chelation in [Ag(9S3)Cl] originates in the unique conformation of the nine-membered ring.

Strong coordination by 9S3 qualitatively influences the electrochemical behavior of $[Ag(9S3)_2]^+$. First, by promoting six-coordination, it presumably generates high electron density on the metal and thereby promotes oxidation to $[Ag(9S3)_2]^{2+}$ at a relatively low potential.

Second, it improves the reversibility of the $[Ag(9S3)_2]^{2+/+}$ couple. Typically ligands form stable complexes either with Ag(I) or with Ag(II), but not both. For example, the stable $[Ag(cyclam)]^{2+}$ cation[32] (cyclam = 1,4,8,11-tetraazacyclotetradecane) disproportionates on reduction.[33] Larger N_4 macrocycles form stable complexes with Ag(I) but not Ag(II).[34] Irreversibility results in either case, since only half of the couple exists in solution. Thioethers thermodynamically stabilize lower oxidation states of metal ions by binding more strongly to them than to those in higher oxidation states.[35] Oxidation therefore decrements the stability of a thioether complex. Complexes of 9S3, however, are so stable that even the more weakly bound oxidized form still has sufficient stability to resist ligand substitution by solvent molecules. Electrochemical reversibility results, since both oxidized and reduced forms can exist in solution.

Conclusions

Coordination of conformationally favorable crown thioethers imposes not only different coordination behavior on Ag(I)—in this case six- instead of four-coordination—but also different electrochemistry. The facile oxidation of $[Ag9S3)_2]^+$ apparently results from the great stability of 9S3 complexes; as a consequence of this stability, oxidation to the dication yields a reasonably stable complex that can be observed by cyclic voltammetry. These results underscore once again the singular attributes conferred on 9S3 by its conformation, which uniquely suits it for chelation. In a broader context, they demonstrate the importance of conformational considerations to ligand design.

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Registry No. $[Ag(9S3)_2](CF_3SO_3)$, 110922-45-7; $[Ag(9S3)](CF_3SO_3)$, 110899-85-9; [Ag(9S3)Cl], 122539-96-2; [Ag(18S6)Br], 122539-99-5; $[Ag(18S6)NO_3]$, 122566-64-7; $[Ag(12S3)](CF_3SO_3)$, 122539-98-4; $[Ag(12S3)](CF_3O_3)\cdot MeCN$, 122540-01-6; $[Ag(9S3)_2]^{2+}$, 110899-86-0.

Supplementary Material Available: Tables containing full crystallographic data, bond distances and angles, anisotropic thermal parameters, hydrogen atomic coordinates, and torsional angles (17 pages); tables of structure factors (60 pages). Ordering information is given on any current masthead page.

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Notes

Contribution from the Faculty of Chemistry,
University of Bielefeld,
D-4800 Bielefeld 1, West Germany

Formation of the Metal–Sulfide Aggregate $[W_3S_{10}]^{2-}$ through a Novel Balanced Intramolecular Condensation Redox Process with Principal Relevance to the Formation of Amorphous Metal Sulfides like WS_3

A. Müller,* E. Diemann, U. Wienböker, and H. Bögge

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Although the formation of isopoly anions by protonation of oxoanions of the transition metals has been studied in numerous investigations, little is known about corresponding reproducible stoichiometric reactions of thioanions.[1,2] We have now obtained $[W_3S_{10}]^{2-}$ (**1**) with the new $[WS_5]^{2-}$ ligand in the mixed-crystal compounds $(PPh_4)_2[W_3S_{10}]_{0.7}[W_3S_9]_{0.3}\cdot DMF$ (**2**) (DMF = *N*,*N*-dimethylformamide) and $((PPh_3)_2N)_2[W_3S_{10}]_{0.3}[W_3S_9]_{0.7}\cdot {}^1/_2CH_2Cl_2$ (**3**) by controlled acidification of a methanolic solution of $(NH_4)_2[WS_4]$ with gaseous HCl; **2** only forms in the presence of manganese chloride (see below).

