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Synthesis and Characterization of Two Novel Oxo–Persulfido Complexes with a Doubly Bridging S_7^{2-} Ligand and an "End-to-End" Bridging Hydrazine Ligand: $[Et_4N]_2[\{MO(S_2)_2\}_2(\mu_2\text{-}S_7)(\mu_2\text{-}NH_2NH_2)]\cdot CH_3CN$ (M = Mo, W)

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The two title complexes, $[Et_4N]_2[\{MO(S_2)_2\}_2(\mu_2\text{-}S_7)(\mu_2\text{-}NH_2NH_2)]\cdot CH_3CN$ (M = Mo (I) W, (II)), were obtained by the reaction of $MO_2S_2^{2-}$ with elemental sulfur in the presence of $NH_2NH_2\cdot 2HCl$ in DMF solvent in the air at ambient temperature. I crystallizes in the space group $P2_1/c$, with the following unit cell parameters: $a = 14.912$ (8) Å, $b = 17.066$ (7) Å, $c = 17.81$ (1) Å, $\beta = 113.87$ (4)°, $V = 4144$ (4) Å³, $Z = 4$; $\mu = 13.45$ cm⁻¹, $F(000) = 2120$, $2\theta_{max} = 52.1°$; $d_{calcd} = 1.66$ g·cm⁻³, $T = 296$ K; Mo Kα radiation ($\lambda = 0.710\,69$ Å); final R = 0.060 for 4358 observed reflections with $I > 3\sigma(I)$ and 443 variables. II crystallizes in the monoclinic space group $P2_1/c$, with the following unit cell parameters: $a = 14.86$ (1) Å, $b = 17.14$ (2) Å, $c = 17.81$ (3) Å, $\beta = 114.04$ (8)°, $V = 4145$ (9) Å³, $Z = 4$; $\mu = 64.19$ cm⁻¹, $F(000) = 2376$, $2\theta_{max} = 48.1°$, $d_{calcd} = 1.95$ g·cm⁻³, $T = 296$ K, Mo Kα radiation ($\lambda = 0.710\,69$ Å); final R = 0.049 for 3962 observed reflections with $I > 3\sigma(I)$ and 443 variables. The two complexes are isomorphous. In the anion of I (or II), the two Mo (or W) atoms, which are each coordinated by two persulfido S_2^{2-} ligands and one double-bonded terminal oxo ligand, are linked by a S_7^{2-} bridge and a H_2NNH_2 bridge. The coordination polyhedron of each Mo (or W) atom is a pentagonal bipyramid, whose two apices are formed by the terminal oxo atom and the coordinating atom of the H_2NNH_2 ligand. The equatorial five sulfur atoms of each pentagonal bipyramid, which is defined by two $\eta^2\text{-}S_2^{2-}$ ligands and a coordinating sulfur atom of the S_7^{2-} ligand, are almost planar within 0.05 Å. The average Mo–N (W–N) bond length of 2.490 (8) Å (2.46 (1) Å) is relatively long, due to the N atom being trans to the Mo=O (W=O) double bond (average O–Mo–N angle 175.6 (4)°; average O–W–N angle 175.9 (6)°). The N–N bond lengths of the H_2NNH_2 ligand are 1.40 (1) Å for I and 1.35 (2) Å for II. The two metals are in the trans position in the structure of the doubly bridging hydrazine and the four non-hydrogen atoms of the fragment $M(\mu_2\text{-}H_2NNH_2)M$ are almost planar within 0.11 Å. The two M=O double bonds locate in the plane of $M(\mu_2\text{-}H_2NNH_2)M$. The spectroscopic properties of the two complexes are also reported.

Introduction

The chemistry of transition metal polysulfido complexes,[1,2] especially the polysulfido–molybdenum complexes in connection with the hydrodesulfurization (HDS) catalyst, has attracted much interest. The family of soluble binary molybdenum (tungsten) sulfides, $Mo_xS_y^{2-}$ ($W_xS_y^{2-}$), has been developed recently, which includes the following examples: $[(S_4)_2MoS]^{2-}$,[3] $[(S_4)MoS(MoS_4)]^{2-}$,[4] $[(MS_4)_2MS]^{2-}$ (M = Mo,[5] W[6]), $[(S)_2Mo(\mu\text{-}S)]_2^{2-}$,[4] $[(S)_2SM(\mu\text{-}S)_2MS(S_2)]^{2-}$,[4] $[(S_2)SMo(\mu\text{-}S)]_2^{2-}$,[7] $[(S_2)SMo(\mu\text{-}S)_2MoS(S_4)]^{2-}$,[3,8] $[(S_4)SM(\mu\text{-}S)]_2^{2-}$ (M = Mo,[3,9] W[9,10]), $[(S_2)_2Mo(\mu\text{-}S_2)]_2^{2-}$,[11] $[Mo_3(\mu\text{-}S)(\mu\text{-}S_2)_3(S_2)_3]^{2-}$,[12] $[WS_4\{W_2S_2(\mu\text{-}S)_2\}WS_4]^{2-}$.[13] In most cases the binary Mo(W)/S complex contains molybdenum (tungsten) in oxidation states lower than +6, with the exception of the MS_4^{2-} (M = Mo, W) group in $[(MS_4)_2MS]^{2-}$, $[(S_4)MoS(MoS_4)]^{2-}$, and $[WS_4\{W_2S_2(\mu\text{-}S)_2\}WS_4]^{2-}$. However, in these complexes Mo (or W) is bound to S only in the form of sulfido (S^{2-}), persulfido (S_2^{2-}), or tetrasulfido (S_4^{2-}). The molybdenum–nitrosyl complex anion $[Mo_2(NO)_2(\mu_2\text{-}\eta^2\text{-}\eta^2\text{-}S_2)(S_2)_2(S_5)(O)]^{3-}$[14] features an S_5^{2-} doubly bridging chain strapped across the Mo–O–Mo bent bridge. In polysulfido molybdenum (tungsten) complexes,[1,2] no S_X^{2-} ligand with $X > 5$ has been found.

As is known, MS_4^{2-} reacting with elemental sulfur can afford $MoS(S_4)_2^{2-}$[3] (in CH_3CN) or $M_2S_4(S_4)_2^{2-}$[10] (in DMF; M = Mo, W), in which a redox reaction takes place. Little is known about the oxo–thiomolybdate (or -tungstate) reacting with elemental sulfur. Reaction of $MoO_2S_2^{2-}$[15] or $MoOS_3^{2-}$[16] with elemental sulfur can produce $OMo(S_4)_2^{2-}$. In recent years, the reaction system with $MO_nS_{4-n}^{2-}$ and elemental sulfur in the presence of $NH_2NH_2\cdot 2HCl$ has been studied in this group. A convenient synthetic method for $W_2S_4(S_4)_2^{2-}$ in DMF at room temperature in the presence of WS_4^{2-}, elemental sulfur, and $NH_2NH_2\cdot 2HCl$ has been illustrated.[17]

Recently, some polynuclear oxo(sulfido)–persulfido–molybdate(VI) (or –tungsten(VI)) anions have been reported, such as $[Mo_2O_2S_9]^{2-}$,[18c] $[\{Mo_2O_2S_9\}_{0.86}\{Mo_2O_2S_{10}\}_{0.14}]^{2-}$,[18a,b] $[Mo_4O_4S_{18}]^{2-}$,[18a,b] $[W_2(S)_2(\mu\text{-}S)(S_2)_4]^{2-}$,[19] and $[W_2O_2(S)(S_2)_4]^{2-}$ [20] anions. There are some common structural features in these complexes, where (a) the Mo(VI) or W(VI) atom has a pseudo-pentagonal-bipyramidal coordination geometry, (b) the two η^2-persulfido ligands are located in the equatorial positions. (c) one terminal oxo (or sulfido) atom per Mo(VI) or W(VI) occupies one of the axial sites, while the other axial site is occupied by an intramolecularly weakly interacting sulfur atom of persulfido ligand with a bond length ca. 2.8 Å, and (d) all possess the neutral $EM(S_2)_2$ subunit (E = O, S; M = Mo, W). In this paper, we describe the synthesis and characterization of two novel oxo–persulfido–molybdate(VI) (or –tungsten(VI)) complexes, which feature the structure containing a doubly bridging hydrazine H_2NNH_2 and a S_7^{2-} ligand connecting two $OM(S_2)_2$ subunits.

