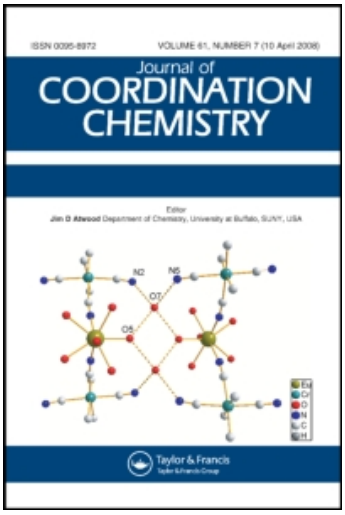

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SYNTHESIS, STRUCTURE AND CHARACTERIZATION OF THE CUBANE-LIKE CLUSTER $\{WAG_3S_3[S_2P(OCH_2CH_3)_2]\}(O)(PH_3P)_3$ AND THE DOUBLE CUBANE-LIKE CLUSTER $\{W_2AG_6S_6[SC(CH_3)_3]_2\}(O)_2(PH_3P)_4$

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Two novel W-Ag-S cubane-like and double cubane-like heterometallic clusters $\{WAg_3S_3[S_2P(OCH_2CH_3)_2]\}(O)(Ph_3P)_3$ **I** and $\{W_2Ag_6S_6[SC(CH_3)_3]_2\}(O)_2(Ph_3P)_4$ **II** were obtained from the reaction of the butterfly compound $\{WAg_2S_3\}(O)(Ph_3P)_3$ with $AgS_2P(OCH_2CH_3)_2$ and $AgSC(CH_3)_3$, respectively. Cluster **I** is triclinic, space group $P\bar{1}$ with cell parameters a = 14.275(3), b = 19.96(1), c = 11.746(4) Å, α = 98.58(4), β = 107.68(2), γ = 87.88(3)°, U = 3153(2) Å^3, Z = 2, Cluster **II** is also triclinic, space group $P\bar{1}$, with cell parameters a = 13.529(6), b = 15.825(9), c = 11.348(5) Å, α = 102.11(4), β = 102.53(4), γ = 66.99(4)°, U = 2162(2) Å^3, Z = 1. Triply bridging modes of the $S_2P(OCH_2CH_3)_2^-$ and $SC(CH_3)_3^-$ ligands were found. The bidentate $S_2P(OCH_2CH_3)_2^-$ ligand completes the cubane-like core of cluster **I** and the monodentate $SC(CH_3)_3^-$ links two cubane-like fragments in cluster **II**.

KEYWORDS: Cubanes, tungsten, silver, thio ligands, X-ray structures

INTRODUCTION

Recently, the synthetic and structural chemistry of transition metal clusters containing sulphido ligands has developed rapidly.[1–3] One reason is because of their bioinorganic relevance, *e.g.*, single or double cubane-like clusters with cores $\{MoFe_3S_4\}$,[4] $\{NiFe_3S_4\}$,[5] $\{VFe_3S_4\}$,[6] and $\{MoFe_3S_4S_4Fe_3Mo\}$[7] are synthetic analogues of the active sites of some enzymes. The MoS_4^{2-} anion has been claimed to be the most effective antagonist[8] of copper metabolism. In particular, structure models which contain double and single cubanes for the nitrogenase FeMo-cofactor and P-cluster are based on crystallographic analysis of the nitrogenase molybdenum-iron (MoFe)-protein from *Azotobacter vinelandii* at 2.7 angstrom resolution.[9] It is clear that the single cubane- and double cubane-like clusters are important structure types.

Chemistry and structures of Mo(W)-Cu-S and Mo(W)-Ag-S complexes are similar. To date, five types of Mo(W)-Ag-S compounds are known. One is the linear

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di- or tri-nuclear species $[Pr^iN][(CN)\text{-}AgS_2MS_2]$[10] or $(PR_3)_nAg_2MS_4$[11] (M = Mo, W; R_3 = Ph_3, $MePh_2$; n = 3, 4). Another is the cage species of formula $(Ag_4M_2S_6)(PR_3)_4S_2$[12] (M = Mo, W; R_3 = Ph_3, $MePh_2$). Incomplete cubane-like compounds $[Et_4N][M_2AgS_4](Ph_3P)$[13] (M = Mo, W), single cubane-like compounds $\{MoAg_3S_3Cl\}(X)(Ph_3P)_3$[14](X = 0,S) and the double cubane-like compound $\{Mo_2Ag_6S_6[SC(CH_3)_3]_2\}(O)_2(Ph_3P)_4$,[15] prepared in our laboratory, are also known. Herein, structures of a novel example of a W/Ag/S double cubane-like cluster $\{W_2Ag_6S_6[SC(CH_3)_3]_2\}(O)_2(Ph_3P)_4$ and the single cubane-like cluster $\{WAg_3S_3[S_2P(OCH_2CH_3)_2]\}(O)(Ph_3P)_3$ are reported.

EXPERIMENTAL

All reagents and solvents were above CP grade and were used directly. $AgS_2P(OCH_2CH_3)_2$ and $AgSC(CH_3)_3$ were obtained from EtOH by reaction of $AgNO_3$ with $HS_2P(OCH_2CH_3)_2$ (P_2S_5 dissolved in EtOH) and a mixture of $HSC(CH_3)_3$ and NEt_3, respectively. $(NH_4)_2WOS_3$ was prepared according to the literature.[16] Elemental analyses were carried out by the Elemental Analysis Laboratories of our Institute. IR spectra were recorded on on Perkin Elmer 577 spectrophotometer.

$\{WAg_2S_3\}(O)(Ph_3P)_3$

Some 1.03 g of $AgNO_3$ (6.0 mmol) and 4.8 g of Ph_3P (18.3 mmol) were heated and dissolved in 60 cm^3 CH_2Cl_2 and then 1.0 g $(NH_4)_2WOS_3$ (3.0 mmol) was added. After stirring for 2.0 hours, the solution was filtered and 40 cm^3 *i*-PrOH and 40 cm^3 Et_2O were added to the filtrate. Some 2.2 g of yellow crystals were obtained by evaporating the filtrate in air (yield: 56.5%). *Anal:* calcd. for $C_{54}H_{45}Ag_2WOP_3S_3$: C, 50.0; H, 3.5; Ag, 16.6; W, 14.2; P, 7.2: S, 7.4%. Found: C, 50.4; H, 3.0; Ag, 15.8; W, 13.8; P, 6.4; S, 7.8%. IR (KBr pellet): δ(C-H) in Ph_3P, 750(s) and 700(s); ν(Ag-P), 520s, 515s, 500s and 495m; υ(W-μ_2-S) and (W-μ_3-S), 455s, 436s and 415s; υ(W-O), 935vs cm^{-1}.