Experimental Section

Synthesis. The products are prepared in an argon atmosphere. The solvents used were analytically pure and were dried over molecular sieves.

$(PPh_4)_2[W_3S_{10}]_{0.7}[W_3S_9]_{0.3}\cdot DMF$ (2). $MnCl_2\cdot 4H_2O$ (2.38 g, 12 mmol) is added to a solution of $(NH_4)_2[WS_4]$ (4.20 g, 12 mmol) in 1200 mL of methanol, and then gaseous HCl (7.5 L/h) is passed for 60–70 s through the solution under vigorous stirring. After 20 min a solution of PPh_4Cl (3.00 g, 8 mmol) in 40 mL of methanol is added and the mixture is stirred for 2 h. The precipitate is filtered off, washed with toluene, methanol, and ether, and dissolved in 90 mL of CH_2Cl_2/DMF (2:1). The solution is filtered, and the filtrate is carefully covered with a layer of 100 mL of *n*-hexane (in a cylindrical vessel, diameter ca. 3 cm) and kept for 6–8 days at 5–7 °C. Dark red crystals of **2** are filtered off, washed with toluene, methanol (to remove the small amount of coprecipitated yellow $(PPh_4)_2[WS_4]$), and ether, and dried in vacuum, yield 1.70 g (26%). Anal. Calcd (found): C, 37.9 (37.9); H, 2.9 (2.9); N, 0.9 (1.0); S, 19.3 (19.3). IR (CsI pellet): 527 ($\nu(WS_{cent})$, ν(S–S), and a cation band), 495 ($\nu(WS_{term})$), 465, 435 ($\nu(WS_{br})$), 320 ($\nu(W-S_2)$) cm^{-1}. Ra-

Table I. Crystal Data, Intensity Measurement, and Refinement Parameters for **2–4**

	2	**3**	**4**
mol wt	1614.5	1969.4	1593.5
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, pm	1158.7 (17)	1330.2 (3)	1186.3 (4)
b, pm	1525.6 (21)	1387.7 (3)	1282.4 (5)
c, pm	1847.7 (24)	2126.0 (4)	2043.5 (7)
α, deg	76.65 (10)	93.73 (2)	83.04 (3)
β, deg	72.73 (10)	95.03 (2)	88.25 (3)
γ, deg	67.46 (10)	99.18 (2)	63.74 (2)
V, pm^3	2855.2×10^6	3846.8×10^6	2766.7×10^6
Z	2	2	2
ρ_{calcd}, $g\cdot cm^{-3}$	1.88	1.70	1.91
μ(Mo Kα), cm^{-1}	65.93	49.72	68.59
radiation	Mo Kα (graphite monochromator; λ = 71.069 pm)		
temp, K	294	294	294
R^a	0.086	0.086	0.078
R_w^b	0.084	0.130	0.086
g^c	0.0001	0.002	0.0002

[a] $\sum||F_o| - |F_c||/\sum|F_o|$. [b] $[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. [c] $1/w = \sigma^2(F_o) + gF_o^2$.

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* To whom correspondence should be addressed.

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Table II. Atomic Coordinates ($\times 10^4$) for $(PPh_4)_2[W_3S_{10}]_{0.7}[W_3S_9]_{0.3}\cdot DMF$ (**2**)