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Some schemes involving the reduction of dinitrogen bridging two metal atoms have been proposed.[21,22] The feasibility of introducing nitrogenase substrates in an "end-to-end" bridging mode between two metals within two μ_2-S cubane subunits was demonstrated,[23] in which CN^- and NH_2NH_2 were used as substrates. Therefore, exploration of the coordination of the NH_2NH_2 ligand to the Mo or W atom will be helpful in understanding the coordination mode of nitrogenase substrates. Very few Mo or W complexes containing the doubly bridging NH_2NH_2 ligand[23,24] have been reported.

Experimental Section

Synthesis. The chemicals in this research were used as purchased. $(NH_4)_2MoO_2S_2$ and $(NH_4)_2WO_2S_2$ were prepared according to the literature.[25] Elemental analyses were carried out by the Elemental Analysis Groups of our institute. Visible and UV electronic spectra were obtained on a Schimadzu UV-3000 spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer 577 spectrometer.

$[Et_4N]_2\{[MoO(S_2)_2]_2(\mu_2\text{-}S_7)(\mu_2\text{-}H_2NNH_2)\}\cdot CH_3CN.$ A 1.2-g (5.26-mmol) amount of $(NH_4)_2MoO_2S_2$ was dissolved in 30 mL of DMF. To this solution was added with stirring 0.675 g (21.04 mmol) of solid elemental sulfur; the solution color changed to reddish-brown for a while. After 1.5 h of stirring, 0.3 g (2.86 mmol) of $NH_2NH_2\cdot2HCl$ was added to the reddish-brown reaction solution. After additional stirring for 3 h, 1.5 g (7.14 mmol) of Et_4NBr was added. After a further 1.5 h of stirring, the solution was filtered and the filtrate was layered with 50 mL of 2-propanol and then allowed to stand at $-15\,°C$ for several days. The dark brown precipitates were recrystallized from mixed NCMe/ether, and 1.15 g of pure reddish-brown crystals was obtained; yield 53% (referenced to the amount of sulfur used). Anal. Found (calcd for $C_{18}H_{47}N_5O_2S_{15}Mo_2$): Mo, 18.9 (18.5); S, 47.2 (46.2); C, 20.1 (20.8); H, 4.5 (4.5); N, 5.7 (6.7).

IR spectra data for complex I (KBr pallet, cm^{-1}): 3290 (vw), 3210 (w), 2980 (w), 2940 (w), 1480–1420 (m), 1390 (m), 1365 (m), 1295 (w), 1184 (m), 1172 (m), 1115 (s), 1025 (w), 1000 (m), 925 (vs), 780 (m), 532 (s), 485 (w, sh), 470 (w), 344 (s).

UV-vis spectra [in NCMe solution, $\lambda_{max}(\epsilon)$ nm $(10^3\,M^{-1}\,cm^{-1})$]: 530 (2.43), 452 (4.00), 317 (14.9), 248 (25.0).

$[Et_4N]_2\{[WO(S_2)_2]_2(\mu_2\text{-}S_7)(\mu_2\text{-}H_2NNH_2)\}\cdot CH_3CN.$ The procedure is similar to that given above. A 2.0-g (6.33-mmol) amount of $(NH_4)_2WO_2S_2$ was dissolved in 30 mL of DMF. To this solution was added with stirring 0.81 g (25 mmol) of solid elemental sulfur, and after a while the solution color changed to reddish-brown. After 1.5 h of stirring, 0.5 g (4.77 mmol) of $NH_2NH_2\cdot2HCl$ was added to the reddish-brown reaction solution, and immediately the solution color changed to reddish-orange. After additional stirring for 3 h, 2.0 g (9.51 mmol) of Et_4NBr was added. After 1.5 h more stirring, the solution was filtered and the filtrate was layered with 50 mL of 2-propanol and then allowed to stand at $-15\,°C$ for several days. The reddish-orange precipitates were recrystallized from the mixed NCMe/ether, and 0.81 g of pure reddish-orange crystals was obtained; yield 27% (referenced to the amount of sulfur used). Anal. Found (calcd for $C_{18}H_{47}N_5O_2S_{15}W_2$): W, 31.2 (30.3); S, 37.7 (39.5); C, 17.7 (17.8); H, 3.6 (3.9); N, 5.9 (5.8).

IR spectral data for complex II (KBr pallet, cm^{-1}): 3280 (w), 3210 (w), 2980 (w), 2940 (w), 1545 (w), 1520 (w, sh), 1470–1420 (m), 1380 (m), 1360 (m), 1292 (w), 1175 (m), 1165 (m), 1125 (s), 1025 (w), 990 (m), 930 (vs), 776 (s), 518 (s), 466 (w), 455 (w, sh), 325 (s), 315 (s), 300 (w, sh).

UV-vis spectral data [in NCMe solution, λ_{max}, nm ϵ, $10^3\,M^{-1}\,cm^{-1}$)]: 470 (1.2), 350 (11.0), 236 (29.5).

X-ray Structure Determination. $[Et_4N]_2\{[MoO(S_2)_2]_2(\mu_2\text{-}S_7)(\mu_2\text{-}H_2NNH_2)\}\cdot CH_3CN$ (M = Mo (I), W (II)). A crystal was mounted in

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Table I. Crystallographic Data for $[Et_4N]_2\{[MO(S_2)_2]_2(\mu_2\text{-}S_7)(\mu_2\text{-}H_2NNH_2)\}\cdot CH_3CN$ (M = Mo (I), W (II))

	I	II
chem formula	$C_{18}H_{47}N_5O_2S_{15}Mo_2$	$C_{18}H_{47}N_5O_2S_{15}W_2$
fw	1038.4	1214.2
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
unit cell params		
a, Å	14.912 (8)	14.86 (1)
b, Å	17.066 (7)	17.14 (2)
c, Å	17.81 (1)	17.81 (3)
β, deg	113.87 (4)	114.04 (8)
V, Å^3	4144 (4)	4145 (9)
Z	4	4
μ, cm^{-1}	13.45	64.19
d_{calcd}, g·cm^{-3}	1.66	1.94
temp, K	296	296
radiation	Mo Kα (λ = 0.710 69 Å)	Mo Kα
residuals:^{a} R, R_w	0.060, 0.076	0.049, 0.061

$^a R = \sum ||F_o| - |F_c||/\sum|F_o|$, $R_w = [\sum(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

a random orientation on a glass fiber. Some experimental conditions are reported in Table I. Data were collected on a Rigaku AFC5R diffractometer using Mo Kα radiation at ca. 296 K. Cell constants were obtained by least-squares analysis on 25 diffraction maxima (search limits of 2θ: 12.0–55.0°). Scan speed was varied on the basis of SEARCH intensity, and a total of 8832 (7095 for II) [include 8494 (6806 for II) unique ones] reflections were collected. R_{int} = 5.9% (5.0% for II). Three standard reflections were measured periodically, with no random deviations, indicating crystal and electronic stability. Intensity was defined as $C - \frac{1}{2}(t_c/t_b)(b_1 + b_2)$, 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 background counts; the intensity error was $\sigma(F^2) = (C + \frac{1}{4}(t_c/t_b)^2(b_1 + b_2) + (pI)^2)^{1/2}$, where I is the intensity and p is the factor that downweights strong reflections, taken to be 0.03 (0.05 for II). The data were corrected for Lorentz and polarization factors and for absorption using empirical scan data and DIFABS.[26] Linear decay correction was applied. A total of 4358 (3962 for II) reflections with $I \geq 3\sigma(I)$ are considered observed, and all were used in the refinement.