$\{WAg_3S_3[S_2P(OCH_2CH_3)_2]\}(O)(Ph_3P)_3$

Some 0.6 g (0.46 mmol) of $\{WAg_2S_3\}(O)(Ph_3P)_3$ and 0.13 g (0.44 mmol) of $AgS_2P(OCH_2CH_3)_2$ were reacted in 40 cm^3 of CH_2Cl_2 for about 1 hour and then filtered. The yellow filtrate was added to 30 cm^3 of *i*-PrOH and 30 cm^3 Et_2O. The filtrate was left to evaporate in air and 0.2 g of yellow crystals were obtained (yield: 28.6%). *Anal:* calcd. for $C_{58}H_{55}Ag_3WO_3P_4S_5$: C, 43.7; H, 3.5; Ag, 20.3; W, 11.6 P, 7.8; S, 10.1%. Found: C, 43.6; H, 3.4: W, 11.6; P, 6.5; S, 10.0%. IR (KBr pellet): δ(C-H) in Ph_3P, 750(s) and 700(s); υ(Ag-P), 510s, 500s, and 490m; υ(W-μ_2-S) and (W-μ_3-S), 446s, 430s and 415s; υ(W-O), 942s cm^{-1}.

$\{W_2Ag_6S_6[SC(CH_3)_3]_2\}(O)_2(Ph_3P)_4$

A mixture of 0.2 g (0.15 mmol) $\{WAg_2S_3\}(O)(Ph_3P)_3$ and 0.03 g (0.15 mmol) $AgSC(CH_3)_3$ in 30 cm^3 CH_2Cl_2 was stirred for 20 min. The orange solution was

filtered and 20 cm^3 Et_2O was added to the filtrate. The filtrate was stored at *ca* 5–10° for two days, when 0.1 g of yellow crystals were obtained (yield: 54.1%). *Anal:* calcd. for $C_{80}H_{78}O_2P_4S_8W_2Ag_6$: Ag, 26.2; P, 5.0; C, 39.0; H, 3.2%. Found: Ag, 24.4; P, 4.6; C, 39.2; H, 3.3%. IR (KBr pellet): δ(C-H) in Ph_3P, 757s, 745(vs), 710s and 695vs; υ(Ag-P), 520s, 508s and 500s; υ(W-μ_3-S), 425s; ν(W-O), 949vs cm^{-1}

Crystal Structure Determination

Crystal data for **I** and **II** are summarized in Table 1, together with some experimental details. Crystals were mounted in random orientation on glass fibres. Diffraction data were collected on a RIGAKU AFC5R diffractometer using MoK_α radiation (λ = 0.71073Å) at *ca* 296K. Cell constants were obtained by

Table 1 Crystallographic data for $\{WAg_3S_3[S_2P(OCH_2CH_3)_2]\}(O)(Ph_3P)_3$ (**I**) and $\{W_2Ag_6S_6[SC(CH_3)_3]_2\}(O)_2(Ph_3P)_4$ (**II**).

	I	**II**
Chemical formula	$C_{58}H_{55}O_3P_4S_5WAg_3$	$C_{80}H_{78}O_2P_4S_8W_2Ag_6$
Formula weight	1591.72	2466.78
colour	Yellow	Yellow
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell parameters		
a(Å)	14.275(3)	13.529(6)
b(Å)	19.96(1)	15.825(9)
c(Å)	11.746(4)	11.348(5)
α(°)	98.58(4)	102.11(4)
β(°)	107.68(2)	102.53(4)
γ(°)	87.88(3)	66.99(4)
V(Å^3)	3153(2)	2162(2)
Z	2	1
μ(cm^{-1})	30.66	43.25
F(000)	1564	1192
2θ(°)	50.0	50.0
^{d}*cald* (g/cm^3)	1.68	1.89
Temperature (K)	296	296
Diffractometer	Rigaku AFC5R	Rigaku AFC5R
Radiation λ (Å)	Mo-K_α (0.71069)	Mo-K_α (0.71069)
Max/min. transmission factors	0.770/1.233	0.786/1.207
Solution method	direct methods	Patterson synthesis
Correction	Lp, Ψ, DIFABS	Lp, Ψ, DIFABS
Residuals: *R*, R_W	0.053, 0.087	0.048, 0.057
Goodness of fit: *S*	2.24	1.20
No. of unique data	11076	7619
No. obs. with $I > 3\sigma(I)$	8225	4524
No. of variables	377	280
Max. shift $(\Delta/\sigma)_{max}$ in final cycle	0.26	0.26
Largest peaks in final diff. map(eÅ^{-3})	1.05, −1.16	0.99, −0.81
scan type	ω	ω

$R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$;
$S = [\Sigma w(|F_o| - |F_c|)^2/(N_o - N)]^{1/2}$; $w = 1/\sigma^2(F_o)$.

least-squares analysis of 20 reflections. Scan repeat times varied on the basis of $I/\sigma(\mathbf{I})$ values. A total 11567 of reflections for **I** (7985 for **II**) was collected. Three standard reflections were measured periodically, indicating crystal and electronic stability. The collected intensity was defined as $C - 1/2(t_c/t_b)(b_1 + b_2)$, where C = total number of counts, t_c = time spent counting peak intensity, t_b = time spent counting one side of the background, b_1 = high-angle background counts and b_2 = low-angle backgrounds counts; the intensity error was defined as $\sigma(F)^2 = [C + 1/4(t_c/t_b)^2(b_1 + b_2) + (pI)^2]^{1/2}$, where I is the intensity and p is a factor that downweights strong reflections, taken to be 0.05. The data were corrected for Lorentz and polarization factors and for absorption by empirical scan data and DIFABS.[17] Reflections with $I > 3\sigma(I)$ were considered to be observed, and were used in the refinement.

The structure of **I** was solved using direct methods, which located W and Ag. The structure of **II** was solved by locating W from a Patterson synthesis. Most non-hydrogen atoms were deduced from a *DIRDIF* calculation[18] and successive difference-Fourier syntheses. Both structures were refined by full-matrix least-square techniques with anisotropic thermal parameters for W, Ag, S, P, O and C atoms in the $SC(CH_3)_3$ ligand, and isotropic thermal parameters for all C atoms in Ph_3P and $S_2P(OCH_2CH_3)_2^-$. All calculations were performed on a *VAX 785* computer using the *TEXSAN*[19] program package. Non-hydrogen scattering factors were taken from Cromer and Waber.[20] Atomic coordinates and equivalent isotropic thermal parameters are listed in Table 2 for **I** (Table 3 for **II**); important bond lengths and angles are given in Tables 4 and 5 for **I** (Tables 6 and 7 for **II**).

