	A	B	C^b	D^c
		Distances		
Fe–Fe^d	3.766 (3, 11)	3.785 (3, 10)	3.790 (3, 8)	3.791 (6, 5)
Fe–Fe^e	2.747 (3, 14)	2.761 (3, 10)	2.765 (3, 3)	2.757 (6, 5)
Fe–S^d	2.333 (3, 3)	2.333 (3, 3)	2.284 (3, 3)	2.268 (6, 8)
Fe–S^e	2.284 (6, 6)	2.286 (6, 5)	2.272 (6, 2)	2.254 (12, 8)
Mo–Fe	2.99 (3, 2)	3.005 (3, 11)		
Mo–S	2.608 (3, 6)	2.619 (3, 3)		
Mo–C	1.943 (3, 13)	1.958 (3, 11)		
		Angles		
Fe–S–Fe^d	111.1 (3, 6)	111.8 (3, 5)	113.2 (3, 3)	114.5 (6, 6)
Fe–S–Fe^e	73.0 (6, 3)	73.4 (6, 2)	74.7 (6, 1)	75.1 (12, 4)
S–Fe–S^d	113.2 (3, 5)	113.0 (3, 4)	113.7 (3, 3)	112.0 (6, 9)
Fe–Mo–F^e	78.1 (3, 3)	78.07 (3, 2)		
Fe–S–Mo	75.0 (6, 4)	75.2 (6, 3)		
S–Mo–S	93.9 (3, 6)	93.4 (3, 2)		

[a] See Figure 1 for the labeling scheme. The mean values of chemically equivalent bonds are given. In parentheses the first entry represents the number of independent distances or angles averaged out, the second entry represents the larger of the standard deviations for an individual value estimated from the inverse matrix or of the standard deviation: $\sigma = [\sum_{i=1}^{N}(x_i - \bar{x})^2/N(N-1)]^{1/2}$. [b] From ref 9b. [c] From ref 9c. [d] Distances or angles within the Fe_3S_3 structural units. [e] Distances or angles within the Fe_2S_2 rhombic units.

The crude product, as initially isolated in the synthesis of I, shows a weak EPR signal (g_x = 2.064) and two additional CO vibrations of minor intensity at 1921 and 1855 cm^{-1}. The paramagnetic, minor component that accounts for these spectral characteristics very likely is the $[Fe_6Mo_2Cl_6(Mo(CO)_3)_2]^{3-}$ trianion. The latter would be analogous to the paramagnetic, $S = {}^1/_2$, $[Fe_6S_6(p\text{-}CH_3C_6H_4O)_6(Mo(CO)_3)_2]^{3-}$ trianion for which the

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