The structure was solved by direct methods using MITHRIL,[27] the Mo (W for II) atoms were located in the E map. Most of the non-hydrogen atoms were located by use of the DIRDIF[28] program, and some non-hydrogen atoms were located in the succeeding difference Fourier syntheses. At this stage, the structure was refined by the full-matrix least-squares technique with anisotropic thermal parameters for most atoms except S(5), S(6), S(7), and the S atoms around Mo(2) which were refined with isotropic parameters; the difference Fourier electron density map revealed an alternative position, S(6'), for S(6). It also shows other alternative positions [S(5'), S(7'), S(21')–S(22') and S(23')–S(24')] for the corresponding isotropically refined sulfur atoms. The occupancy factor of S(6) converged to 0.61 (0.66 for II) while the alternative position S(6') converged to the complementary occupancy factor of 0.39 (0.34 for II). The refinement of the occupancy factors of the other disordered sulfido or disulfido ligands yielded occupancies close to the above values, respectively, and their occupancy factors were set as 0.61 (0.66 for II) and 0.39 (0.34 for II) correspondingly according to the convergence results of S(6) and S(6'). In the final least-squares cycle, the structure was refined by the full-matrix least-squares technique with anisotropic thermal parameters for all atoms (443 variables for both complexes). Final $R = \sum ||F_o| - |F_c||/\sum|F_o| = 0.060$ (0.049 for II), $R_w = [\sum(|F_o| - |F_c|)^2\sum wF_o^2]^{1/2} = 0.076$ (0.061 for II) and $S = [\sum w(|F_o| - |F_c|)^2/(N_o - N)]^{1/2} = 2.63$ (1.51 for II), $w = 1/\sigma^2(F_o)$. $(\Delta/\sigma)_{max} = 0.63$ (0.66 for II). All calculations were performed on a VAX 785 computer using the TEXSAN[29] program package. Non-hydrogen scattering factors were taken from the work of Cromer and Waber.[30]

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Table II. Positional Parameters and $B(eq)^a$ for $[Et_4N]_2[\{MO(S_2)_2\}_2(\mu_2\text{-}S_7)(\mu_2\text{-}NH_2NH_2)]\cdot CH_3CN$

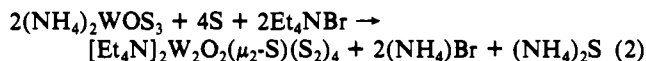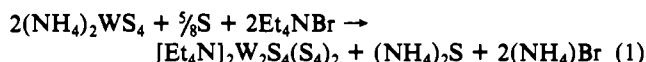| atom	x	y	z	$B(eq)$, Å^2	atom	x	y	z	$B(eq)$, Å^2
			a. M = Mo, $[Et_4N]_2\{[OMo(S_2)_2]_2(S_7)(NHNH)\}\cdot CH_3CN$						
Mo(1)	0.34672 (6)	0.03912 (5)	0.63912 (6)	3.90 (4)	S(22')	−0.068 (1)	0.0331 (7)	0.591 (1)	6.1 (6)
Mo(2)	0.00164 (6)	0.09499 (6)	0.71419 (6)	4.52 (4)	S(23')	0.0284 (8)	−0.0364 (8)	0.7769 (7)	5.5 (4)
N(1)	0.1550 (6)	0.0499 (6)	0.7036 (6)	5.6 (4)	S(24')	0.109 (2)	0.052 (1)	0.854 (2)	6.3 (7)
N(2)	0.2130 (7)	0.0929 (5)	0.6735 (6)	5.5 (4)	N(11)	0.6460 (6)	0.2329 (5)	0.5566 (5)	4.3 (4)
O(1)	0.4425 (5)	0.0085 (5)	0.6212 (5)	5.8 (4)	C(11)	0.5992 (8)	0.2630 (7)	0.6140 (7)	5.6 (6)
O(2)	−0.1011 (5)	0.1193 (5)	0.7250 (5)	6.4 (4)	C(12)	0.633 (1)	0.2184 (9)	0.6954 (8)	8.4 (8)
S(1)	0.4435 (3)	0.0957 (2)	0.7760 (2)	6.6 (2)	C(13)	0.6022 (8)	0.2853 (7)	0.4822 (7)	5.1 (5)
S(2)	0.4735 (2)	0.0166 (3)	0.8682 (2)	7.3 (2)	C(14)	0.636 (1)	0.2642 (8)	0.4128 (8)	7.1 (7)
S(3)	0.3570 (2)	0.0158 (2)	0.8997 (2)	5.9 (1)	C(15)	0.7578 (8)	0.238 (1)	0.5941 (9)	7.7 (7)
S(4)	0.3741 (2)	0.1111 (2)	0.9740 (2)	6.0 (2)	C(16)	0.796 (1)	0.324 (1)	0.620 (1)	10 (1)
S(5)	0.291 (1)	0.195 (2)	0.898 (2)	7.3 (6)	C(17)	0.624 (1)	0.1458 (7)	0.5358 (8)	7.0 (7)
S(6)	0.1616 (5)	0.1871 (5)	0.9104 (4)	7.1 (3)	C(18)	0.511 (1)	0.1292 (9)	0.494 (1)	9.3 (9)
S(7)	0.100 (1)	0.0837 (7)	0.860 (1)	5.7 (5)	N(12)	0.2480 (6)	0.0701 (5)	0.1800 (5)	4.6 (4)
S(11)	0.2538 (2)	0.1085 (2)	0.5156 (2)	5.6 (1)	C(21)	0.230 (1)	0.077 (1)	0.257 (1)	10 (1)
S(12)	0.3456 (2)	0.1767 (2)	0.6082 (2)	5.6 (1)	C(22)	0.286 (1)	0.021 (1)	0.3263 (9)	8.3 (8)
S(13)	0.2340 (2)	−0.0663 (2)	0.5853 (2)	5.9 (1)	C(23)	0.213 (2)	−0.014 (1)	0.145 (1)	12 (1)
S(14)	0.3224 (2)	−0.0732 (2)	0.7079 (2)	6.0 (2)	C(24)	0.229 (2)	−0.028 (1)	0.064 (1)	11 (1)
S(21)	−0.010 (1)	0.1816 (5)	0.6015 (9)	6.5 (5)	C(25)	0.196 (1)	0.137 (1)	0.121 (1)	12 (1)
S(22)	0.0635 (8)	0.2251 (8)	0.7170 (6)	6.7 (5)	C(26)	0.081 (1)	0.120 (1)	0.081 (1)	12 (1)
S(23)	0.0031 (6)	−0.0428 (6)	0.7272 (5)	6.6 (3)	C(27)	0.358 (1)	0.078 (1)	0.200 (1)	10 (1)
S(24)	−0.0578 (9)	−0.0061 (5)	0.6083 (8)	7.3 (4)	C(28)	0.404 (1)	0.155 (1)	0.247 (1)	10 (1)
S(5')	0.318 (2)	0.208 (3)	0.899 (3)	7 (1)	N(')	0.864 (2)	0.195 (1)	0.902 (2)	17 (2)
S(6')	0.1774 (7)	0.2326 (7)	0.8773 (7)	6.9 (5)	C	0.904 (2)	0.247 (2)	0.888 (1)	10 (1)
S(7')	0.100 (1)	0.215 (1)	0.751 (1)	5.5 (6)	C(1)	0.955 (1)	0.309 (1)	0.877 (1)	10 (1)
S(21')	−0.022 (2)	0.1444 (8)	0.589 (1)	5.5 (6)					
			b. M = W, $[Et_4N]_2\{(S_2)_2WO(S_7)WO(S_2)_2(NH_2NH_2)\}\cdot CH_3CN$						
W(1)	0.34445 (5)	0.04022 (4)	0.63879 (4)	3.61 (3)	S(22')	−0.068 (1)	0.032 (2)	0.591 (2)	6 (1)
W(2)	0.00194 (4)	0.09537 (4)	0.71301 (4)	4.18 (3)	S(23')	0.026 (2)	−0.041 (2)	0.771 (2)	7 (1)
N(1)	0.155 (1)	0.053 (1)	0.706 (1)	6.3 (8)	S(24')	0.091 (3)	0.061 (3)	0.843 (2)	10 (2)
N(2)	0.208 (1)	0.0915 (8)	0.671 (1)	7.0 (8)	N(11)	0.6461 (9)	0.2334 (8)	0.5556 (7)	4.2 (6)
O(1)	0.4437 (7)	0.0098 (7)	0.6231 (7)	5.5 (5)	C(11)	0.600 (1)	0.263 (1)	0.615 (1)	5.2 (8)
O(2)	−0.1050 (7)	0.1186 (7)	0.7209 (7)	5.8 (6)	C(12)	0.637 (2)	0.214 (1)	0.696 (1)	8 (1)
S(1)	0.4402 (4)	0.0970 (3)	0.7752 (3)	6.7 (3)	C(13)	0.601 (1)	0.285 (1)	0.479 (1)	5.3 (8)
S(2)	0.4734 (4)	0.0174 (4)	0.8676 (3)	7.1 (3)	C(14)	0.634 (2)	0.262 (1)	0.412 (1)	7 (1)
S(3)	0.3578 (3)	0.0160 (3)	0.9007 (3)	5.6 (2)	C(15)	0.760 (1)	0.240 (1)	0.595 (1)	7 (1)
S(4)	0.3757 (3)	0.1109 (3)	0.9757 (3)	5.5 (2)	C(16)	0.795 (1)	0.325 (2)	0.615 (2)	9 (1)
S(5)	0.291 (1)	0.196 (1)	0.901 (1)	6.0 (6)	C(17)	0.628 (2)	0.148 (1)	0.537 (1)	7 (1)
S(6)	0.1610 (7)	0.1855 (6)	0.9119 (5)	6.5 (5)	C(18)	0.512 (2)	0.128 (1)	0.496 (2)	10 (1)
S(7)	0.105 (1)	0.080 (1)	0.862 (1)	5.2 (6)	N(12)	0.249 (1)	0.0686 (8)	0.1815 (8)	4.6 (6)
S(11)	0.2532 (4)	0.1092 (3)	0.5152 (3)	5.7 (2)	C(21)	0.230 (2)	0.075 (2)	0.260 (2)	10 (2)
S(12)	0.3455 (4)	0.1770 (3)	0.6093 (3)	5.4 (2)	C(22)	0.287 (2)	0.022 (1)	0.329 (1)	8 (1)
S(13)	0.2332 (4)	−0.0652 (3)	0.5844 (3)	5.6 (2)	C(23)	0.214 (2)	−0.015 (2)	0.147 (2)	12 (2)
S(14)	0.3209 (4)	−0.0719 (3)	0.7078 (3)	5.9 (2)	C(24)	0.232 (2)	−0.030 (2)	0.066 (1)	11 (2)
S(21)	−0.009 (2)	0.183 (1)	0.604 (1)	7 (1)	C(25)	0.194 (2)	0.140 (2)	0.127 (2)	14 (2)
S(22)	0.066 (1)	0.222 (1)	0.7185 (7)	5.7 (6)	C(26)	0.078 (2)	0.115 (2)	0.086 (2)	12 (2)
S(23)	0.004 (1)	−0.039 (1)	0.7272 (8)	6.6 (6)	C(27)	0.361 (2)	0.078 (2)	0.201 (2)	10 (1)
S(24)	−0.053 (1)	−0.0051 (8)	0.609 (1)	7.1 (7)	C(28)	0.402 (2)	0.157 (1)	0.247 (1)	9 (1)
S(5')	0.320 (3)	0.200 (3)	0.896 (4)	8 (2)	N(')	0.859 (2)	0.192 (2)	0.905 (2)	18 (3)
S(6')	0.177 (1)	0.231 (1)	0.878 (1)	8 (1)	C	0.900 (2)	0.242 (2)	0.890 (2)	9 (2)
S(7')	0.098 (2)	0.217 (2)	0.754 (1)	6 (1)	C(1)	0.952 (2)	0.304 (2)	0.877 (2)	10 (2)
S(21')	−0.019 (4)	0.148 (3)	0.590 (3)	6 (2)					