Table 2 Positional parameters and B(eq) for $\{WAg_3S_3[S_2P(OCH_2CH_3)_2]\}(O)(Ph_3P)_3$; $B_{eq} = 4/3\ \Sigma i\Sigma j Bijai\ aj$.

atom	x/a	y/b	z/c	B(eq)
Ag(1)	0.51213(7)	0.27163(5)	0.3166(1)	4.16(4)
Ag(2)	0.71566(9)	0.16868(5)	0.2777(1)	5.20(5)
Ag(3)	0.80580(7)	0.29207(5)	0.51768(9)	4.60(4)
W	0.69233(3)	0.32401(2)	0.26816(4)	3.18(2)
O	0.6891(8)	0.3957(4)	0.193(1)	5.9(4)
S(1)	0.6493(2)	0.3580(2)	0.4370(3)	4.0(1)
S(2)	0.5869(2)	0.2479(2)	0.1391(3)	4.8(1)
S(3)	0.8413(2)	0.2784(2)	0.3079(3)	4.0(1)
S(4)	0.7663(3)	0.1634(2)	0.5203(4)	5.0(1)
S(5)	0.5249(4)	0.1525(2)	0.3808(5)	8.0(2)
P(1)	0.3513(2)	0.3241(2)	0.2895(3)	3.8(1)
P(2)	0.7680(2)	0.0660(1)	0.1769(3)	3.4(1)
P(3)	0.9419(2)	0.3377(2)	0.6874(3)	3.3(1)
P(4)	0.6328(3)	0.1599(2)	0.5344(3)	4.7(1)
O(1)	0.6258(8)	0.1016(6)	0.610(1)	7.2(5)
O(2)	0.6258(7)	0.2238(6)	0.632(1)	6.4(5)
C(1)	0.639(2)	0.033(1)	0.562(2)	9.0(5)
C(2)	0.646(2)	−0.008(1)	0.653(2)	11.7(7)
C(3)	0.535(2)	0.244(1)	0.655(3)	11.9(7)
C(4)	0.546(3)	0.280(2)	0.768(4)	17(1)
C(111)	0.327(1)	0.3884(7)	0.190(1)	4.4(3)

Table 2 *Continued.*

atom	x/a	y/b	z/c	B(eq)
C(112)	0.269(1)	0.442(1)	0.198(2)	7.3(4)
C(113)	0.255(1)	0.490(1)	0.119(2)	8.5(5)
C(114)	0.298(2)	0.481(1)	0.033(2)	10.7(6)
C(115)	0.357(2)	0.428(2)	0.018(3)	12.1(7)
C(116)	0.370(1)	0.379(1)	0.100(2)	8.1(5)
C(121)	0.3431(9)	0.3692(6)	0.432(1)	4.0(2)
C(122)	0.293(1)	0.3421(8)	0.498(1)	5.6(3)
C(123)	0.296(1)	0.375(1)	0.612(2)	7.0(4)
C(124)	0.344(1)	0.430(1)	0.660(2)	6.7(4)
C(125)	0.398(1)	0.461(1)	0.598(2)	8.4(5)
C(126)	0.392(1)	0.428(1)	0.480(2)	7.2(4)
C(131)	0.242(1)	0.2692(7)	0.231(1)	4.4(3)
C(132)	0.255(2)	0.204(1)	0.225(2)	9.4(5)
C(133)	0.173(2)	0.156(1)	0.187(2)	11.0(7)
C(134)	0.081(2)	0.182(1)	0.144(2)	8.4(5)
C(135)	0.068(2)	0.247(1)	0.154(2)	8.5(5)
C(136)	0.147(1)	0.292(1)	0.197(2)	7.3(4)
C(211)	0.7974(8)	0.0783(6)	0.041(1)	3.7(2)
C(212)	0.760(1)	0.1347(7)	−0.014(1)	4.8(3)
C(213)	0.784(1)	0.1486(8)	−0.113(1)	5.6(3)
C(214)	0.849(1)	0.1069(8)	−0.157(1)	5.8(3)
C(215)	0.886(1)	0.0518(7)	−0.104(1)	5.3(3)
C(216)	0.862(1)	0.0379(7)	−0.005(1)	4.6(3)
C(221)	0.8816(8)	0.0302(6)	0.264(1)	3.3(2)
C(222)	0.8934(9)	−0.0386(6)	0.270(1)	4.2(2)
C(223)	0.984(1)	−0.0627(7)	0.336(1)	4.5(3)
C(224)	1.060(1)	−0.0179(7)	0.393(1)	5.1(3)
C(225)	1.049(1)	0.0496(7)	0.389(1)	5.2(3)
C(226)	0.959(1)	0.0747(7)	0.325(1)	4.7(3)
C(231)	0.6786(9)	−0.0032(6)	0.132(1)	3.8(2)
C(232)	0.633(1)	−0.0154(9)	0.212(2)	6.7(4)
C(233)	0.564(1)	−0.067(1)	0.187(2)	7.5(4)
C(234)	0.538(1)	−0.105(1)	0.080(2)	7.3(4)
C(235)	0.581(2)	−0.094(1)	0.000(2)	8.5(5)
C(236)	0.652(1)	−0.0417(9)	0.023(2)	6.7(4)
C(311)	0.9765(8)	0.4213(5)	0.669(1)	3.3(2)
C(312)	0.900(1)	0.4647(6)	0.624(1)	4.2(2)
C(313)	0.920(1)	0.5304(7)	0.610(1)	4.8(3)
C(314)	1.015(1)	0.5522(7)	0.639(1)	4.7(3)
C(315)	1.090(1)	0.5097(7)	0.681(1)	5.0(3)
C(316)	1.0727(9)	0.4435(6)	0.699(1)	4.0(2)
C(321)	0.9219(8)	0.3517(6)	0.835(1)	3.2(2)
C(322)	0.9778(9)	0.3962(6)	0.931(1)	4.0(2)
C(323)	0.958(1)	0.4059(7)	1.040(1)	4.4(3)
C(324)	0.880(1)	0.3724(7)	1.052(1)	5.0(3)
C(325)	0.821(1)	0.3297(7)	0.958(1)	5.2(3)
C(326)	0.843(1)	0.3185(7)	0.850(1)	4.9(3)
C(331)	1.053(1)	0.2876(6)	0.708(1)	4.2(2)
C(332)	1.077(1)	0.2600(8)	0.607(1)	5.8(3)
C(333)	1.162(1)	0.217(1)	0.619(2)	7.3(4)
C(334)	1.217(1)	0.207(1)	0.727(2)	8.3(5)
C(335)	1.196(2)	0.233(1)	0.826(2)	9.2(5)
C(336)	1.113(1)	0.274(1)	0.820(2)	7.1(4)