	x	*y*	*z*
W(1)	8761 (1)	7210 (1)	6146 (1)
W(2)	9344 (1)	7373 (1)	7590 (1)
W(3)	9536 (1)	8589 (1)	8553 (1)
S(1)	8162 (7)	8304 (5)	5231 (3)
S(2)	8929 (7)	5830 (5)	5921 (3)
S(3)	7377 (6)	7586 (5)	7259 (3)
S(4)	10592 (6)	7204 (5)	6299 (3)
S(5)	9884 (7)	5987 (5)	8197 (3)
S(6)	10995 (6)	7970 (5)	7515 (3)
S(7)	7745 (6)	8396 (5)	8464 (3)
S(8)	10087 (7)	7754 (6)	9564 (4)
S(9)[a]	8324 (17)	10205 (10)	8808 (9)
S(10)[a]	10266 (19)	9947 (12)	8338 (9)
S(11)[b]	9220 (29)	10035 (27)	8393 (30)
P(1)	5083 (6)	4626 (5)	1731 (3)
P(2)	5478 (6)	8842 (4)	3056 (3)
C(1)	2457 (15)	5315 (10)	2089 (7)
C(2)	1251	5931	1982
C(3)	1150	6726	1421
C(4)	2256	6906	966
C(5)	3462	6290	1073
C(6)	3562	5495	1635
C(7)	6296 (11)	5951 (9)	1284 (6)
C(8)	7234	6337	837
C(9)	8181	5859	253
C(10)	8190	4994	118
C(11)	7251	4608	565
C(12)	6304	5086	1148
C(13)	4431 (15)	3840 (12)	3210 (9)
C(14)	4463	3630	3981
C(15)	5272	3908	4239
C(16)	6048	4396	3725
C(17)	6016	4607	2953
C(18)	5207	4329	2696
C(19)	6243 (14)	2712 (14)	1576 (8)
C(20)	6410	1876	1312
C(21)	5593	1884	886
C(22)	4609	2727	724
C(23)	4442	3564	988
C(24)	5260	3556	1414
C(25)	3645 (13)	8300 (10)	4173 (8)
C(26)	2391	8379	4577
C(27)	1357	9120	4341
C(28)	1577	9781	3702
C(29)	2831	9702	3299
C(30)	3865	8961	3534
C(31)	5075 (14)	10373 (15)	3712 (10)
C(32)	5437	11019	3942
C(33)	6735	10902	3807
C(34)	7670	10138	3443
C(35)	7307	9492	3213
C(36)	6010	9609	3347
C(37)	6723 (14)	9256 (12)	1597 (9)
C(38)	7001	9276	806
C(39)	6184	9104	476
C(40)	5090	8911	936
C(41)	4812	8891	1726
C(42)	5629	9064	2057
C(43)	6855 (13)	7002 (11)	2783 (6)
C(44)	7679	6071	2940
C(45)	8178	5810	3589
C(46)	7852	6480	4082
C(47)	7028	7411	3926
C(48)	6530	7672	3276
O	3961 (19)	6962 (15)	2739 (10)
C(49)	2775 (33)	7404 (26)	2788 (18)
N(1)	1931 (23)	7085 (18)	3380 (12)
C(50)	2197 (34)	6354 (26)	3950 (18)
C(51)	608 (40)	7661 (31)	3347 (22)

[a] Occupancy factor 0.7. [b] Occupancy factor 0.3.

man (λ_e = 647.1 nm): 520 ($\nu(WS_{cent})$), 497 ($\nu(WS_{term})$), 447 ($\nu(WS_{br})$) cm^{-1}.

$((PPh_3)_2N)_2[W_3S_{10}]_{0.3}[W_3S_9]_{0.7}\cdot{}^1/_2CH_2Cl_2$ (3). Gaseous HCl (7.5 L/h) is passed for 10–12 s through a solution of $(NH_4)_2[WS_4]$ (0.70 g, 2 mmol) in 200 mL of methanol under vigorous stirring. After 20 min a solution of $((PPh_3)_2N)Cl$ (0.77 g, 1.34 mmol) in 20 mL of methanol is added and the mixture is stirred for 12 h. The orange precipitate is filtered off, washed with toluene, methanol, and ether, and dissolved in 30 mL of CH_2Cl_2/DMF (2:1). The solution is covered with a layer of 30 mL of *n*-hexane and kept for 3–5 days at 5 °C. Dark red crystals of **3** are filtered off, washed with toluene, methanol, and ether, and dried in vacuum, yield 1.07 g (27%). Anal. Calcd (found): C, 44.2 (44.6); H, 3.1 (3.3); N, 1.4 (1.3); S, 15.1 (14.9). IR (CsI pellet): 526 ($\nu(WS_{cent})$, ν(S-S), and a cation band), 494 ($\nu(WS_{term})$), 461, 434 ($\nu(WS_{br})$), 325 ($\nu(W-S_2)$) cm^{-1}. Raman (λ_e = 647.1 nm): 523 ($\nu(WS_{cent})$), 498 ($\nu(WS_{term})$), 448 ($\nu(WS_{br})$) cm^{-1}.