^{a} All atoms were refined anisotropically. $B(eq) = {}^4/_3\sum_i\sum_j B_{ij}a_i\cdot a_j$.

The atomic coordinates and thermal parameters are listed in Table IIa (IIb); the important bond lengths and bond angles are given in Table IIIa (IIIb) and IVa (IVb).

Results and Discussion

Synthesis. The reaction of $MO_2S_2^{2-}$ (M = Mo, W) with elemental sulfur in the presence of $NH_2NH_2\cdot 2HCl$ in DMF solvent in the air [in a molar ratio $(NH_4)_2MoO_2S_2$:S:$NH_2NH_2\cdot 2HCl$ of 1:4:0.53 or $(NH_4)_2WO_2S_2$:S:$NH_2NH_2\cdot 2HCl$ of 1:4:0.75] proceeds at ambient temperature, and the product, $[Et_4N]_2[\{MO(S_2)_2\}_2$-$(\mu_2\text{-}S_7)(\mu_2\text{-}H_2NNH_2)]\cdot CH_3CN$ (M = Mo (I), W (II)), is obtained by recrystallization in a mixed CH_3CN/Et_2O solution. When the $WO_2S_2^{2-}$ was replaced by WS_4^{2-} [in a molar ratio $(NH_4)_2W$-S_4:S:$NH_2NH_2\cdot 2HCl$ of 1:4:0.83] or WOS_3^{2-} [in a molar ratio $(NH_4)_2WOS_3$:S:$NH_2NH_2\cdot 2HCl$ of 1:4:0.79], the product is $W_2S_4(S_4)_2^{2-}$ [17] (eq 1) or $W_2O_2(\mu_2\text{-}S)(S_2)_4^{2-}$ [31] (eq 2), respectively.

This told us that the content of the oxo ligand may decide which product will be formed.

$$2(NH_4)_2WS_4 + {}^5/_8S + 2Et_4NBr \rightarrow$$
$$[Et_4N]_2W_2S_4(S_4)_2 + (NH_4)_2S + 2(NH_4)Br \quad (1)$$

$$2(NH_4)_2WOS_3 + 4S + 2Et_4NBr \rightarrow$$
$$[Et_4N]_2W_2O_2(\mu_2\text{-}S)(S_2)_4 + 2(NH_4)Br + (NH_4)_2S \quad (2)$$

In this paper, the reactions may take place according to eq 3, where the doubly bridging ligand is NH_2NH_2. However, it is

$$2(NH_4)_2MO_2S_2 + 11S + NH_2NH_2 + 2HCl + 2Et_4NBr \rightarrow$$
$$[Et_4N]_2[\{MO(S_2)_2\}_2(\mu\text{-}S_7)(\mu\text{-}NH_2NH_2)] + 2H_2O +$$
$$2(NH_4)Br + 2NH_3 + 2Cl^- \quad (3)$$

obvious that the total charges of the two sides are not in equilibrium. From this, two questions arise: (a) Where do the protons in H_2O come from when one oxygen atom of the $MO_2S_2^{2-}$ anion

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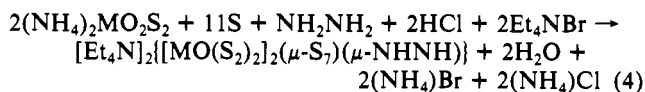
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Table III. Selected Bond Lengths (Å)

a. Compound I

Mo(1)-O(1)	1.669 (6)	S(5)-S(6)	2.03 (2)
Mo(1)-S(11)	2.387 (4)	S(6)-S(7)	2.03 (2)
Mo(1)-S(12)	2.410 (3)	S(11)-S(12)	2.029 (5)
Mo(1)-S(13)	2.383 (3)	S(13)-S(14)	2.047 (5)
Mo(1)-S(14)	2.381 (3)	S(21)-S(22)	2.04 (2)
Mo(1)-S(1)	2.472 (4)	S(23)-S(24)	2.04 (1)
Mo(1)-N(2)	2.487 (8)	Mo(2)-S(7')	2.45 (2)
Mo(2)-O(2)	1.671 (6)	Mo(2)-S(21')	2.27 (2)
Mo(2)-S(21)	2.44 (1)	Mo(2)-S(22')	2.27 (2)
Mo(2)-S(22)	2.40 (1)	Mo(2)-S(23')	2.46 (1)
Mo(2)-S(23)	2.36 (1)	Mo(2)-S(24')	2.46 (3)
Mo(2)-S(24)	2.44 (1)	S(4)-S(5')	2.07 (5)
Mo(2)-S(7)	2.42 (2)	S(5')-S(6')	2.02 (3)
Mo(2)-N(1)	2.492 (8)	S(6')-S(7')	2.09 (2)
S(1)-S(2)	2.030 (5)	S(21')-S(22')	2.03 (2)
S(2)-S(3)	2.031 (5)	S(23')-S(24')	2.06 (3)
S(3)-S(4)	2.047 (5)	N(1)-N(2)	1.40 (1)
S(4)-S(5)	2.02 (3)		

b. Compound II

W(1)-O(1)	1.692 (9)	S(4)-S(5)	2.03 (2)
W(2)-O(2)	1.699 (9)	S(5)-S(6)	2.03 (2)
W(1)-N(2)	2.48 (1)	S(6)-S(7)	2.03 (2)
W(2)-N(1)	2.44 (1)	S(11)-S(12)	2.041 (7)
N(1)-N(2)	1.35 (2)	S(13)-S(14)	2.051 (8)
W(1)-S(1)	2.462 (6)	S(21)-S(22)	2.01 (2)
W(1)-S(11)	2.377 (6)	S(23)-S(24)	2.01 (2)
W(1)-S(12)	2.404 (5)	W(2)-S(7')	2.46 (4)
W(1)-S(13)	2.374 (5)	W(2)-S(21')	2.28 (5)
W(1)-S(14)	2.383 (5)	W(2)-S(22')	2.27 (3)
W(2)-S(7)	2.48 (2)	W(2)-S(23')	2.52 (3)
W(2)-S(21)	2.41 (2)	W(2)-S(24')	2.24 (5)
W(2)-S(22)	2.37 (2)	S(4)-S(5')	2.02 (5)
W(2)-S(23)	2.32 (2)	S(5')-S(6')	2.09 (4)
W(2)-S(24)	2.42 (2)	S(6')-S(7')	2.05 (3)
S(1)-S(2)	2.038 (8)	S(21')-S(22')	2.13 (6)
S(2)-S(3)	2.032 (7)	S(23')-S(24')	2.15 (6)
S(3)-S(4)	2.053 (7)		

is converted to H_2O, and (b) how is the $S_7{}^{2-}$ ligand formed from neutral sulfur? It has been shown that the disproportionation product $MOS_3{}^{2-}$ obtained from $MO_2S_2{}^{2-}$ will preferentially lead to other complexes. Therefore, if the bridging ligand is H_2NNH_2, other explanations for the reaction may exist.