Table 3 Positional parameters and *B(eq)* for $[W_2Ag_6S_6(SC_4H_9)_2](O)_2(Ph_3P)_4$; *B(eq)* = 4/3 Σ*i*Σ *jBijai aj*.

atom	*x/a*	*y/b*	*z/c*	B(eq)
W	-0.13007(4)	0.23341(4)	0.20349(5)	2.79(3)
Ag(1)	-0.14152(9)	0.25713(8)	-0.0606(1)	3.97(6)
Ag(2)	0.10919(8)	0.1734(1)	0.1545(1)	4.54(7)
Ag(3)	-0.0709(1)	0.03512(8)	0.1154(1)	4.37(7)
S	0.0507(3)	0.1247(2)	-0.0691(3)	3.2(2)
S(1)	-0.0765(3)	0.3366(3)	0.1552(3)	3.6(2)
S(2)	-0.2251(3)	0.1749(3)	0.0416(3)	4.1(2)
S(3)	0.0128(3)	0.1222(3)	0.2920(3)	3.7(2)
P(1)	-0.2396(3)	0.3280(2)	-0.2383(3)	2.9(2)
P(2)	0.2861(3)	0.1708(3)	0.2569(3)	3.6(2)
O	-0.2151(8)	0.2901(7)	0.3106(9)	5.1(6)
C(1)	0.143(1)	0.136(1)	-0.161(1)	4.1(9)
C(2)	0.257(1)	0.066(1)	-0.129(1)	5(1)
C(3)	0.098(1)	0.124(1)	-0.293(1)	5(1)
C(4)	0.140(1)	0.237(1)	-0.122(2)	6(1)
C(111)	-0.259(1)	0.243(1)	-0.369(1)	3.1(2)*
C(112)	-0.336(1)	0.270(1)	-0.470(1)	3.7(3)*
C(113)	-0.342(1)	0.200(1)	-0.571(1)	5.3(3)*
C(114)	-0.279(1)	0.113(1)	-0.567(1)	4.9(3)*
C(115)	-0.204(1)	0.089(1)	-0.467(2)	5.7(4)*
C(116)	-0.193(1)	0.151(1)	-0.367(1)	4.7(3)*
C(121)	-0.376(1)	0.411(1)	-0.224(1)	3.4(3)*
C(122)	-0.432(1)	0.393(1)	-0.152(1)	4.2(3)*
C(123)	-0.539(1)	0.451(1)	-0.139(2)	5.8(4)*
C(124)	-0.587(1)	0.524(1)	-0.199(1)	5.4(4)*
C(125)	-0.534(1)	0.544(1)	-0.270(2)	6.0(4)*
C(126)	-0.426(1)	0.486(1)	-0.286(2)	5.6(4)*
C(131)	-0.173(1)	0.391(1)	-0.287(1)	4.0(3)*
C(132)	-0.163(1)	0.391(1)	-0.405(1)	5.4(4)*
C(133)	-0.108(1)	0.443(1)	-0.432(2)	6.1(4)*
C(134)	-0.071(2)	0.497(1)	-0.342(2)	6.9(4)*
C(135)	-0.078(1)	0.498(1)	-0.228(2)	6.5(4)*
C(136)	-0.132(1)	0.449(1)	-0.196(1)	5.0(3)*
C(211)	-0.363(1)	0.204(1)	0.172(1)	3.5(3)*
C(212)	0.450(1)	0.140(1)	0.119(1)	5.0(3)*
C(213)	0.499(1)	0.170(1)	0.049(2)	6.7(4)*
C(214)	0.464(2)	0.258(2)	0.030(2)	7.2(5)*
C(215)	0.376(2)	0.326(1)	0.084(2)	6.8(4)*
C(216)	0.324(1)	0.296(1)	0.152(1)	5.5(4)*
C(221)	0.375(1)	0.056(1)	0.285(1)	4.3(3)*
C(222)	0.341(1)	-0.018(1)	0.246(1)	5.3(3)*
C(223)	0.409(2)	-0.108(2)	0.261(2)	7.6(5)*
C(224)	0.515(2)	-0.123(1)	0.318(2)	6.8(4)*
C(225)	0.550(1)	-0.051(1)	0.362(2)	5.6(4)*
C(226)	0.481(1)	0.039(1)	0.351(1)	5.0(3)*
C(231)	0.283(1)	0.247(1)	0.401(1)	3.8(3)*
C(232)	0.353(1)	0.295(1)	0.448(1)	4.7(3)*
C(233)	0.343(2)	0.352(1)	0.558(2)	7.2(5)*
C(234)	0.264(1)	0.363(1)	0.622(2)	6.6(4)*
C(235)	0.194(1)	0.317(1)	0.580(1)	5.4(4)*
C(236)	0.203(1)	0.259(1)	0.471(1)	4.6(3)*

* The starred atoms are refined isotropically.

Table 4 Selected bond lengths for **I**(Å).

atom	atom	distance	atom	atom	distance
Ag(1)	W	3.049(1)	Ag(3)	S(4)	2.656(4)
Ag(2)	W	3.121(2)	S(4)	P(4)	1.968(5)
Ag(3)	W	3.036(2)	S(5)	P(4)	1.975(6)
W	O	1.785(8)	P(4)	O(1)	1.59(1)
W	S(1)	2.254(3)	P(4)	O(2)	1.61(1)
W	S(2)	2.229(3)	O(1)	C(1)	1.43(2)
W	S(3)	2.225(3)	O(2)	C(3)	1.43(3)
Ag(1)	S(1)	2.578(4)	C(1)	C(2)	1.42(3)
Ag(1)	S(2)	2.594(4)	C(3)	C(4)	1.38(4)
Ag(1)	S(5)	2.583(4)	P(1)	C(111)	1.82(1)
Ag(1)	P(1)	2.439(3)	P(1)	C(121)	1.82(1)
Ag(2)	P(2)	2.421(3)	P(1)	C(131)	1.83(1)
Ag(2)	S(2)	2.696(4)	P(2)	C(211)	1.82(1)
Ag(2)	S(3)	2.794(4)	P(2)	C(231)	1.82(1)
Ag(2)	S(4)	2.735(4)	P(2)	C(221)	1.82(1)
Ag(3)	P(3)	2.411(3)	P(3)	C(321)	1.82(1)
Ag(3)	S(1)	2.548(3)	P(3)	C(331)	1.82(1)
Ag(3)	S(3)	2.636(3)	P(3)	C(311)	1.82(1)

Table 5 Selected bond angles for **I** (degrees).

