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A Novel Bimetallic Sulfur Cluster. Crystal and Molecular Structure of a Dimer of Bis[methyldiphenylphosphinesilver]tetrathiotungsten, $[(C_6H_5)_2PCH_3]_4Ag_4W_2S_8$

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Abstract: The title compound, I, is formed from $[(C_6H_5)_2PCH_3]_4Ag_2WS_4$ (II) with loss of phosphine in polar solvents. The crystal and molecular structure of I has been determined from three-dimensional X-ray data collected by counter methods. The molecular compound I crystallizes in the monoclinic space group $P2_1/n$ with $Z = 2$ and cell dimensions $a = 11.901$ (4) Å, $b = 12.233$ (5) Å, $c = 20.375$ (10) Å, $\beta = 92.25$ (3)°. The observed and calculated densities are 2.04 and 2.08 g/cm³, respectively. The structure has been refined to a final R factor on F of 0.049 for 2096 observed reflections. The structure of I consists of a 12-atom cluster containing four silver atoms, two tungsten atoms, and six sulfur atoms; the cluster possesses a crystallographic center of symmetry. Based on ^{31}P NMR data for II and the structures of the closely related $[(C_6H_5)_2PCH_3]_2Au_2MS_4$ compounds (M = Mo, W), a mechanism for the formation of I from II is proposed.

Introduction

The chemistry of molecular metal sulfides is currently a subject of much interest. Iron–sulfur aggregates, in particular, have been closely studied because of analogies to biological electron-transfer components.[2-4] Sulfur-bridged molybdenum compounds have been scrutinized in order to learn about the role of this group 6B metal in nitrogen fixation[5] and in redox-active molybdoenzymes such as xanthine, aldehyde and sulfite oxidases, and nitrate reductase.[6,7]

Following the development of a general synthesis for bimetallic sulfur arrays of the type $L_nM_2M'S_4$ (L = tertiary phosphine; M = Cu, Ag, Au; M' = Mo, W),[8] systematic X-ray crystallographic studies have been carried out to obtain further insight into the structure and bonding of these materials. This paper reports the crystal and molecular structure of $[(C_6H_5)_2PCH_3]_4Ag_4W_2S_8$, a novel bimetallic sulfur cluster with surprisingly different architecture from that of the stoichiometric gold analogue, $[(C_6H_5)_2PCH_3]_2Au_2WS_4$.[8]

Experimental Section

Preparation of $[(C_6H_5)_2PCH_3]_4Ag_4W_2S_8$ (I). $[(C_6H_5)_2PCH_3]_4Ag_2WS_4$ (II) was prepared as previously described.[8] A solution of 0.58 g (4.4 mmol) of II in 50 mL of 1:1 acetone-1,2-dichloroethane was degassed by two freeze–pump–thaw cycles and allowed to stand at room temperature. After 7 days 0.11 g (22%) of crystalline I had separated. The crystals were washed with a small amount of 1,2-dichloroethane and vacuum dried. Anal. Calcd: C, 33.62; H, 2.80; Ag, 23.27; P, 6.68; S, 13.79; W, 19.83. Found: C, 33.64; H, 2.82; Ag, 23.24; P, 6.67; S, 13.81; W, 19.81. Recrystallization from acetonitrile yielded small, orange crystals suitable for X-ray analysis.

Unit Cell and Space Group. Precession photographs of the $h0l$, $h1l$, and $0kl$ zones indicated monoclinic symmetry with systematic absences $0k0$, $k \neq 2n$, and $h0l$, $h + l \neq 2n$, uniquely establishing space group C_{2h}^5-$P2_1/n$ [equivalent positions: $\pm(x, y, z)$; $\pm (\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$]. The cell dimensions, obtained using Mo Kα radiation ($\lambda = 0.7107$ Å) by centering 15 reflections on an automated diffractometer, are $a = 11.904$ (4) Å, $b = 12.233$ (5) Å, $c = 20.375$ (10) Å, $\beta = 92.25$ (3)°. The observed density of 2.04 g/cm³ obtained by flotation agrees with the calculated value of 2.080 g/cm³ assuming $Z = 2$ on the basis of the dimeric structure subsequently determined. A crystallographic center of symmetry thus is imposed upon the metal cluster I.