Another possible way to solve these two questions may be to assume the neutral doubly bridging ligand NH_2NH_2 to be instead the neutral ligand diazene, NH=NH. At this point, a satisfactory relationship is given in eq 4.

$$2(NH_4)_2MO_2S_2 + 11S + NH_2NH_2 + 2HCl + 2Et_4NBr \rightarrow$$
$$[Et_4N]_2\{[MO(S_2)_2]_2(\mu\text{-}S_7)(\mu\text{-}NHNH)\} + 2H_2O +$$
$$2(NH_4)Br + 2(NH_4)Cl \quad (4)$$

However, no direct evidence has been obtained to identify which choice is correct for the ligand: NH_2NH_2 or NH=NH. The ^{1}H NMR measurements (on Varian FT-80 NMR spectrometer) fail to give useful information about this point. Considering that the N—N bond length is much longer than a normal N=N double bond length (1.25 Å in $[(\mu_2\text{-NHNH})\{Cr(CO)_5\}_2]\cdot 2THF^{32}$), we tentatively suggest that the ligand is NH_2NH_2. The identification of the ligand as H_2NNH_2 or NHNH needs further investigation.

Spectroscopic Properties. In the IR spectra, the vibration of the Mo=O or W=O bond is observed in the region around 925–930 cm^{-1}. The strong vibration absorption at around 530 cm^{-1} is assigned^{2,33} to ν(S–S) of the S_X group. The strong peaks at 344 (s) cm^{-1} for I and 325 (s), 315 (s), and 300 (w, sh) cm^{-1} for II are confidently assigned^{33} to ν(Mo–S) and ν(W–S), respectively. ν(N–H) is observed at 3290 (vw) and 3210 (w) cm^{-1} for I and 3280 (w) and 3210 (w) cm^{-1} for II. Except for those peaks due to the Et_4N^+ cation, the peaks around 1295 (w), 1125

(s), and 1025 (w) cm^{-1} for both title complexes and 1545 (w) and 1520 (w, sh) cm^{-1} for only II may be due to the hydrazine or diazene ligand.

The electronic spectral data for the two complexes are given in the Experimental Section. In the three-center MS_2 core of the side-on persulfido complexes, the antibonding orbital π^* of the S_2 ligand splits into two components: the in-plane $\pi_h{}^*$ orbital forms a strong σ bond to the metal, leaving the $\pi_V{}^*$ orbital, which is perpendicular to the MS_2 plane at a higher energy. Two ligand to metal charge-transfer (LMCT) transitions are expected:^{33} $\pi_V{}^*$(S) d(Mo, or W) and $\pi_h{}^*$ d(Mo, or W). The former is observed as a low-energy absorption in the visible region. The latter is found at higher energies (due to the stabilization of the $\pi_h{}^*$ σ-bonding orbital) in the ultraviolet region. The energies of the electronic excitations of the former $\pi_V{}^*$(S) d(Mo or W) LMCT transitions depend also on the oxidation state of the Mo or W, the metal–metal bonding, and the nature of the other ligands. In the spectrum of the complex $Mo^{VI}O(S_2)(Et_2NCS_2)_2$ the absorption at 581 nm ($\epsilon = 1300$) has been previously assigned^{34} to this LMCT, but in the spectrum of the complex $Mo^V{}_2O_2S_2(S_2){}_2{}^{2-}$, containing the $Mo^VO(S_2)$ fragment with a +5 oxidation state for the Mo atom, this LMCT is^{33} at 463 nm ($\epsilon = 2000$). In the related oxopersulfidomolybdate (or -tungstate) complexes, this LMCT is around 522 ($\epsilon = 1950$), 510 ($\epsilon = 7850$), 455, and 450 nm for $[Mo_2O_2S_{9,14}]^{2-,18a,b}$ $[Mo_4O_4S_{18}]^{2-,18a,b}$ $[W_2O_2S_{9,23}]^{2-,31}$ and $[W_2O_2(S)(S_2)_4]^{2-,20}$ respectively. As a result, the band at 530 nm of the electronic spectrum of I is assigned to the $\pi_V{}^*$(S) d(Mo) LMCT transition. In the spectrum of II, the band at 470 nm is assigned to the $\pi_V{}^*$(S) d(W) LMCT transition. It is noted that the $\pi_V{}^*$(S) d(Mo, or W) LMCT transitions of the title complexes have some red-shifts relative to those for the above-related complexes, correspondingly.

In the CV (in NCMe solution vs SCE with a platinum electrode) of complex I, there are two irreversible reduction waves at −0.69 and −0.92 V and one irreversible oxidation wave at +0.78 V. Complex II displays one irreversible reduction wave at −1.21 V and one irreversible oxidation wave at +0.82 V. The irreversible reductions may occur on the metal atoms, because I and II have different reduction potentials since they have different metals, Mo and W. Meanwhile, I shows lower and greater reduction potentials. If the CV properties of the two complexes are compared, the irreversible oxidation waves at +0.78 V for I and +0.82 V for II are approximately the same.

The magnetic measurement show that the two title complexes are diamagnetic. ^{1}H NMR measurements (on a Varian FT-80 NMR spectrometer) have not given peaks belonging to either the NH_2NH_2 or the NH=NH ligand.

Structures of $[Et_4N]_2\{[MO(S_2)_2]_2(\mu_2\text{-}S_7)(\mu_2\text{-}H_2NNH_2)\}\cdot CH_3CN$ (M = Mo (I), W (II)). The two title complexes are isomorphous. Each crystal structure of $[Et_4N]_2\{[MO(S_2)_2]_2(\mu_2\text{-}S_7)(\mu_2\text{-}H_2NNH_2)\}\cdot CH_3CN$ (M = Mo (I), W (II) consists of four discrete anions, eight cations, and four solvent molecule in the unit cell. The $S_7{}^{2-}$ ligand spanning the two M(VI) atoms is disordered in two different sets of positions (shown in Figures 1–4 with different occupancy factors.

In the anion, the two Mo (or W) atoms, which are each coordinated by two persulfido $S_2{}^{2-}$ ligands and one double-bonded terminal oxo ligand, are linked by a $S_7{}^{2-}$ bridge and a H_2NNH_2 bridge (Figures 1–4). The coordination polyhedron of each Mo (or W) atom is a pentagonal bipyramid, whose two axial positions are occupied by the terminal oxo atom and the coordinating atom of the H_2NNH_2 ligand. The five equatorial sulfur atoms of each pentagonal bipyramid, which are defined by two η^2-$S_2{}^{2-}$ ligands and a coordinating sulfur atom of the $S_7{}^{2-}$ ligand, are almost planar within 0.09 Å. Meanwhile S(2) and S(6) [or S(6')] atoms are located in the respective equaterial least-square planes (see Figures 1–4) within 0.09 Å. In the $[\{MO(S_2)_2\}_2(\mu_2\text{-}S_7)(\mu_2\text{-}H_2NNH_2)]^{2-}$ (M = Mo (I), W (II)) anion, the two molybdenum (or tungsten) atoms are elevated from the respective pentagonal planes by 0.42 Å (0.40 Å).