atom	atom	atom	angle	atom	atom	atom	angle
Ag(1)	W	Ag(2)	71.36(4)	P(3)	Ag(3)	S(4)	112.9(1)
Ag(3)	W	Ag(1)	85.75(4)	W	S(1)	Ag(1)	77.9(1)
Ag(3)	W	Ag(2)	67.24(5)	W	S(1)	Ag(3)	78.2(1)
S(2)	W	S(1)	112.1(1)	Ag(3)	S(1)	Ag(1)	107.8(1)
S(3)	W	S(1)	112.2(1)	W	S(2)	Ag(1)	78.0(1)
S(3)	W	S(2)	107.6(1)	W	S(2)	Ag(2)	78.0(1)
O	W	S(1)	108.3(3)	Ag(1)	S(2)	Ag(2)	85.7(1)
O	W	S(2)	106.7(4)	W	S(3)	Ag(2)	76.0(1)
O	W	S(3)	109.8(3)	W	S(3)	Ag(3)	76.8(1)
S(1)	Ag(1)	S(2)	91.9(1)	Ag(3)	S(3)	Ag(2)	77.7(1)
S(1)	Ag(1)	S(5)	117.3(1)	P(4)	S(4)	Ag(2)	98.0(2)
S(5)	Ag(1)	S(2)	100.0(2)	P(4)	S(4)	Ag(3)	107.3(2)
P(1)	Ag(1)	S(1)	110.2(1)	Ag(3)	S(4)	Ag(2)	78.5(1)
P(1)	Ag(1)	S(2)	120.9(1)	P(4)	S(5)	Ag(1)	105.1(2)
P(1)	Ag(1)	S(5)	114.6(2)	O(1)	P(4)	O(2)	98.2(7)
S(2)	Ag(2)	S(4)	131.0(1)	O(1)	P(4)	S(4)	109.8(5)
S(2)	Ag(2)	S(3)	81.8(1)	O(1)	P(4)	S(5)	111.4(5)
S(4)	Ag(2)	S(3)	93.2(1)	O(2)	P(4)	S(4)	105.6(4)
P(2)	Ag(2)	S(2)	117.5(1)	O(2)	P(4)	S(5)	114.7(4)
P(2)	Ag(2)	S(3)	112.4(1)	S(4)	P(4)	S(5)	115.6(3)
P(2)	Ag(2)	S(4)	109.5(1)	C(1)	O(1)	P(4)	119(1)
S(1)	Ag(3)	S(3)	91.6(1)	C(3)	O(2)	P(4)	122(1)
S(1)	Ag(3)	S(4)	111.5(1)	C(2)	C(1)	O(1)	108(2)
S(3)	Ag(3)	S(4)	98.8(1)	C(4)	C(3)	O(2)	114(3)
P(3)	Ag(3)	S(1)	123.2(1)	C(111)	P(1)	C(121)	104.3(6)
P(3)	Ag(3)	S(3)	114.3(1)	C(111)	P(1)	C(131)	104.1(6)
C(121)	P(1)	C(131)	105.3(6)	C(211)	P(2)	C(231)	106.1(6)
C(211)	P(2)	C(221)	101.9(5)	C(231)	P(2)	C(221)	105.1(5)
C(321)	P(3)	C(331)	105.0(5)	C(321)	P(3)	C(311)	103.4(5)
C(331)	P(3)	C(311)	105.4(5)				

Table 6 Selected bond lengths for **II** (Å).

atom	atom	distance	atom	atom	distance
W	O	1.717(8)	Ag(2)	S(3)	2.653(4)
W	S(1)	2.228(4)	Ag(3)*	S	2.390(4)
W	S(2)	2.253(4)	Ag(3)	S(2)	2.522(4)
W	S(3)	2.255(4)	Ag(3)	S(3)	2.504(4)
W	Ag(1)	3.061(2)	S	C(1)	1.87(1)
W	Ag(2)	3.138(2)	C(1)	C(2)	1.53(2)
W	Ag(3)	2.925(2)	C(1)	C(3)	1.50(2)
Ag(1)	S	2.632(4)	C(1)	C(4)	1.56(2)
Ag(1)	S(1)	2.643(4)	P(1)	C(111)	1.83(1)
Ag(1)	S(2)	2.581(4)	P(1)	C(121)	1.82(1)
Ag(1)	P(1)	2.390(4)	P(1)	C(131)	1.81(1)
Ag(2)	P(2)	2.412(4)	P(2)	C(211)	1.83(1)
Ag(2)	S	2.538(4)	P(2)	C(221)	1.79(2)
Ag(2)	S(1)	2.812(4)	P(2)	C(231)	1.82(1)

* The starred atom is symmetry-related.

Table 7 Selected bond angles for **II** (degrees).

atom	atom	atom	angle	atom	atom	atom	angle
Ag(1)	W	Ag(2)	72.59(5)	C(1)	S	Ag(3)	104.4(5)
Ag(3)	W	Ag(1)	86.19(6)	Ag(2)	S	Ag(1)	90.4(1)
Ag(3)	W	Ag(2)	76.82(5)	Ag(3)	S	Ag(1)	121.5(1)
O	W	S(1)	107.6(4)	Ag(3)	S	Ag(2)	113.3(1)
O	W	S(2)	107.4(4)	W	S(1)	Ag(1)	77.3(1)
O	W	S(3)	106.7(4)	W	S(1)	Ag(2)	76.0(1)
S(1)	W	S(2)	111.7(1)	Ag(1)	S(1)	Ag(2)	84.5(1)
S(1)	W	S(3)	110.6(1)	W	S(2)	Ag(1)	78.2(1)
S(2)	W	S(3)	112.5(1)	W	S(2)	Ag(3)	75.3(1)
S	Ag(1)	S(1)	92.4(1)	Ag(3)	S(2)	Ag(1)	106.6(1)
S(2)	Ag(1)	S	97.7(1)	W	S(3)	Ag(2)	79.0(1)
S(2)	Ag(1)	S(1)	90.5(1)	W	S(3)	Ag(3)	75.6(1)
P(1)	Ag(1)	S	119.9(1)	Ag(3)	S(3)	Ag(2)	93.9(1)
P(1)	Ag(1)	S(1)	128.3(1)	C(3)	C(1)	S	109(1)
P(1)	Ag(1)	S(2)	120.2(1)	C(2)	C(1)	S	109(1)
S	Ag(2)	S(3)	109.8(1)	C(4)	C(1)	S	105(1)
S	Ag(2)	S(1)	90.6(1)	C(3)	C(1)	C(2)	114(1)
S(3)	Ag(2)	S(1)	84.8(1)	C(3)	C(1)	C(4)	109(1)
P(2)	Ag(2)	S	128.8(1)	C(2)	C(1)	C(4)	111(1)
P(2)	Ag(2)	S(3)	110.9(1)	C(121)	P(1)	C(111)	104.1(6)
P(2)	Ag(2)	S(1)	122.6(1)	C(131)	P(1)	C(121)	105.3(6)
S	Ag(3)	S(3)	131.6(1)	C(131)	P(1)	C(111)	105.9(6)
S	Ag(3)	S(2)	129.3(1)	C(221)	P(2)	C(231)	107.9(7)
S(3)	Ag(3)	S(2)	96.5(1)	C(221)	P(2)	C(211)	102.8(6)
C(1)	S	Ag(1)	117.7(5)	C(231)	P(2)	C(211)	104.7(6)
C(1)	S	Ag(2)	108.7(5)				