Collection and Reduction of the Intensity Data. A small crystal of approximate dimensions $0.05 \times 0.06 \times 0.08$ mm was mounted parallel to the [100] direction. Diffractometer data were obtained using graphite-monochromated Mo Kα radiation by the bisecting mode, θ–2θ scan technique. The peaks were scanned from 1.0° on the low-angle side of the $K\alpha_1$ peak to 1.1° on the high-angle side of the $K\alpha_2$ peak using a variable scan rate; background counts were taken at each end of the scan with the ratio of total background time/scan time = 1.0.

A unique data set was collected to $2\theta = 40°$. Three reflections, monitored periodically, showed no significant change in intensity during data collection. The intensities were corrected for background, and standard deviations were assigned according to the equation $\sigma(I) = [I + (KI)^2]^{1/2}$, where the value of 0.017 13 used for K was obtained from a statistical analysis of the intensity distributions of the three standard reflections.[9] The data were also corrected for Lorentz and polarization effects. Because the crystal faces were poorly defined and the absorption coefficient was 59.2 cm⁻¹, no absorption correction was applied. Transmission coefficients ranged from 0.62 to 0.74. Of the 2786 unique data collected, 2096 reflections were considered to be observed with $I \geq 3\sigma(I)$, although all data were used in the final structure refinement.

Solution and Refinement of the Structure. Conventional Patterson and Fourier techniques readily yielded the positions of all nonhydrogen

Table I. Positional and Thermal Parameters for [(C$_6$H$_5$)$_2$PCH$_3$]$_4$Ag$_4$W$_2$S$_8$

atom[a]	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
W	0.484 41 (6)[b]	0.370 64 (6)	0.596 62 (4)	33.3 (4)	24.9 (4)	29.8 (5)	−0.6 (4)	4.1 (3)	2.6 (4)
Ag(1)	0.332 01 (12)	0.341 35 (12)	0.478 80 (7)	45.0 (9)	45.4 (10)	49.9 (10)	−2.8 (7)	−7.4 (7)	−9.7 (8)
Ag(2)	0.435 40 (12)	0.613 79 (12)	0.597 58 (7)	63.3 (10)	33.8 (9)	55.2 (10)	3.9 (8)	12.0 (8)	−10.4 (8)
S(1)	0.4898 (4)	0.2639 (4)	0.6794 (3)	69 (4)	46 (3)	43 (3)	−0 (3)	10 (3)	15 (3)
S(2)	0.5274 (4)	0.2696 (4)	0.5108 (2)	46 (3)	42 (3)	37 (3)	7 (3)	2 (2)	−1 (3)
S(3)	0.3103 (4)	0.4403 (4)	0.5857 (2)	37 (3)	42 (3)	53 (3)	1 (2)	8 (2)	−7 (3)
S(4)	0.6152 (4)	0.4972 (4)	0.6138 (2)	41 (3)	38 (3)	63 (3)	−11 (2)	−8 (3)	4 (3)
P(1)	0.1844 (4)	0.2649 (4)	0.4097 (2)	42 (3)	35 (3)	36 (3)	−3 (2)	−3 (2)	2 (2)
P(2)	0.3481 (4)	0.7357 (4)	0.6746 (3)	59 (3)	35 (3)	42 (3)	−0 (3)	15 (3)	−1 (3)
C(1)	0.1544 (16)	0.3392 (15)	0.3327 (9)	78 (14)	47 (13)	30 (12)	−9 (11)	−9 (10)	13 (10)
C(2)	0.2292 (16)	0.6680 (16)	0.7129 (9)	61 (13)	63 (15)	51 (13)	−31 (11)	7 (11)	5 (11)