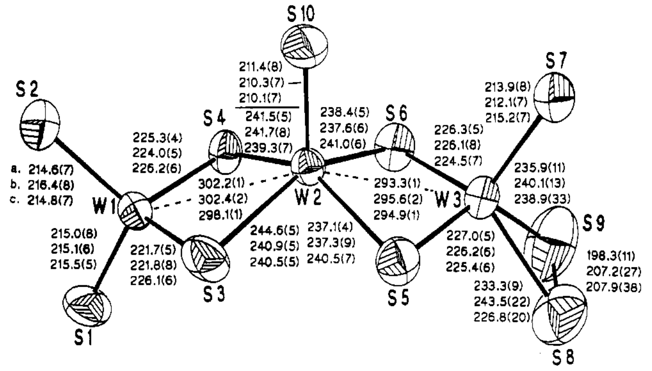

Figure 1. Ellipsoid plot of the $[W_3S_{10}]^{2-}$ anion in **4** with bond lengths (a, in pm). Below the values for **4** the "formal" corresponding bond lengths for the equivalent atoms in the $[W_3S_{10}]^{2-}$ anions in the mixed-crystal compounds **2** (b) and **3** (c) are given. Bond angles (deg) for the anion in **4**: S(1)-W(1)-S(2) = 110.8 (3), S(1)-W(1)-S(3) = 109.7 (2), S(1)-W(1)-S(4) = 110.4 (2), S(2)-W(1)-S(3) = 110.7 (2), S(2)-W(1)-S(4) = 111.1 (2), S(3)-W(1)-S(4) = 103.9 (2), S(3)-W(2)-S(4) = 92.8 (2), S(3)-W(2)-S(5) = 76.7 (2), S(3)-W(2)-S(6) = 150.4 (2), S(3)-W(2)-S(10) = 105.0 (2), S(4)-W(2)-S(5) = 146.8 (2), S(4)-W(2)-S(6) = 77.6 (2), S(4)-W(2)-S(10) = 105.3 (2), S(5)-W(2)-S(6) = 96.0 (2), S(5)-W(2)-S(10) = 107.9 (2), S(6)-W(2)-S(10) = 104.5 (2), S(5)-W(3)-S(6) = 102.4 (2), S(5)-W(3)-S(7) = 107.9 (3), S(5)-W(3)-S(8) = 91.1 (2), S(5)-W(3)-S(9) = 133.9 (3), S(6)-W(3)-S(7) = 110.2 (2), S(6)-W(3)-S(8) = 129.8 (3), S(6)-W(3)-S(9) = 90.0 (3), S(7)-W(3)-S(8) = 111.0 (3), S(7)-W(3)-S(9) = 108.9 (3), S(8)-W(3)-S(9) = 50.0 (3), W(1)-S(3)-W(2) = 80.6 (1), W(1)-S(4)-W(2) = 80.6 (1), W(2)-S(5)-W(3) = 78.3 (1), W(2)-S(6)-W(3) = 78.2 (1), W(3)-S(8)-S(9) = 65.7 (4), W(3)-S(9)-S(8) = 64.3 (4).

Crystallographic Data Collection and Refinement of the Structure. The structures of **2**–**4** were determined from single-crystal X-ray diffraction data (Syntex P2₁ four-circle diffractometer). Crystal data and details concerning the intensity, data collection, and structure refinement are given in Table I. The structures of **2** and **3** were each determined twice by using crystals from different lots. The results of the better determinations (the two determinations of the same substance lead to approximately the same results) are given in this work. Room-temperature unit cell parameters were obtained by the least-squares refinement of the angular settings of 15 high-angle reflections (20° < 2θ < 30°). Empirical absorption corrections were applied. The data were corrected for Lorentz and polarization effects. No extinction corrections were performed. The structures were solved by conventional heavy-atom methods (SHELXTL program package).[3] During the last cycles of the refinement no parameter shifted more than 0.1σ, where σ is the standard deviation of the parameter.