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Table IV. Selected Bond Angles (deg)

a. Compound I

O(1)-Mo(1)-S(11)	101.6 (3)	O(2)-Mo(2)-N(1)	175.9 (3)	O(2)-Mo(2)-S(21)	100.2 (4)	S(6)-S(7)-Mo(2)	112.0 (7)
O(1)-Mo(1)-S(12)	100.9 (3)	S(23)-Mo(2)-S(22)	158.7 (3)	O(2)-Mo(2)-S(22)	97.5 (4)	S(12)-S(11)-Mo(1)	65.6 (1)
O(1)-Mo(1)-S(13)	101.9 (3)	S(23)-Mo(2)-S(7)	80.6 (4)	O(2)-Mo(2)-S(23)	102.0 (3)	S(11)-S(12)-Mo(1)	64.4 (1)
O(1)-Mo(1)-S(14)	99.6 (3)	S(23)-Mo(2)-S(21)	132.8 (3)	O(2)-Mo(2)-S(24)	101.6 (4)	S(14)-S(13)-Mo(1)	64.5 (1)
O(1)-Mo(1)-S(1)	96.2 (3)	S(23)-Mo(2)-S(24)	50.1 (3)	S(13)-S(14)-Mo(1)	64.6 (1)	S(6')-S(5')-S(4)	114 (2)
O(1)-Mo(1)-N(2)	175.3 (3)	S(23)-Mo(2)-N(1)	74.2 (3)	S(22)-S(21)-Mo(2)	64.0 (1)	S(5')-S(6')-S(7')	105 (1)
S(14)-Mo(1)-S(11)	136.2 (1)	S(22)-Mo(2)-S(7)	89.5 (4)	S(21)-S(22)-Mo(2)	66.2 (5)	S(6')-S(7')-Mo(2)	114.6 (8)
S(14)-Mo(1)-S(12)	156.0 (1)	S(22)-Mo(2)-S(21)	49.9 (4)	S(24)-S(23)-Mo(2)	67.0 (4)	S(22')-S(21')-Mo(2)	63.6 (7)
S(14)-Mo(1)-S(13)	50.9 (1)	S(22)-Mo(2)-S(24)	133.4 (4)	S(23)-S(24)-Mo(2)	62.9 (5)	S(21')-S(22')-Mo(2)	63.5 (8)
S(14)-Mo(1)-S(1)	87.5 (1)	S(22)-Mo(2)-N(1)	86.0 (4)	O(2)-Mo(2)-S(7')	103.7 (5)	S(24')-S(23')-Mo(2)	65.2 (8)
S(14)-Mo(1)-N(2)	82.3 (2)	S(7)-Mo(2)-S(21)	138.0 (5)	O(2)-Mo(2)-S(21')	103.6 (6)	S(23')-S(24')-Mo(2)	65 (1)
S(13)-Mo(1)-S(11)	87.3 (1)	S(7)-Mo(2)-S(24)	130.2 (4)	O(2)-Mo(2)-S(22')	98.3 (6)	O(2)-Mo(2)-S(23')	99.3 (4)
S(13)-Mo(1)-S(12)	134.8 (1)	S(7)-Mo(2)-N(1)	83.3 (4)	O(2)-Mo(2)-S(24')	102.0 (6)	S(21')-Mo(2)-S(22')	52.9 (5)
S(13)-Mo(1)-S(1)	136.6 (1)	S(21)-Mo(2)-S(24)	84.8 (4)	S(21')-Mo(2)-S(7')	77.9 (5)	S(21')-Mo(2)-S(23')	135.6 (5)
S(13)-Mo(1)-N(2)	82.7 (2)	S(21)-Mo(2)-N(1)	83.6 (4)	S(21')-Mo(2)-S(24')	152 (1)	S(21')-Mo(2)-N(1)	79.8 (6)
S(11)-Mo(1)-S(12)	50.1 (1)	S(24)-Mo(2)-N(1)	77.3 (4)	S(22')-Mo(2)-S(7')	129.6 (5)	S(22')-Mo(2)-S(23')	86.7 (4)
S(11)-Mo(1)-S(1)	127.2 (1)	S(2)-S(1)-Mo(1)	112.8 (2)	S(22')-Mo(2)-S(24')	133.8 (5)	S(22')-Mo(2)-N(1)	81.8 (5)
S(11)-Mo(1)-N(2)	79.6 (2)	S(1)-S(2)-S(3)	107.1 (2)	S(7')-Mo(2)-S(23')	132.1 (4)	S(7')-Mo(2)-S(24')	84.8 (7)
S(12)-Mo(1)-S(1)	78.0 (1)	S(2)-S(3)-S(4)	106.0 (2)	S(7')-Mo(2)-N(1)	79.2 (4)	S(24')-Mo(2)-S(23')	49.4 (6)
S(12)-Mo(1)-N(2)	76.4 (2)	S(5)-S(4)-S(3)	104.4 (8)	S(24')-Mo(2)-N(1)	75.2 (6)	S(23')-Mo(2)-N(1)	76.6 (3)
S(1)-Mo(1)-N(2)	79.6 (3)	S(4)-S(5)-S(6)	103 (1)	S(3)-S(4)-S(5')	108 (1)	N(2)-N(1)-Mo(2)	126.7 (6)
O(2)-Mo(2)-S(7)	94.5 (4)	S(7)-S(6)-S(5)	107 (1)	N(1)-N(2)-Mo(1)	125.7 (6)		

b. Compound II

|							
N(2)-N(1)-W(2)	127 (1)	O(2)-W(2)-S(23)	101.3 (6)	S(1)-W(1)-N(2)	80.3 (5)	S(4)-S(5)-S(6)	103.4 (9)
N(1)-N(2)-W(1)	128 (1)	O(2)-W(2)-S(24)	101.1 (6)	O(2)-W(2)-N(1)	176.0 (5)	S(7)-S(6)-S(5)	105.7 (8)
O(1)-W(1)-N(2)	175.4 (6)	O(2)-W(2)-S(7)	97.3 (5)	O(2)-W(2)-S(21)	99.4 (7)	S(6)-S(7)-W(2)	109.8 (9)
O(1)-W(1)-S(1)	95.3 (4)	S(23)-W(2)-S(21)	134.4 (6)	O(2)-W(2)-S(22)	99.1 (6)	S(12)-S(11)-W(1)	65.4 (2)
O(1)-W(1)-S(11)	101.9 (4)	S(23)-W(2)-S(22)	157.5 (6)	S(11)-S(12)-W(1)	64.1 (2)	N(1)-W(2)-S(23')	76.7 (8)
O(1)-W(1)-S(12)	100.4 (4)	S(23)-W(2)-S(24)	50.1 (5)	S(14)-S(13)-W(1)	64.7 (2)	S(5')-S(4)-S(3)	103 (2)
O(1)-W(1)-S(13)	102.0 (4)	S(23)-W(2)-S(7)	78.7 (6)	S(13)-S(14)-W(1)	64.2 (2)	S(4)-S(5')-S(6')	114 (2)
O(1)-W(1)-S(14)	99.1 (4)	S(23)-W(2)-N(1)	74.8 (6)	S(22)-S(21)-W(2)	64.0 (9)	S(7')-S(6')-S(5')	103 (2)
S(13)-W(1)-S(11)	87.8 (2)	S(22)-W(2)-S(21)	49.7 (6)	S(21)-S(22)-W(2)	66.3 (9)	S(6')-S(7')-W(2)	115 (2)
S(13)-W(1)-S(12)	136.0 (2)	S(22)-W(2)-S(24)	133.9 (5)	S(24)-S(23)-W(2)	67.4 (7)	S(22')-S(21')-W(2)	62 (2)
S(13)-W(1)-S(14)	51.1 (2)	S(22)-W(2)-S(7)	89.3 (6)	S(23)-S(24)-W(2)	62.4 (9)	S(21')-S(22')-W(2)	62 (1)
S(13)-W(1)-S(1)	136.9 (2)	S(22)-W(2)-N(1)	84.5 (5)	O(2)-W(2)-S(21')	103 (1)	S(24')-S(23')-W(2)	57 (2)
S(13)-W(1)-N(2)	82.2 (4)	S(21)-W(2)-S(24)	86.2 (6)	O(2)-W(2)-S(22')	96 (1)	S(23')-S(24')-W(2)	70 (1)
S(11)-W(1)-S(12)	50.5 (2)	S(21)-W(2)-S(7)	137.6 (7)	O(2)-W(2)-S(23')	99.3 (8)	O(2)-W(2)-S(24')	99 (1)
S(11)-W(1)-S(14)	137.0 (2)	S(21)-W(2)-N(1)	84.2 (7)	O(2)-W(2)-S(7')	103.1 (9)	S(24')-W(2)-S(21')	154 (2)
S(11)-W(1)-S(1)	126.8 (2)	S(24)-W(2)-N(1)	77.3 (6)	S(24')-W(2)-S(22')	136 (1)	S(24')-W(2)-S(23')	53 (1)
S(11)-W(1)-N(2)	79.9 (4)	S(24)-W(2)-S(7)	128.0 (6)	S(24')-W(2)-S(7')	84 (1)	S(24')-W(2)-N(1)	79 (1)
S(14)-W(1)-S(12)	156.2 (2)	N(1)-W(2)-S(7)	81.0 (5)	S(22')-W(2)-S(21')	56 (1)	S(22')-W(2)-S(23')	83 (1)
S(14)-W(1)-S(1)	87.5 (2)	S(2)-S(1)-W(1)	112.6 (3)	S(22')-W(2)-S(7')	132 (1)	S(22')-W(2)-N(1)	83 (1)
S(14)-W(1)-N(2)	82.0 (3)	S(3)-S(2)-S(1)	106.7 (3)	S(21')-W(2)-S(7')	78 (1)	S(21')-W(2)-S(23')	135 (1)
S(12)-W(1)-S(1)	77.1 (2)	S(2)-S(3)-S(4)	106.2 (3)	S(21')-W(2)-N(1)	80 (1)	S(7')-W(2)-S(23')	134 (1)
S(12)-W(1)-N(2)	77.5 (3)	S(5)-S(4)-S(3)	105.1 (7)	N(1)-W(2)-S(7')	80.0 (9)		
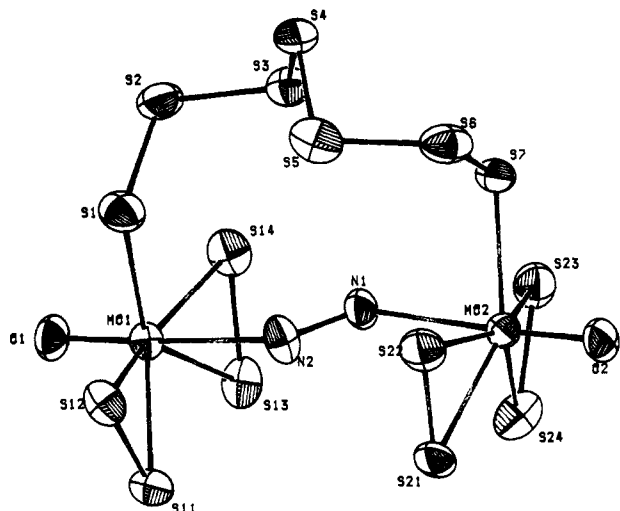
Figure 1. Configuration of the anion {[MoO(S$_2$)$_2$]$_2$(μ_2-S$_7$)(μ_2-NH$_2$NH$_2$)}$^{2-}$ with the first kind of conformation (a) of the S$_7^{2-}$ ligand.