atom[c]	x	y	z	U	atom	x	y	z	U
		Phenyl Ring 1					Phenyl Ring 3		
C(1)	0.0500	0.2581	0.4474	34 (5)	C(1)	0.4414	0.7802	0.7416	38 (5)
C(2)	0.0148	0.1617	0.4766	60 (6)	C(2)	0.5547	0.7942	0.7295	47 (5)
C(3)	−0.0880	0.1581	0.5067	95 (8)	C(3)	0.6282	0.8336	0.7788	58 (6)
C(4)	−0.1558	0.2508	0.5074	77 (7)	C(4)	0.5883	0.8590	0.8403	67 (6)
C(5)	−0.1206	0.3472	0.4784	85 (7)	C(5)	0.4749	0.8449	0.8525	69 (6)
C(6)	−0.0177	0.3508	0.4483	72 (7)	C(6)	0.4014	0.8055	0.8032	54 (6)
		Phenyl Ring 2					Phenyl Ring 4		
C(1)	0.2103	0.1270	0.3815	37 (4)	C(1)	0.2960	0.8657	0.6450	43 (5)
C(2)	0.1416	0.0776	0.3332	44 (5)	C(2)	0.1899	0.9052	0.6591	68 (6)
C(3)	0.1644	−0.0285	0.3129	58 (6)	C(3)	0.1572	1.0094	0.6386	79 (7)
C(4)	0.2558	−0.0852	0.3408	60 (6)	C(4)	0.2307	1.0742	0.6040	74 (7)
C(5)	0.3244	−0.0357	0.3892	63 (6)	C(5)	0.3368	1.0347	0.5899	73 (7)
C(6)	0.3016	0.0704	0.4095	48 (5)	C(6)	0.3694	0.9305	0.6104	53 (5)

[a] x, y, and z are fractional coordinates. The U_{ij} are the mean-square amplitudes of vibration in Å^2 ($\times 10^3$) from the general temperature expression $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. [b] The standard deviations of the least significant figures are given in parentheses. [c] The fractional coordinates of the group carbon atoms have been derived from the refined group parameters. The atoms are numbered so that C(1) is attached to P; C(4) is para to C(1). The isotropic U is in Å^2 ($\times 10^3$).

atoms. All atoms were refined with anisotropic thermal parameters, except that the phenyl rings were treated as rigid groups of D_{6h} symmetry (C–C = 1.392 Å) with individual isotropic thermal parameters. The hydrogen atoms were not located or refined, but phenyl hydrogen atoms were included in fixed positions in the final refinement assuming C–H = 1.0 Å and an isotropic U of 0.08 Å^2.

The model was refined to a conventional R, based on F, of 0.049 and a weighted R_w of 0.048 for the observed reflections, where

$$R = \sum ||F_o| - |F_c|| / \sum |F_o|$$

and

$$R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$$

The weights, w, were taken as $1/[\sigma(F_o)]^2$ where $\sigma(F_o) = [F_o^2 + \sigma(I)/Lp]^{1/2} - F$, and the function minimized was $\sum w(|F_o| - |F_c|)^2$. The scattering factors for H were taken from Stewart et al.;[10] the scattering factors for C, P, S, Ag, and W were computed from numerical Hartree–Fock wave functions.[11] Anomalous dispersion factors $\Delta f'$ and $\Delta f''$ for P, S, Ag, and W were taken from the International Tables for X-ray Crystallography.[12] On the final cycle of least-squares refinement the average and the maximum shift/error were 0.004 and 0.036, respectively, for all nongroup parameters and 0.003 and 0.010 for group parameters. A difference Fourier map showed several peaks between 1.3 and 2.0 e$^-$/Å^3 in the vicinity of the heavy metal atoms; all other residual peaks were below 1.1 e$^-$/Å^3, approximately 25% of the height of a carbon atom. No evidence of extinction was observed.

The final positional and thermal parameters are presented in Table I. Table I also gives the positional parameters for the group carbon atoms which may be derived from the refined group parameters. A table of the final values of $|F_o|$ and $|F_c|$ is available as supplementary material.

Description of the Structure

The crystal structure consists of discrete 12-atom clusters containing four silver atoms, two tungsten atoms, and six

bridging sulfur atoms. Each tungsten atom is additionally bonded to a terminal sulfur atom, while each silver atom is also bonded to a methyldiphenylphosphine ligand. Figure 1 presents a stereoscopic view of the cluster, omitting the methyl and phenyl groups; in Figure 2, the methyl and phenyl carbon atoms have been included. The numbering of the atoms is indicated in Figure 1.

A crystallographic center of symmetry is located in the center of the molecule; each molecule can thus be considered to be formed by the dimerization of two identical (C$_6$H$_5$)$_2$-(CH$_3$)PAg(WS$_4$)AgP(CH$_3$)(C$_6$H$_5$)$_2$ moieties. Bond lengths and angles are given in Table II; the primed atoms are related to the unprimed atoms by the symmetry center.