The atomic scattering factors for all atoms were taken from standard sources.[4] Anomalous dispersion corrections were applied to all atoms. Atomic parameters for **2**–**4** are given in Tables II–IV. Bond lengths and bond angles are presented in Figure 1.

Results and Discussion

2–**4** were characterized by X-ray structure analyses (see Table I and Figure 1). **1** does *not* show the $[Cr_3O_{10}]^{2-}$ structure,[5] namely $[(WS_3(\mu\text{-}S))_2WS_2]^{2-}$. Instead an intramolecular redox process

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(3) "SHELXTL", revision 5.1, Nicolet Analytical Instruments, Dec 1985.

(4) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

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Table III. Atomic Coordinates ($\times 10^4$) for $((PPh_3)_2N)_2[W_3S_{10}]_{0.3}[W_3S_9]_{0.7}\cdot{}^1/_2CH_2Cl_2$ (**3**)

	x	*y*	*z*		*x*	*y*	*z*
W(1)	−1325 (1)	−1051 (1)	2793 (1)	C(31)	7191 (10)	5214 (10)	893 (6)
W(2)	336 (1)	475 (1)	2452 (1)	C(32)	7482	6062	1300
W(3)	1222 (1)	2231 (1)	1853 (1)	C(33)	8194	6072	1824
S(1)	−2960 (4)	−1357 (5)	2560 (3)	C(34)	8615	5235	1940
S(2)	−850 (6)	−2130 (5)	3382 (3)	C(35)	8325	4387	1533
S(3)	−545 (5)	−1025 (4)	1890 (3)	C(36)	7613	4377	1009
S(4)	−811 (5)	483 (4)	3258 (3)	C(37)	7487 (11)	588 (10)	4459 (6)
S(5)	606 (5)	734 (4)	1367 (3)	C(38)	7598	−396	4438
S(6)	445 (5)	2197 (4)	2749 (3)	C(39)	8239	−722	4903
S(7)	2858 (6)	2387 (5)	2044 (4)	C(40)	8770	−64	5390
S(8)[a]	781 (9)	3388 (7)	1274 (5)	C(41)	8660	920	5411
S(8a)[b]	835 (25)	3855 (23)	1906 (16)	C(42)	8018	1246	4945
S(8b)[b]	687 (15)	3052 (13)	1033 (9)	C(43)	8178 (9)	2767 (11)	3763 (7)
S(9)	1681 (5)	102 (5)	2894 (3)	C(44)	7951	3028	3150
P(1)	5609 (4)	2847 (4)	−539 (3)	C(45)	7016	3323	2982
P(2)	7213 (4)	3267 (4)	518 (3)	C(46)	6308	3357	3427
P(3)	7778 (4)	2459 (4)	4999 (3)	C(47)	6536	3096	4039
P(4)	6365 (4)	2468 (4)	6043 (3)	C(48)	7471	2801	4207
N(1)	6798 (13)	2581 (11)	5363 (8)	C(49)	9886 (13)	3079 (11)	5158 (8)
N(2)	6206 (13)	3410 (11)	87 (8)	C(50)	10778	3727	5381
C(1)	4834 (11)	3458 (9)	−1668 (7)	C(51)	10724	4563	5769
C(2)	4744	4137	−2117	C(52)	9778	4753	5934
C(3)	5352	5061	−2029	C(53)	8886	4105	5711
C(4)	6050	5307	−1491	C(54)	8940	3269	5323
C(5)	6140	4628	−1042	C(55)	5361 (10)	3956 (11)	5734 (8)
C(6)	5532	3703	−1131	C(56)	4549	4481	5711
C(7)	3721 (12)	1579 (10)	−755 (7)	C(57)	3645	4114	5963
C(8)	2713	1264	−634	C(58)	3552	3222	6237
C(9)	2293	1750	−153	C(59)	4364	2697	6260
C(10)	2882	2552	208	C(60)	5269	3064	6008
C(11)	3891	2867	87	C(61)	5818 (15)	1044 (12)	6823 (8)
C(12)	4310	2381	−395	C(62)	5513	82	6970
C(13)	6684 (12)	1920 (9)	−1371 (7)	C(63)	5372	−683	6494
C(14)	7153	1146	−1583	C(64)	5535	−486	5873
C(15)	7044	280	−1279	C(65)	5839	476	5727
C(16)	6465	187	−764	C(66)	5981	1241	6202
C(17)	5996	961	−552	C(67)	7083 (12)	3869 (11)	7040 (9)
C(18)	6105	1827	−855	C(68)	7773	4293	7553
C(19)	5944 (9)	2081 (10)	1207 (7)	C(69)	8607	3849	7744
C(20)	5725	1399	1651	C(70)	8751	2982	7421
C(21)	6505	960	1933	C(71)	8062	2558	6908
C(22)	7503	1203	1771	C(72)	7228	3002	6717
C(23)	7721	1885	1327	C(73)[c]	2649 (42)	2764 (37)	3771 (26)
C(24)	6942	2324	1045	Cl(1)[d]	3582 (19)	2753 (17)	4441 (12)
C(25)	8492 (11)	2139 (8)	−68 (7)	Cl(2)[e]	2334 (28)	3858 (24)	3832 (18)
C(26)	9272	2024	−451	Cl(3)[e]	2768 (32)	3947 (27)	3567 (20)
C(27)	9814	2838	−694	Cl(4)[f]	3877 (39)	2915 (34)	4217 (26)
C(28)	9577	3767	−555	Cl(5)[f]	3750 (62)	3183 (58)	3923 (43)
C(29)	8798	3882	−173	Cl(6)[g]	1959 (37)	3366 (34)	4147 (23)
C(30)	8255	3068	71				