RESULTS AND DISCUSSION

Synthesis

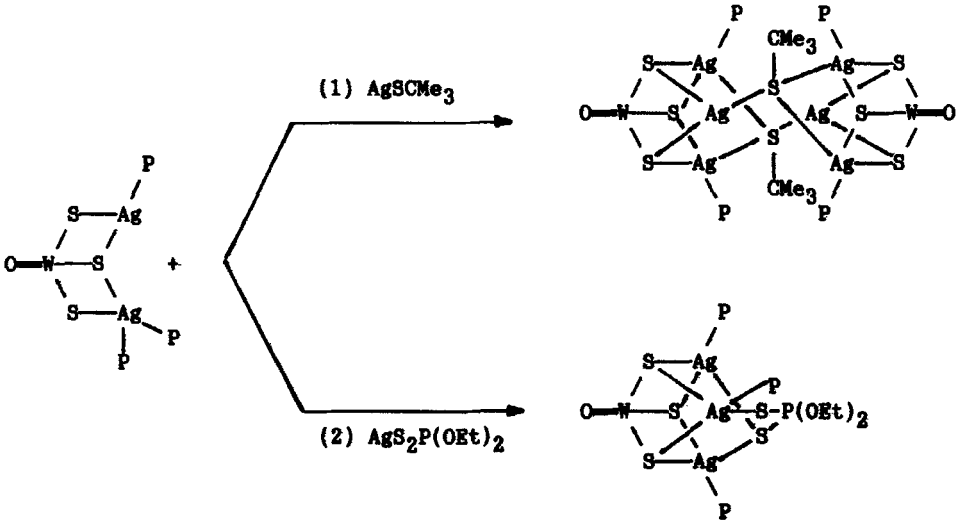
"Unit-construction"[21] is a convenient method for the rational synthesis of transition metal clusters by use of reactive fragments as building blocks. It was shown that

a "unit", which contains sulphido ligands with a lone-pair of electrons and unsaturated coordination, may add to another metal complex which has unsaturated coordination positions or easily displaceable ligands. Following this idea, the butterfly fragment $\{WAg_2S_3\}(O)(Ph_3P)_3$ may be expected to combine with another metal complex to form a cubane-like cluster because of the existence of two unsaturated μ_2-S atoms, and the two cubane-like cores would be connected by the active S atoms in $AgSC(CH_3)_3$.

It is worth noting that syntheses of $\{WAg_2S_3\}(O)(Ph_3P)_3$ with silver-thiolate complexes adopt two different strategies depending on the thiolate ligands used: monodentate thiolate ligands lead to dimerization to form a double cubane-like cluster; bidentate 1,1-dithiolate ligands cause the formation of a single cubane-like cluster (Scheme 1).

Crystal structure of $\{WAg_3S_3[S_2P(OCH_2CH_3)_2]\}(O)(Ph_3P)_3$

Cluster **I** consists of two neutral molecules in the unit cell. An ORTEP drawing of the molecule is shown in Figure 1. The $\{WAg_3S_3\}$ core is an incomplete cubane-like fragment composed of three Ag atoms and the terdentate WS_3O^{2-} ligand. Each Ag atom has one terminally coordinated PPh_3 ligand. In the bridging $S_2P(OCH_2CH_3)_2^-$ ligand, one sulfur links to one Ag atom, while the other bridges the other two Ag atoms. The coordination geometry of the W atom is a distorted tetrahedron; the O–W–S angle (av. 108.27(3)°) is different from S–W–S (av. 110.63(1)°). Each Ag atom is tetrahedrally coordinated by S and Ph_3P ligands, but the Ag(2) tetrahedron [angle range: 81.8(1)°–131.0(1)°] is much more distorted than those of Ag(1) [91.9(1)°–120.9(1)°] and Ag(3) [91.6(1)°–123.2(1)°], corresponding to the longer average Ag(2)-S bond length.



Scheme 1. The reaction of the butterfly compound $\{WAg_2S_3\}(O)(Ph_3P)_3$ with (1) the monodentate thiolate ligand and (2) the bidentate, 1,1-dithiolate ligand.