Figure 2. Configuration of the anion {[MoO(S$_2$)$_2$]$_2$(μ_2-S$_7$)(μ_2-NH$_2$NH$_2$)}$^{2-}$ with the second kind of conformation (b) of the S$_7^{2-}$ ligand.

In related complexes with a similar structural character, [Mo$_2$O$_2$S$_9$]$^{2-}$,[18c] [{Mo$_2$O$_2$S$_9$}$_{0.86}${Mo$_2$O$_2$S$_{10}$}$_{0.14}$]$^{2-}$,[18a,b] [Mo$_4$O$_4$S$_{18}$]$^{2-}$,[18a,b] [{W$_2$O$_2$S$_9$}$_{0.77}${W$_2$O$_2$S$_{10}$}$_{0.23}$]$^{2-}$,[31] and [W$_2$O$_2$-(S)(S$_2$)$_4$]$^{2-}$,[20] the anions are composed of neutral MO(S$_2$)$_2$ subunits bridging by a sulfide (in M$_2$O$_2$S$_9^{2-}$ anion), a η^1,η^1-disulfide (in M$_2$O$_2$S$_{10}^{2-}$ anion), or a η^1,η^2-disulfide and a η^1,η^1-disulfide (in

[Mo$_4$O$_4$S$_{18}$]$^{2-}$ anion). The metal ions are in pseudo-pentagonal-bipyramidal environments, for the seventh coordinating atom is a weakly interacting intramolecular sulfur atom at ca. 2.8 Å. In the two title complexes, the two neutral MO(S$_2$)$_2$ subunits are bridged by a H$_2$NNH$_2$ ligand and a long S$_7^{2-}$ chain ligand, in which the M(VI) metal ion is coordinated by seven atoms in a

Table V. Comparisons of Torsion Angles and Conformations of Different S_7^{2-} Ligands

	I		II		$Pd_2(S_7)_4^{4-}$	$(Ph_4P)_2S_7$	$(Ph_4P)(NH_4)S_7$
	one	two	one	two			
angle, deg							
MS1S2/S1S2S3	-85.6	-85.6	-87.0	-87.0	77.5		
S1S2S3/S2S3S4	-80.1	-80.1	-79.9	-79.9	82.6	73.3	-77.9
S2S3S4/S3S4S5	96.5	83.7	96.1	82.2	-96.9	74.4	-96.2
S3S4S5/S4S5S6	95	94	93	100	-102.2	65.2	72.7
S4S5S6/S5S6S7	-68	-115	-66	-121	82.8	79.9	71.3
S5S6S7/S6S7M	-87	105	-90	100	82.8		
M-M dist, Å	5.894		5.835		6.300 (1)		
conformation[e]	a	b	a	b	a	c	d
ref	this work		this work		46	47	48

[a] (trans-)cis-trans-cis(-trans). [b] (trans-)cis-trans-cis(-cis). [c] trans-trans-cis. [d] trans-cis-trans. [e] The definition of conformation is according to: Wells, A. F. *Structural Inorganic Chemistry*, 4th ed.; Oxford University Press: London, 1975; p 591.
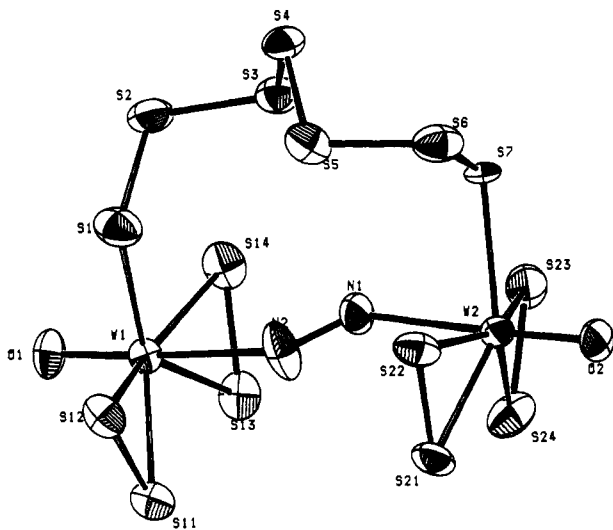

Figure 3. Configuration of the anion $\{[WO(S_2)_2]_2(\mu_2\text{-}S_7)(\mu_2\text{-}NH_2NH_2)\}^{2-}$ with the first kind of conformation (a) of the S_7^{2-} ligand.
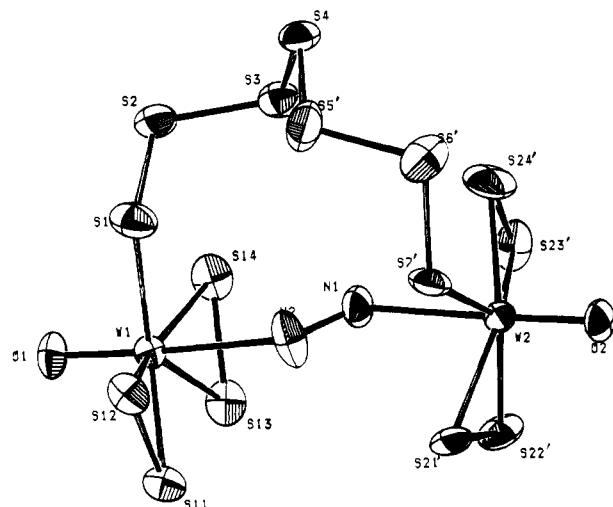

Figure 4. Configuration of the anion $\{[WO(S_2)_2]_2(\mu_2\text{-}S_7)(\mu_2\text{-}NH_2NH_2)\}^{2-}$ with the second kind of conformation (b) of the S_7^{2-} ligand.

real pentagonal-bipyramidal environment, unlike in the related complexes with a pseudo-pentagonal-bipyramidal environment. The bond lengths and bond angles for the neutral $MO(S_2)_2$ subunit are very similar among these related complexes. It is noted that the seventh coordinating site in this kind of complex has the ability to loosely coordinate a ligand.

The average Mo-N (W-N) bond length of 2.490 (8) Å (2.46 (1) Å is relatively long, due to the N atom being in the position opposite the Mo=O (W=O) double bond (average O-Mo-N angle of 175.6 (4)° and average O-W-N angle of 175.7 (6)°).