[a] Occupancy factor 0.7. [b] Occupancy factor 0.3. [c] Occupancy factor 0.5. [d] Occupancy factor 0.3. [e] Occupancy factor 0.15. [f] Occupancy factor 0.1. [g] Occupancy factor 0.2.

occurs with formation of an S_2^{2-} group accompanied by a formal two-electron reduction of a W_3 unit.[6]

The ion **1** is of particular interest because it represents, after the $[WS_3(SH)]^{2-}$ ion,[12] one more defined step during the formation of noncrystalline WS_3, which is the final product of the protonation reaction. This and related compounds may be precursors for heterogeneous catalysts and cathodes in lithium cells.[13] The amorphous nature of these materials has hindered their complete structural characterization.[14] But there is now evidence for S_2^{2-} groups, and in addition, arguments have been given for the

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(6) This represents a balanced intramolecular redox reaction. The formulation of **1** is $[SW^{IV}(W^{VI}S_4)(W^{VI}S_3(S_2))]^{2-}$ with the new $[WS_5]^{2-}$ ligand rather than $[(W^{VI}S_4)W^V{}_2S_4(S_2)]^{2-}$.[7] Unbalanced intramolecular redox reactions with formation of S_2^{2-} ligands are known, i.e. during the formation of $[Mo_2S_4(S_2)_2]^{2-}$ from $[MoS_4]^{2-}$ with an external oxidant[10] and probably also during the formation of $[Mo_2O_2S_2(S_2)_2]^{2-}$ from $[MoO_2S_2]^{2-}$,[11] which was the first reported reaction of that type.