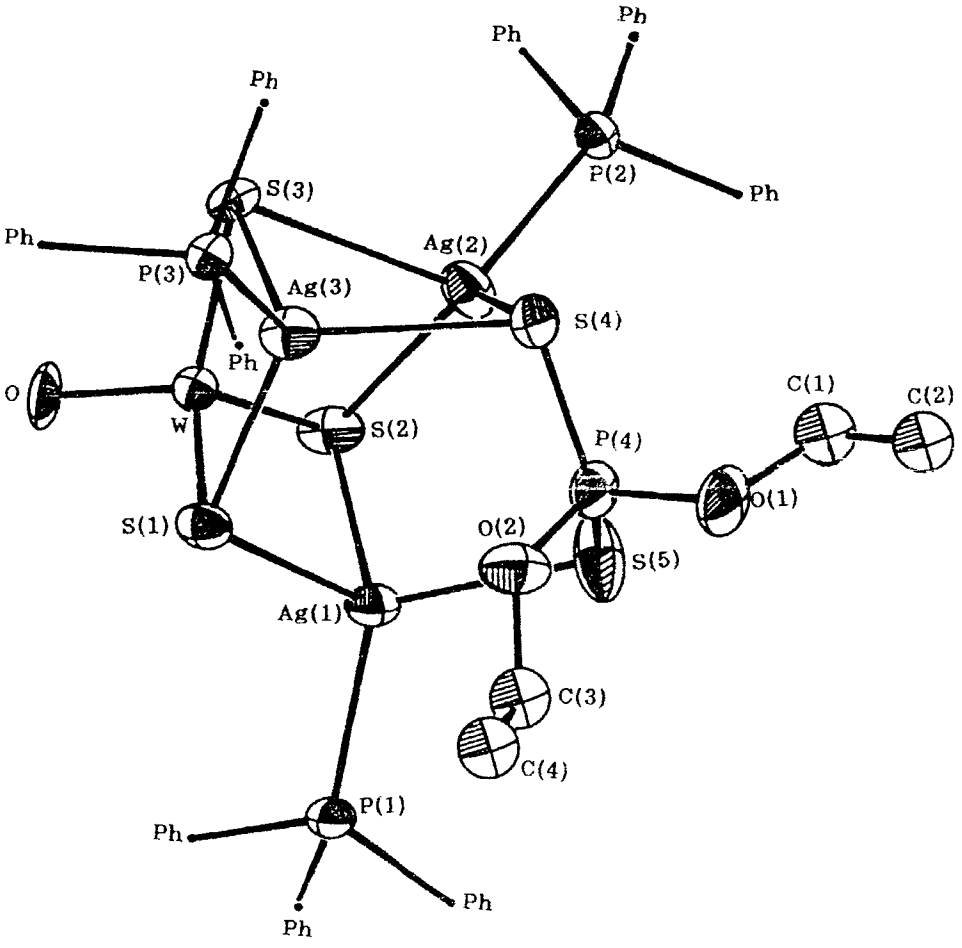


Figure 1 ORTEP drawing of cluster I $\{WAgS_3[S_2P(OCH_2CH_3)_2]\}(O)(Ph_3P)_3$ with 30% probability levels for thermal ellipsoids.

Structure of $\{W_2Ag_6S_6[SC(CH_3)_3]_2\}(O)_2(Ph_3P)_4$

The molecular structure of cluster **II** is presented in Figure 2. The structure consists of one neutral molecule in the unit cell. The crystallographic inversion centre is the centre of the molecule. The W atom [angle range: 106.7(4)–112.5(1)°] is tetrahedrally coordinated. The coordination geometry of the two Ag atoms which are attached to Ph_3P ligands is that of a distorted tetrahedron [angles vary between 128.8(1) and 84.8(1)°], while the other Ag atom is in an approximately planar triangular environment [the sum of three angles 357.4°]. In the cubane-like core of the half molecule, W-Ag(3) [2.925(2) Å] is somewhat shorter than W-Ag(1) [3.061(2) Å] and W-Ag(2) [3.138(2) Å], and the three Ag-S [at $SC(CH_3)_3^-$] distances are not equivalent, being 2,390(4), 2.538(4) and 2.632(4) Å, respectively. Meanwhile, the angles around the organosulfur atoms are quite different: [Ag(2)-S-Ag(1)]

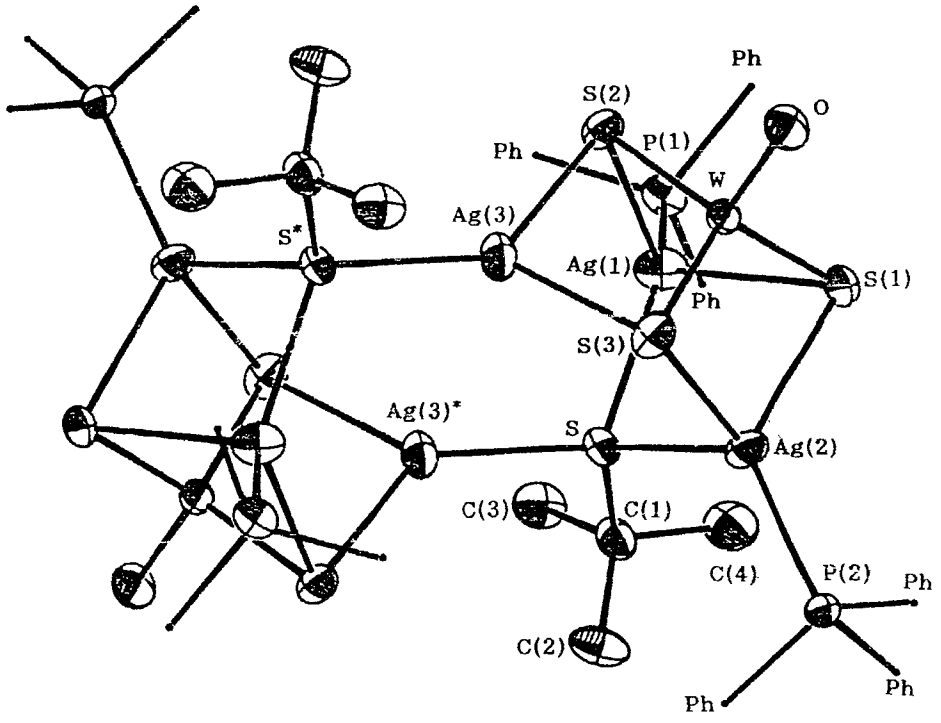


Figure 2 ORTEP drawing of cluster **II** $\{W_2Ag_6S_6[SCMe_3]_2\}(O)_2(Ph_3P)_4$ with 30% probability levels for thermal ellipsoids.

90.4(1)°; [C(1)-S-Ag(2)] 108.7(5)°; [C(1)-S-Ag(1)] 117.7(4)°. The $SC(CH_3)_3^-$ ligand acts as a bridge to connect two cluster fragments.

Table 8 represents a comparison of some related clusters. In these clusters, the average lengths for M-Ag are too long for effective bonding. All M-μ_3-S bond lengths are relatively short and close to that of the double M = S bond in the MS_4^{2-} anion.[22] Average Ag-μ_3-S bond lengths can be considered to be single bonds and are a little longer than those of Mo(W)-Cu-S compounds[23] owing to the large size of Ag(I).

The structure of **I** is similar to that of $\{MoAg_3S_3Cl\}(O)(Ph_3P)_3$[14(b)] except that the chloride ion is replaced by the 1,1-dithiophosphato(1-) ligand. The three Ag-S bonds [at $S_2P(OCH_2CH_3)_2^-$] are different, and Ag(2)-S(4) [2.735(4) Å] is longer than Ag(1)-S(5) [2.583(4) Å] and Ag(3)-S(4) [2.656(4) Å]. Otherwise, in $\{MoAg_3S_3Cl\}(O)(Ph_3P)_3$, the interaction between Cl and the three Ag atoms is relatively weak, in which one of the three Ag-Cl bond lengths [Ag(2)-Cl, 2.843(4) Å] is a little longer than the others [Ag(1)-Cl, 2.792(4) Å; Ag(3)-Cl, 2.795(5) Å].

It is noted that when Ag has a tetrahedral coordination, one of the Ag-S distances is always a little longer than the others and silver thus tends to be trigonally coordinated. In **II** Ag(2)-S(1) [2.812(4)Å] is too long to form a bond, as in **I** [Ag(2)-S(3) 2.794(4) Å] and $\{Mo_2Ag_6S_6[SCMe_3]_2\}(O)_2(Ph_3P)_4$ [Ag(1)-S(2) 2.762(3)Å].

Table 8 Comparison of bond lengths in some related M-Ag-S clusters, (M = Mo or W; X = Cl or S).