It can be seen from Table II that the WS$_4$ group retains tetrahedral geometry, with S–W–S angles ranging from 106 to 113°. The terminal W–S bond length of 2.131 (5) Å is similar to previously reported W^{VI}–S distances, such as 2.165 Å in (NH$_4$)$_2$WS$_4$[13] and 2.098 (8) and 2.08 (2) Å in WSCl$_4$ and WSBr$_4$, respectively.[14] The bridging W–S bond lengths, in which the sulfur atoms bridge one tungsten and two silver atoms, range from 2.213 to 2.244 (5) Å and are comparable to those of 2.217–2.222 (3) Å found in the closely related compound [(C$_6$H$_5$)$_2$PCH$_3$]$_2$Au$_2$WS$_4$, in which the sulfur atoms bridge two tungsten atoms.[8,15]

The geometry about the two crystallographically independent silver atoms is also basically tetrahedral, but quite distorted; the S–Ag–S and P–Ag–S bond angles range from 92 to 127°. The Ag–P distances of 2.398 and 2.427 (5) Å are close to the sum of the covalent radii of 2.44 Å,[16] and are similar to the distances reported in other tetrahedral silver complexes, such as 2.369 (6) Å in AgNO$_3$·P(C$_6$H$_5$)$_3$[17] and the average Ag–P bond lengths of 2.382–2.458 Å reported for the (R$_3$P)$_4$Ag$_4$X$_4$ series (R = C$_6$H$_5$, C$_2$H$_5$; X = Cl, Br, I).[18] The bridging Ag–S distances range from 2.514 to 2.820 (5) Å, comparable to those reported for Ag$_3$AsS$_3$ of 2.45–2.76 Å.[19]
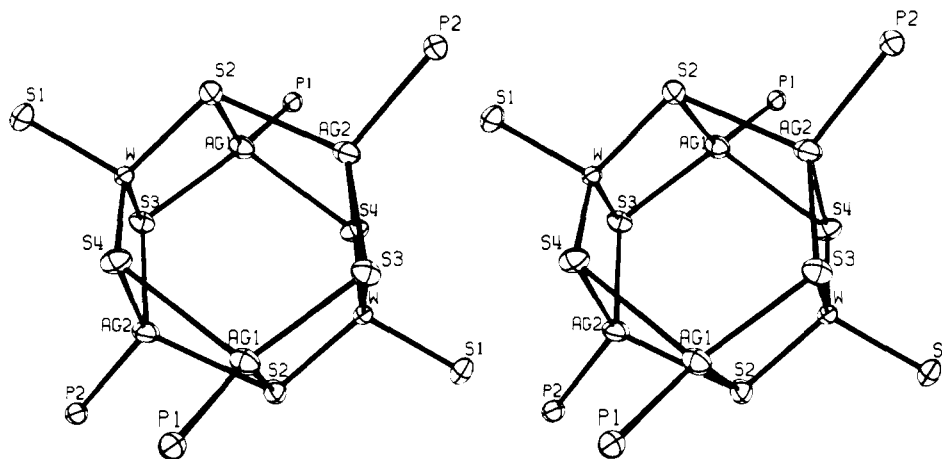
Figure 1. Stereoscopic view of $[(C_6H_5)_2PCH_3]_4Ag_4W_2S_8$ (I), omitting methyl and phenyl groups.
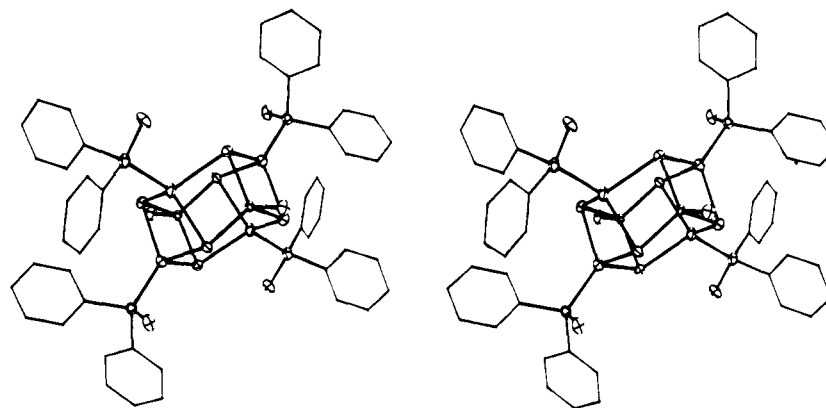

Figure 2. Stereoscopic view of $[(C_6H_5)_2PCH_3]_4Ag_4W_2S_8$ (I).