(7) In species with the central $M^V{}_2S_2^{2+}$ unit (M = Mo, W; with an M–M single bond) like e.g. those in $[Mo_2O_2S_2(S_4)_2]^{2-}$, $[Mo_2OS_3(S_2)_2]^{2-}$, $[Mo_2O_2S_2(S_2)_2]^{2-}$, $[W_2S_4(S_4)_2]^{2-}$, $[W_2O_2S_2(S_4)_2]^{2-}$, and $[W_2S_4(S_2)(S_4)]^{2-}$, the MS_{br} distances are practically equal[8]—in contrast to those in **1**, $[SW^{IV}(W^{VI}S_4)_2]^{2-}$,[9] and similar species (see also: Do, Y.; Simhon, E. D.; Holm, R. H. *Inorg. Chem.* **1985**, *24*, 2827).

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Table IV. Atomic Coordinates (×10^4) for $(PPh_4)_2[W_3S_{10}]\cdot{}^1/_2CH_2Cl_2$ (**4**)

	x	*y*	*z*
W(1)	2606 (1)	847 (1)	3485 (1)
W(2)	4590 (1)	327 (1)	2447 (1)
W(3)	6017 (1)	–939 (1)	1365 (1)
S(1)	1296 (6)	142 (5)	3764 (3)
S(2)	2411 (7)	2174 (5)	4088 (3)
S(3)	4550 (5)	–584 (4)	3565 (3)
S(4)	2348 (5)	1553 (4)	2408 (2)
S(5)	6237 (5)	–1595 (4)	2459 (3)
S(6)	4091 (5)	611 (4)	1298 (2)
S(7)	7431 (6)	–361 (5)	1118 (3)
S(8)	6634 (9)	–2830 (7)	1097 (4)
S(9)	5513 (10)	–1569 (9)	426 (4)
S(10)	5410 (6)	1465 (5)	2554 (3)
P(1)	1758 (5)	6194 (4)	985 (2)
P(2)	2389 (5)	6653 (4)	4492 (2)
C(1)	4289 (12)	5580 (8)	914 (6)
C(2)	5556	4787	902
C(3)	5900	3602	881
C(4)	4977	3209	871
C(5)	3709	4002	883
C(6)	3366	5188	904
C(7)	2040 (9)	4857 (10)	2191 (6)
C(8)	1603	4484	2771
C(9)	314	4941	2877
C(10)	–537	5772	2404
C(11)	–100	6146	1825
C(12)	1189	5688	1719
C(13)	1526 (13)	7958 (10)	1696 (5)
C(14)	1480	9041	1776
C(15)	1548	9772	1228
C(16)	1661	9420	600
C(17)	1708	8337	520
C(18)	1640	7606	1068
C(19)	1360 (9)	5564 (9)	–207 (6)
C(20)	639	5680	–762
C(21)	–591	6563	–842
C(22)	–1100	7331	–367
C(23)	–378	7215	188
C(24)	852	6331	268
C(25)	3543 (12)	6901 (7)	3337 (6)
C(26)	4267	6501	2789
C(27)	4833	5308	2722
C(28)	4675	4516	3202
C(29)	3950	4917	3750
C(30)	3384	6110	3818
C(31)	3066 (12)	5109 (11)	5640 (6)
C(32)	3037	4195	6074
C(33)	2342	3623	5908
C(34)	1677	3965	5307
C(35)	1706	4879	4872
C(36)	2401	5451	5039
C(37)	–148 (12)	8129 (11)	4608 (4)
C(38)	–1378	8798	4364
C(39)	–1655	8871	3696
C(40)	–702	8276	3273
C(41)	528	7607	3517
C(42)	805	7534	4184
C(43)	2436 (10)	7817 (11)	5533 (6)
C(44)	2963	8318	5923
C(45)	4062	8401	5730
C(46)	4634	7982	5148
C(47)	4108	7482	4759
C(48)	3009	7399	4951
C(49)[a]	8987 (54)	2200 (45)	2326 (25)
Cl(1)[a]	8343 (15)	1498 (12)	2132 (7)
Cl(2)[a]	8227 (18)	3436 (15)	2641 (8)

[a] Occupancy factor 0.5.

presence of trinuclear M_3 units[14b,e] or a chainlike arrangement of the metal atoms[14c,d] in the noncrystalline materials, which contain (beside the S_2^{2-} groups) only bridging sulfide ligands.[14b–d]

The decrease of the average oxidation state of tungsten from +6 to +5.33 accompanied by the corresponding balanced increase for sulfur from –2 to –1.8 in **1** applies in a similar way to the formation of WS_3 and explains why the stoichiometry of a W^{VI} compound is retained during the decomposition of $[WS_4]^{2-}$.