Compound	$\{MoAg_3S_3Cl\}(O)(Ph_3P)_3$	$\{MoAg_3S_3Cl\}(S)(Ph_3P)_3$	$\{Mo_2Ag_2S_6[SCMe_3]_2\}(O)_2(Ph_3P)_4$	I	II
	3.006(2)	2.959(3)	2.885(2)	3.049(1)	3.061(2)
M-Ag	2.948(2)	2.913(2)	3.100(1)	3.121(2)	3.138(2)
	2.985(2)	2.961(3)	3.003(1)	3.036(2)	2.925(2)
	2.256(4)	2.257(3)	2.234(3)	2.254(3)	2.228(4)
M-μ_3-S	2.246(4)	2.242(3)	2.224(3)	2.229(3)	2.253(4)
	2.251(4)	2.246(3)	2.244(3)	2.225(3)	2.255(4)
	2.616(4)	2.587(3)	2.475(3)	2.578(4)	2.643(4)
	2.552(5)	2.551(3)	2.483(3)	2.594(4)	2.581(4)
	2.515(4)	2.512(3)	2.631(3)	2.696(4)	2.812(4)
Ag-μ_3-S	2.553(4)	2.548(3)	2.762(3)	2.794(4)	2.653(4)
	2.585(5)	2.592(3)	2.595(3)	2.548(3)	2.522(4)
	2.554(4)	2.548(3)	2.545(3)	2.636(3)	2.504(4)
	2.792(4)	2.835(3)	2.389(3)	2.583(4)	2.632(4)
Ag-X	2.843(4)	2.840(3)	2.525(3)	2.735(4)	2.538(4)
	2.795(5)	2.770(3)	2.644(3)	2.656(4)	2.390(4)
Ref.	14(b)	14(a)	15	this work	

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Supplementary material

Lists of anisotropic thermal parameters, complete tables of bond lengths and angles and observed and calculated structure factors are available from the authors on request.

References

1. H. Vahrenkamp, *Angew. Chem., Int. Edn. Engl.*, **14**, 322 (1975).
2. A. Müller, E. Diemann, R. Jostes and H. Bögge, *Angew. Chem., Int. Edt. Engl.*, **20**, 934 (1981).
3. I. G. Dance, *Polyhedron*, **5**, 1037 (1986).
4. (a) R. E. Palermo, R. Singh, J. K. Bashkin and R. H. Holm, *J. Am. Chem. Soc.*, **106**, 2600 (1984), and references therein; (b) Q.-T. Liu, L.-R. Huang, H.-Q. Liu, X.-J. Lie, D.-X. Wu, B.-S. Kang and J.-X. Lu, *Inorg. Chem.*, **29**, 4131 (1990), and references therein.
5. S. Ciurli, S.-B. Yu, R. H. Holm, K. K. P. Srivastava and E. Münck, *J. Am. Chem. Soc.*, **112**, 8169 (1990).
6. J. A. Kovacs and R. H. Holm, *J. Am. Chem. Soc.*, **108**, 340 (1986); *Inorg. Chem.*, **26**, 711 (1987).
7. (a) T. E. Wolff, J. M. Berg, K. O. Hodgson, R. B. Frankel and R. H. Holm, *J. Am. Chem. Soc.*, **101**, 4140 (1979); (b) G. Christou, C. D. Garner, F. E. Mabbs and F. J. King, *J. Chem. Soc., Chem. Comm.*, 740 (1978).
8. C. F. Mills, *Chem. Ber.*, **15**, 512 (1979).
9. J. Kim and D. C. Rees, *Science*, **257**, 1677 (1992).
10. S. F. Gheller, T. W. Hambley, J. R. Rodgers, R. T. C. Brownlee, M. J. O'Connor, M. R. Snow and A. G. Wedd, *Inorg. Chem.*, **23**, 2519 (1984).
11. (a) A. Müller and R. Menge, *Z. Anorg. Allg. Chem.*, **393**, 259 (1972); (b) J. C. Huffman, R. S. Roth and A. R. Siedle, *J. Am. Chem. Soc.*, **98**, 4340 (1976); (c) W. G. Zumft, *Eur. J. Biochem.*,

91, 345 (1978); (d) A. Müller H. Bögge and U. Schimanski, *Inorg. Chim. Acta,* **69,** 5 (1983).
12. (a) A. Müller, H. Bögge, E. Königer-Ahlborn and W. Hellmann, *Inorg. Chem.,* **18,** 2301 (1979); (b) A. Müller, H. Bögge and T. K. Hwang, *Inorg. Chem.,* **39,** 73 (1980); (c) J. K. Stalick, A. R. Siedle, A. D. Minghell and C. R. Hubbard, *J. Am. Chem. Soc.,* **101,** 2903 (1979).
13. N.-Y. Zhu, X.-T. Wu and J.-X. Lu, *J. Chem. Soc., Chem. Comm.,* 235 (1991).
14. (a)N.-Y. Zhu, J.-H. Wu, S.-W. Du, X.-T. Wu and J.-X. Lu, *Inorg. Chim. Acta,* **191** , 65 (1992); (b) J.-H. Wu, N.-Y. Zhu, S.-W. Du and X.-T. Wu, *Polyhedron,* **11,** 1201 (1992).
15. S.-W. Du, N.-Y. Zhu, P.-C. Chen and Xintao Wu, *Polyhedron,* **11,** 2489 (1992).
16. J. W. McDonald and G. D. Friesen, *Inorg. Chim. Acta,* **72,** 205 (1983).
17. N. Walker and D. Stuart, *Acta Cryst,* **A39,** 159 (1983).
18. P. T. Beirskens, "DIRDIF: *Direct Methods for Difference Structures-An Automatic Procedure for Phase Extension and Refinement of Difference Structure Factors,"* Technical Report 1984/1 Crystallography Laboratory, Toernooiveld, 6526 Ed Nijmegen, the Netherlands (1984).
19. "*TEXSAN, TEXRAY Structure Analysis Package,"* Molecular Structure Corp., MSC 3200A Research Forest Drive, The Woodlands, TX77381, USA, (1985).
20. D. T. Cromer and J. T. Waber, *International Tables for X-ray Crystallography* (Kynoch Press, Birmingham, England 1974), Vol. IV, Tables 2.2a, 2.3.1.
21. X.-T. Wu and J.-X. Lu, *Jiegou Huaxue (J. Struct. Chem.),* **8,** 399 (1989).
22. (a) A. Müller, E. Diemann, R. Jostes and H. Bögge, *Angew. Chem., Int. Ed. Engl.,* **20,** 934 (1981), and references therein; (b) K. Sasvari, *Acta Cryst.,* **16,** 719 (1963).
23. N.-Y. Zhu, S.-W. Du, P.-C. Chen and X.-T. Wu, *J. Cluster Science,* **3,** 201 (1992).