The P–C distances and the angles about the phosphorus atoms are normal for phosphine complexes.

The 12-atom cluster can be viewed in two ways. Figure 2 shows the two six-membered rings (each consisting of one tungsten and two silver atoms, with three bridging sulfur atoms) in an approximate chair conformation, joined by metal–sulfur bridges. The intra-ring angles, ideally tetrahedral, range from 106.0 to 123.9 (2)°. However, it is chemically more reasonable to consider the cage as being formed by the dimerization of two $(PAg)_2WS_4$ units (see Discussion and Figure 1). The Ag(1)′–S(4) and Ag(2)–S(2)′ distances of 2.820 and 2.680 (5) Å, respectively, joining the two units, are somewhat longer than the other four Ag–S distances (2.514–2.598 Å); see Figure 3. Figure 3 also presents bond lengths and angles for the three crystallographically independent four-atom faces of the cluster. These faces are not strictly planar (Table III). The two $AgWS_2$ faces have average displacements from the plane of 0.03 Å for the atoms defining the plane, while for the Ag_2S_2 plane the average displacement is 0.16 Å. The acute angles about the sulfur atoms range from 74.5 to 78.0 (2)°, presumably a consequence of geometric constraints due to cage formation. The W–Ag distances of 2.973 and 3.031 (2) Å are approximately 0.33–0.39 Å greater than the sum of the covalent radii[16] of 2.64 Å; similarly, the Ag–Ag distance of 3.275 (2) Å is about 0.60 Å greater than the calculated value of 2.68 Å. Whereas metal–metal interactions are not precluded in this and similar compounds, a detailed analysis will be deferred until more structural data are available.

Discussion

Two questions arise naturally from the structure of $[(C_6H_5)_2PCH_3]_4Ag_4W_2S_8$ (I): (1) what is the relationship of

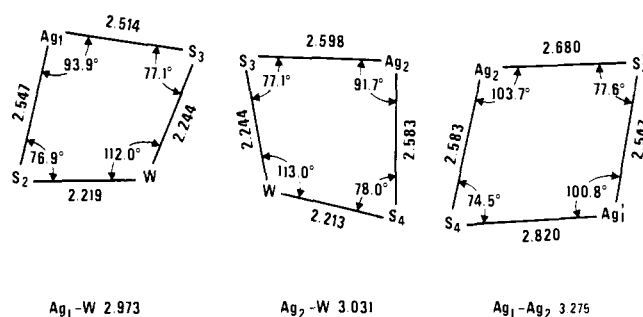Ag_1–W 2.973 Ag_2–W 3.031 Ag_1–Ag_2 3.275

Figure 3. Bond distances and angles for the four-atom faces of the $Ag_4W_2S_6$ cage.

I to its precursor $[(C_6H_5)_2PCH_3]_4Ag_2WS_4$ (II); (2) why does a silver–tungsten–sulfur cage form, rather than the open, net-like structure found for $[(C_6H_5)_2PCH_3]_2Au_2WS_4$ and its isostructural molybdenum analogue?

The precursor II is formed by deoxygenation of $WO_2S_2^{2-}$ with excess methyldiphenylphosphine in the presence of Ag^+; dissociative loss of methyldiphenylphosphine in polar solvents such as acetone or acetonitrile leads to crystallization of the much less soluble I.