During a preparation of **2** without addition of manganese chloride a compound $(PPh_4)_2[W_3S_{10}]\cdot{}^1/_2CH_2Cl_2$ (**4**) could also be isolated; however, reproduction of this experiment turned out to be rather difficult. Initially we wanted to obtain a W–S–Mn cluster compound from the reaction with manganese chloride, which however yielded the new $[W_3S_{10}]^{2-}$ anion. For the reason unknown to us, the presence of manganese chloride is essential for the reproducibility of the preparation of **2**. Notably there exists precedence in literature for the necessicity of manganese chloride to prepare W–S clusters,[15,16] and the reaction did not proceed in this direction even when manganese chloride was substituted by magnesium chloride.

The formation of $[W_3S_9]^{2-}$ is always a competitive reaction; on the other hand, small amounts of **1** may also be present during all preparations of $[W_3S_9]^{2-}$ salts.[17]

Note Added in Proof. The corresponding WOS_4^{2-} ligand has been found in the species $[Br_2FeS_2WO(S_2)]^{2-}$.[18]

Supplementary Material Available: For **2–4**, crystal data (Table S1), bond lengths (Table S2), bond angles (Table S3), anisotropic thermal parameters (Table S4), H atom and isotropic thermal parameters (Table S5), and isotropic parameters for non-hydrogen atoms (Table S6) (7 pages); tables of calculated and observed structure factors (67 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
Northwestern University, Evanston, Illinois 60208

Synthesis and Characterization of $[PPh_4]_2[W_2Se_6]$

Ying-jie Lu, Mohammad A. Ansari, and James A. Ibers*

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An extensive solution chemistry of Mo/S anions has been developed, mainly by Coucouvanis and co-workers.[1,2] Among those anions containing two Mo atoms, various isomers of $Mo_2S_n^{2-}$, $n = 6–12$, are known, as is some of the chemistry of their interconversions.[1] The recent synthesis of the first oligomeric W/Se anions[3] makes possible the study of their reaction chemistry. Here we report the preparation of the new $W_2Se_6^{2-}$ ion from the reaction of BH_4^- with two isomers of $W_2Se_{10}^{2-}$, namely the symmetrical isomer $[(Se_3)SeW(\mu\text{-}Se)_2WSe(Se_3)]^{2-}$ and the unsymmetrical one $[(Se_4)SeW(\mu\text{-}Se)_2WSe(Se_2)]^{2-}$. Although, at this stage in the development of the chemistry of soluble selenide anions of W and Mo, the closest similarities are between the W/Se and Mo/S systems, the chemistry reported here differs from that found in the Mo/S system. Thus, the starting symmetrical $W_2Se_{10}^{2-}$ anion has no known Mo/S counterpart and the reaction of the unsymmetrical $Mo_2S_{10}^{2-}$ anion with BH_4^- affords the $Mo_2S_9^{2-}$ ion and not the $Mo_2S_6^{2-}$ ion.[1]

Experimental Section

$[PPh_4]_2[W_2Se_{10}]$ was prepared by the literature method.[3] All reactions were carried out with the use of standard Schlenk-line techniques under a dry dinitrogen atmosphere. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

The IR spectra were recorded on a Perkin-Elmer 283 spectrometer. Electronic spectra were obtained on a Perkin-Elmer 330 UV-vis spectrophotometer. The ^{77}Se NMR spectra of DMF solutions were recorded on a Varian XLA-400 spectrometer with use of a 10-mm tunable probe

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