This trans influence of the terminal oxo ligand is quite familiar in the extensively studied oxoperoxomolybdates, which have a seven-coordinate Mo(VI) ion with pentagonal-bipyramidal geometry, e.g., $Cs_2[MoO(\eta^2\text{-}S_2)_2(thiooxalato\text{-}S,O)]$,[35] $K_2[MoO-(\eta^2\text{-}O_2)_2(C_2O_4\text{-}O,O')]$,[36] and $K_2[MoO(\eta^2\text{-}O_2)_2(glycolato\text{-}O,-O')]\cdot2H_2O$,[37] all of these complexes show elongation of the axial Mo-O bond across from the terminal oxo ligand. Crystallographic data on the seven-coordinate pentagonal-bipyramidal W(VI) monomer $WO(\eta^2\text{-}S_2)(Et_2NCS_2)_2$[38] show some elongation of the dithiocarbamate S—W bond (2.629 (1) Å) trans to the terminal W=O bond. Similar elongation has also been observed in the complex $WS(\eta^2\text{-}S_2)[(i\text{-}C_4H_9)_2NCS_2]_2$[39] for the dithiocarbamate S—W bond (2.588 (1) Å) trans to the terminal W=S bond.

The N—N bond length of 1.40 (1) Å [1.35 Å (2)] is shorter than that found in free hydrazine (1.44 Å), but longer than the N=N double bond [e.g. in $[(\mu_2\text{-}NHNH)\{Cr(CO)_5\}_2]\cdot2THF$,[32] N=N is 1.25 Å]. In the polymeric chain of $Zn(NH_2NH_2)_2(L)_2$ (L = NCS⁻,[40] Cl⁻[41]), the structure of the hydrazine $[(ZnH_2)N-N(H_2Zn)]$ is "staggered", as in the fragment $[(MH_2)N-N(H_2M)]$ of $[W(NPh)Me_3]_2(\mu_2\text{-}NH_2NH_2)(\mu\text{-}\eta^2,\eta^2\text{-}NHNH)$[24a] or $[\{MoFe_3S_4Cl_2(Cl_4cat)\}_2(\mu_2\text{-}S)(\mu_2\text{-}NH_2NH_2)]^{4-}$. But in the anion of the two title complexes, the structure of the hydrazine $[(MH_2)N-N(H_2M)]$ is very close to the trans form and the $M(\mu_2\text{-}NH_2NH_2)M$ (M = Mo, W) fragment is almost planar within 0.11 Å. This trans form is found in the rare complexes with the μ_2-NHNH (diazene) ligand, such as $[(\mu_2\text{-}NHNH)\{Cr-(CO)_5\}_2]\cdot2THF$,[32] $[\mu\text{-}NHNH\{Ru(Ph_3P)(dttd)\}_2]$,[42] and $[\mu\text{-}NHNH\{Fe(dttd)\}_2]$[43] (where dttd = 2,3,8,9-dibenzo-1,4,7,10-tetrathiadecane(2-)). By the way, the two Mo=O (or W=O) double bonds are almost in the least-square plane of $M(\mu_2\text{-}NH_2NH_2)M$ (M = Mo, W).

Very few complexes containing the S_7^{2-} ligand have been reported.[44-46] The S_7^{2-} ligand can act as a bidentate,[44] a tridentate,[45] and a doubly bridging[46] ligand. So far, only one complex, $[Pd_2(S_7)_4]^{4-}$,[46] purely with four doubly bridging S_7^{2-} ligands has been reported. The features of the doubly bridging S_7^{2-} ligand

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in $[Pd_2(S_7)_4]^{4-}$ and our two complexes are similar; that is, the S–S bond lengths and S–S–S bond angles are close to 2.0 Å and 109°, respectively. In association with $(Ph_4P)_2S_7$,[47] and $(Ph_4P)(NH_4)S_7$,[48] which have the free S_7^{2-} ligand, different conformations of S_7^{2-} ligands are exhibited. Table V gives a comparison of their torsion angles and conformations. In the title complexes, there are two types of conformations observed in bridging two metal atoms. It is noted that in one conformation of the S_7^{2-} ligand of the title complexes one torsion angle is very large at 115 or 121°.

A bimetallic activation and reduction of N_2 has been suggested[21,22] as a possible pathway toward N_2 fixation. The substrate of N_2 between two metals may change from HN=NH (diazene) and H_2NNH_2 (hydrazine) as intermediates to NH_3 (ammonia). In nitrogen fixation, the oxidation state of the center Mo ion may change to a higher state when electrons flow to the substrate. The presence of the loosely coordinated H_2NNH_2 ligand between two sulfur-rich Mo(VI) centers linked by a S_7^{2-} chain may assure a concomitant reduction to ammonia after reduction of the Mo(VI) ion. The isolation of the title complexes implies that the intermediates may still bind to the center ion which is in a higher oxidation state after electrons flow to the substrate or intermediates. Further discussion remains for the future after the identification of the bridging ligand (H_2NNH_2 or NH=NH).

Supplementary Material Available: Tables SI and SII, listing thermal parameters, the angles and distances of all non-hydrogen atoms, and torsion angles associated with the anions for both compounds, and a table listing the complete crystallographic data for both compounds (9 pages); tables of calculated and observed structure factors (24 pages). Ordering information is given on any current masthead page.

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Spin Crossover, Dimerization, and Structural Dynamics of Manganocenes Probed by Deuterium NMR Spectroscopy[†,1]

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The deuteriated manganocenes $(C_5D_5)_2Mn$ (**1**), $(C_5H_4CD_3)_2Mn$ (**2a**), and $(C_5D_4CH_3)_2Mn$ (**2b**) have been prepared and investigated by temperature- and concentration-dependent paramagnetic ^2H NMR spectroscopy. As compared to ^1H NMR, the spectral resolution is far better. This has allowed the detection of the elusive low-spin isomer of the most simple manganocene (in the form of **1**) in solution, the investigation of the spin crossover ($\Delta H° = 12.8$ kJ mol^{-1}, $\Delta S° = 84$ J mol^{-1} K^{-1}), and the formation of antiferromagnetic dimers which contain η^3,η^2-bridging and η^5-terminal Cps. The bridging Cps are involved in a rapid dynamic process so that the η^3 and η^2 fragments are indistinguishable down to 160 K. No interconversion of the bridging and the terminal Cps is visible up to 230 K, and no Cp exchange between monomeric and dimeric manganocene, up to 300 K. Similarly, two spin isomers and dimers have been observed for **2a** and **2b**. The averaged data for the equilibrium of the spin isomers are $\Delta H° \approx 17$ kJ mol^{-1} and $\Delta S° \approx 61$ J mol^{-1} K^{-1}, the energy barrier is $\Delta G^{\ddagger} \approx 46$ kJ mol^{-1}, and the lifetime of the spin isomers lies between 10^{-5} and 10^{-4} s. On the basis of selective deuteriation, the signal assignment shows unambiguously that all signals of the low-spin isomers have small shifts. Hence there is no reason to postulate the population of the $^2A_{1g}$ state in these manganocenes. The temperature dependence of the ^2H NMR signal shifts reflects the presence of the $^2E_{2g}$ and $^6A_{1g}$ states only.

Manganocenes are the most attractive metallocenes as far as the magnetic properties are concerned. It has been shown with various techniques that they can have one or five unpaired electrons and that the spin crossover lies in an easily accessible temperature range when R in $(RCp)_2Mn$ is H, CH_3, and *t*-Bu.[2] The most recently used technique is NMR spectroscopy.[3] In this laboratory it proved to be very efficient in demonstrating that the spin state of manganocenes can be tuned by systematic variation of the number and/or the type of the substituents at the cyclopentadienyl ligands.[3e] The parent sandwich Cp_2Mn appeared to be particularly capricious because in THF the pure high-spin donor adduct $Cp_2Mn(THF)$ formed, which was confirmed later by X-ray analysis.[4] By contrast, in toluene, spin crossover influenced the ^1H NMR signal shift but we were unable to detect the low-spin isomer. On decrease of the temperature, two additional ^1H NMR signals appeared that we ascribed to the formation of manganocene dimers and/or oligomers.

The situation seemed to become confusing when it was claimed[3d,f] that ^1H NMR studies disclose both spin isomers of Cp_2Mn but no dimer. Furthermore, the signal coalescence expected for rapid spin crossover did not occur.

This reflects upon the NMR method which had been used (i) to confirm the structure of manganocenes,[3b-f] (ii) to observe both the low- and high-spin species under slow-exchange conditions,[3d-f]

(iii) to determine the lifetime of a spin isomer,[3e] (iv) to determine the thermodynamic parameters of the spin equilibrium,[3e,f] (v) to

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