We have not yet succeeded in obtaining crystals of II suitable for X-ray diffraction work, and therefore structural deductions must be based on less direct considerations. A pervasive theme in thiatungstate and thiamolybdate chemistry is tetrahedral coordination about the group 6B metal. This has been found, for example, in $[(C_6H_5)_2PCH_3]_2Au_2MS_4$ (M =
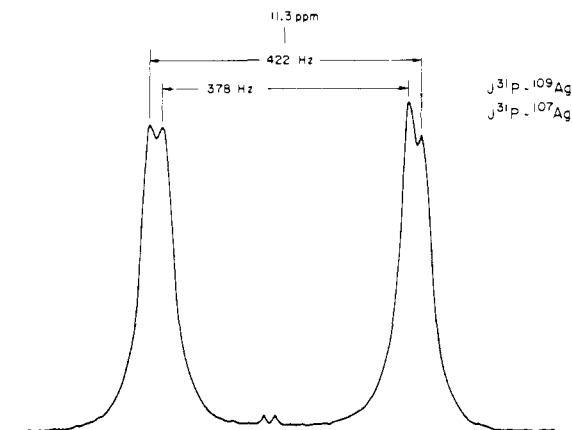
Figure 4. {¹H}³¹P NMR spectrum of [(C₆H₅)₂PCH₃]₄Ag₂WS₄ (II).

Figure 5. Possible mechanism for rearrangement of [(C₆H₅)₂PCH₃]₄-Ag₂WS₄ (II).

Table II. Selected Interatomic Distances (Å) and Angles (deg) for [(C₆H₅)₂PCH₃]₄Ag₄W₂S₈

atoms[a]	dist	atoms	dist
W–S(1)	2.131[b]	P(1)–R(1)C(1)[c]	1.80
W–S(2)	2.219	P(1)–R(2)C(1)	1.81
W–S(3)	2.244	P(2)–R(3)C(1)	1.81
W–S(4)	2.213	P(2)–R(4)C(1)	1.80
Ag(1)–S(2)	2.547	W–Ag(1)	2.973
Ag(1)–S(3)	2.514	W–Ag(2)	3.031
Ag(1)–S(4)′	2.820	Ag(1)–Ag(2)′	3.275
Ag(2)–S(2)′	2.680	W–Ag(1)′	4.451
Ag(2)–S(3)	2.598	W–Ag(2)′	4.111
Ag(2)–S(4)	2.583	Ag(1)–Ag(2)	4.271
Ag(1)–P(1)	2.398	W–W′	5.076
Ag(2)–P(2)	2.427	Ag(1)–Ag(1)′	5.616
P(1)–C(1)	1.84	Ag(2)–Ag(2)′	5.139
P(2)–C(2)	1.84		

atoms	angle	atoms	angle
S(1)–W–S(2)	106.3[d]	Ag(1)–S(2)–Ag(2)′	77.6
S(1)–W–S(3)	108.1	W–S(3)–Ag(1)	77.1
S(1)–W–S(4)	107.7	W–S(3)–Ag(2)	77.1
S(2)–W–S(3)	112.0	Ag(1)–S(3)–Ag(2)	113.3
S(2)–W–S(4)	109.4	W–S(4)–Ag(2)	78.0
S(3)–W–S(4)	113.0	W–S(4)–Ag(1)′	123.9
S(2)–Ag(1)–S(3)	93.9	Ag(2)–S(4)–Ag(1)′	74.5
S(2)–Ag(1)–S(4)′	100.8	Ag(1)–P(1)–C(1)	115.0
S(2)–Ag(1)–P(1)	131.0	Ag(1)–P(1)–R(1)C(1)	114.2
S(3)–Ag(1)–S(4)′	106.0	Ag(1)–P(1)–R(2)C(1)	114.8
S(3)–Ag(1)–P(1)	126.8	C(1)–P(1)–R(1)C(1)	103.9
S(4)′–Ag(1)–P(1)	93.3	C(1)–P(1)–R(2)C(1)	102.7
S(2)′–Ag(2)–S(3)	118.1	R(1)C(1)–P(1)–R(2)C(1)	104.8
S(2)′–Ag(2)–S(4)	103.7	Ag(2)–P(2)–C(2)	110.7
S(2)′–Ag(2)–P(2)	107.1	Ag(2)–P(2)–R(3)C(1)	114.0
S(3)–Ag(2)–S(4)	91.7	Ag(2)–P(2)–R(4)C(1)	118.4
S(3)–Ag(2)–P(2)	107.7	C(2) P(2)–R(3)C(1)	105.9
S(4)–Ag(2)–P(2)	129.1	C(2)–P(2)–R(4)C(1)	106.2
W–S(2)–Ag(1)	76.9	R(3)C(1)–P(2)–R(4)C(1)	100.4
W–S(2)–Ag(2)′	113.8		

[a] The primed atoms are related to the unprimed atoms by the crystallographic center of symmetry. [b] Standard deviations are 0.005 Å for W–S, Ag–S, and Ag–P distances; 0.002 Å for W–W, Ag–Ag, and Ag–W distances; 0.02 Å for P–C distances. [c] R(*i*)C(1) refers to C(1) on phenyl ring *i*. [d] Standard deviations are 0.2° for angles about W, Ag, and S; 0.7° for angles about P.

Table III. Least-Squares Planes for the Ag₄W₂S₆ Cluster

plane 1		plane 2		plane 3	
atom	dist	atom	dist	atom	dist
W	0.03	W	−0.03	Ag(2)	0.16
S(2)	−0.03	S(3)	0.03	S(4)	−0.16
Ag(1)	0.02	Ag(2)	−0.02	Ag(1)′	0.16
S(3)	−0.03	S(4)	0.03	S(2)	−0.16

planes	dihedral angle, deg
1 and 2	60.4
2 and 3	53.2
1 and 3	66.4

[a] dist = distance from plane, Å.

J(³¹P–¹⁰⁷Ag) are 422 and 378 Hz, respectively. The room temperature spectrum is simply a singlet (*W*/2 = 25 Hz), indicating rapid ligand exchange. This phosphine dissociation, in fact, makes molecular weight data unreliable for the characterization of these coinage metal derivatives. The silver-phosphorus coupling constants may be compared with a value of 420 Hz found by Muetterties et al.[23,24] for the nonconducting, anion-bound complex [(*p*-tolyl)₃P]₂AgB₉H₁₂S. A 1 × 10⁻³ M solution of II in nitromethane exhibited a molar conductance of 7.6 Ω⁻¹ mol⁻¹ cm², which excludes an ionic formulation. These data indicate a tetrahedral geometry about silver and are entirely consistent with the structure proposed for II in Figure 5.

The ³¹P NMR and molecular weight data establish lability of the methyldiphenylphosphine ligands, and this suggests a plausible route for the conversion of II to the dimeric cage structure I (Figure 5). Loss of one phosphine ligand and breaking of one of the Ag–S bonds, shown by the dotted line, permits rotation about the Ag–S bond as indicated by the arrow. Re-formation of an Ag–S bond and displacement of a second phosphine ligand results in the conversion of II, in which the WS₄ tetrahedron is bridged by silver on alternate edges, into Ia, in which adjacent edges are bridged. Dimerization of Ia forms I. Factors which may favor the formation of the Ag₄W₂S₆ cage include (1) increase in the coordination number of silver by formation of additional Ag–S bonds, and (2) the relative insolubility of the cage compound I.

The reasons are less obvious why the stoichiometric gold analogue of I, [(C₆H₅)₂PCH₃]₂Au₂WS₄, does not adopt a cage structure, and why [(C₆H₅)₂PCH₃]₄Au₂WS₄, the gold analogue of II, was not isolated. Four-coordinate Au(I) compounds, e.g., the ClO₄⁻ and (C₆H₅)₄B⁻ salts of [(C₆H₅)₃P]₄-Au⁺, have been reported;[25] however, studies of gold–phosphine complexes in solution[23,26] indicate that the ligands are labile

Mo, W),[8,20] [(*p*-C₇H₇)₃P]₄Cu₄W₂O₂S₆,[21] and [(C₂H₅)₃P]₂-PtWS₄,[22] as well as in I, so it is reasonable to expect this feature in II. The {¹H}³¹P NMR spectrum of II in dichloromethane at −90 °C (Figure 4) consists of two doublets centered at 11.3 ppm downfield from H₃PO₄; *J*(³¹P–¹⁰⁹Ag) and

and undergo exchange. This behavior reflects the tendency of Au(I) to form structures with linear or trigonal coordination. The exceptions occur in cases where chelate structures, for example, [(diars)$_2$Au]$^+$I$^-$,[27] or unusual cage structures, such as [(C$_6$H$_5$)$_2$PC≡CP(C$_6$H$_5$)$_2$]$_3$(AuI)$_2$[28] or [(C$_6$H$_5$)$_3$P]$_7$Au$_{11}$X$_3$,[29] are involved.[30] We suggest, then, that the failure to isolate [(C$_6$H$_5$)$_2$PCH$_3$]$_4$Au$_2$WS$_4$ is a consequence of the preference of Au(I) for trigonal coordination and the lability of the phosphine ligands. The net-like structure of [(C$_6$H$_5$)$_2$PCH$_3$]$_2$Au$_2$WS$_4$, as opposed to a dimeric cage structure similar to that found for I, may be explained by the same considerations.

Supplementary Material Available: Final values of |F_o| and F_c (in electrons) for [(C$_6$H$_5$)$_2$PCH$_3$]$_4$Ag$_4$W$_2$S$_8$ (19 pages). Ordering information is given on any current masthead page.

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(30) We have recently isolated a gold analogue of II using the chelating ligand 1,2-bis(diphenylphosphino)ethane (diphos). Treatment of [P(C$_6$H$_5$)$_3$]$_2$-Au$_2$WS$_4$ with excess diphos affords (diphos)$_2$Au$_2$WS$_4$ [Anal. Calcd for C$_{52}$H$_{48}$Au$_2$P$_4$S$_4$W: C, 41.55; H, 3.20; P, 8.26; mol wt, 1502. Found: C, 41.63; H, 3.19; P, 8.00; mol wt, 1487 (osmometric in CHCl$_3$). IR (Nujol): 420, 415 cm^{-1}]. The {^{1}H}^{31}P NMR spectrum contained a single resonance at 23 ppm, indicating that the diphos behaves as a bidentate ligand. A more complex spectrum would be expected for monodentate diphos [R. L. Keiter and D. P. Shah, Inorg. Chem., 11, 191 (1972); R. L. Keiter and L. W. Cary, J. Am. Chem. Soc., 94, 9232 (1972)].

Excited-State Behavior of Polypyridyl Complexes of Chromium(III)[1]

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Abstract: Flash photolysis and luminescence techniques have been used to investigate the properties and the behavior of the ^{2}E excited states of Cr(III) complexes of 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen), 2,2',2''-terpyridine (terpy), and some of their methyl, phenyl, and chloro derivatives. The specific complexes used in the study have been the ClO$_4^-$ salts of Cr(bpy)$_3^{3+}$, Cr(4,4'-Me$_2$bpy)$_3^{3+}$, Cr(4,4'-Ph$_2$bpy)$_3^{3+}$, Cr(phen)$_3^{3+}$, Cr(5-Clphen)$_3^{3+}$, Cr(4,7-Me$_2$phen)$_3^{3+}$, Cr(4,7-Ph$_2$phen)$_3^{3+}$, Cr(3,4,7,8-Me$_4$phen)$_3^{3+}$, and Cr(terpy)$_2^{3+}$. The following aspects of the nature of the metal-centered ^{2}E states have been examined and comparisons made with the behavior of the MLCT excited states of analogous polypyridyl complexes of Ru(II) and Os(II): (a) excited-state absorption and emission spectra; (b) excited-state lifetimes in aqueous solution at room temperature and in methanolic ice at 77 K; (c) solution medium effects on the excited-state lifetimes; (d) relative phosphorescence quantum yields; (e) quenching by O$_2$, Fe$_{aq}^{2+}$, and I$^-$. O$_2$ quenches ^{2}E predominantly via energy transfer and Fe$_{aq}^{2+}$ and I$^-$ quench via reductive electron transfer. An estimate of the (^{2}E)Cr(NN)$_3^{3+}$–Cr(NN)$_3^{2+}$ self-exchange rate yields the value of 4×10^7 M^{-1} s^{-1} in 1 M HCl at 25 °C.

Introduction

Investigations in recent years have demonstrated that excited states of transition-metal complexes can engage in electron transfer and energy transfer in solution.[3] The lowest excited states of polypyridyl complexes of Ru(II) and Os(II) can undergo oxidative and reductive electron transfer reactions and are phosphorescent.[4] These complexes are viewed as having potential applicability in solar energy storage and conversion schemes.[5,6]

The lowest excited state of Cr(bpy)$_3^{3+}$ (bpy = 2,2'-bipyridine) (^{2}E) is phosphorescent,[7] is remarkably long lived (63 μs) in deaerated aqueous solution at room temperature,[8] and is highly reactive toward redox quenchers.[9-12] In this paper we examine in detail the excited-state behavior of polypyridyl complexes of chromium(III), Cr(NN)$_3^{3+}$, containing substi-