Addition of $\{M_2S_2O_2\}^{2+}$, M = Mo, W, to A-α-$[PW_9O_{34}]^{9-}$. Synthesis and Structural Characterizations in the Solid State and in Solution

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The $[P_2W_{18}M_6S_6O_{74}(H_2O)_6]^{12-}$ anions, M = Mo, W, were obtained through the stereospecific addition of the dithiocation $[M_2O_2S_2]^{2+}$ to the trivacant A-α-$[PW_9O_{34}]^{9-}$. $K_{12}[P_2W_{18}Mo_6S_6O_{74}(H_2O)_6]\cdot 26H_2O$ has been isolated as crystals and has been characterized by X-ray diffraction (orthorhombic $Pmn2_1$ with $a = 31.530(6)$ Å, $b = 19.703(4)$ Å, $c = 18.761(4)$ Å, $Z = 4$). The structure of the anion consists of a sandwich-like arrangement of two α-$[PW_9O_{34}]^{9-}$ subunits bridged by three $[Mo_2O_2S_2(H_2O)_2]$ cores. The X-ray diffraction structural analysis showed that one $[Mo_2O_2S_2]$ bridging unit was rotated through an angle of 180° with respect to the other two. Among the six water molecules attached to the Mo centers, four are directed toward the inner cavity while the two remaining ones are directed out of the cavity. According to the X-ray data, ^{183}W NMR characterizations of both compounds show the lowering of the local symmetry of the α-$[PW_9O_{34}]^{9-}$ subunit from C_{3v} to C_s. For $[P_2W_{24}S_6O_{74}(H_2O)_6]^{12-}$, two additional deshielded resonances were observed characteristic of the distribution of the three $[W_2O_2S_2(H_2O)_2]$ bridging units. Infrared data are also given.

Introduction

Heteropolyoxometalates form a large variety of structures and, due to their unique properties, have given rise to numerous applications in diverse areas such as catalysis, medicine, biology, and materials.[1−3] Transition metal sulfides are used commercially in hydrotreating processes[4] and are of current interest for their implications in bioinorganic chemistry.[5] Introduction of sulfur atoms into the framework of a heteropolyoxoanion is expected to modify the properties of the oxo parent, a process which has turned out to be quite difficult since the oxygen/sulfur substitution generally results in the breakdown of the polyanionic architecture. $[TaW_5O_{18}S]^{3-}$ and $[NbW_5O_{18}S]^{3-}$ were the first polyoxothioanions to be unambiguously characterized by Klemperer and co-workers,[6] who succeeded in substituting a terminal oxygen by a sulfur atom in the oxo-parent Lindquist structure. On the basis of the same idea, the Keggin analogues $[PW_{11}O_{39}ME]^{4-}$ (M = Nb, Ta, E = S, Se) were obtained by direct reaction of $[PW_{11}MO_{39}]^{4-}$ with a sulfurating agent.[7,8] Another elegant way to sulfidize the Keggin-type structure consists of the stereospecific addition of the $[M_2S_2O_2]^{2+}$ (M = Mo, W) fragment to the lacunary γ-$[SiW_{10}O_{36}]^{8-}$ and γ-$[PW_{10}O_{36}]^{7-}$ educts, which resulted in derivatives of the γ-Keggin-anion type.[9,10] In the present paper we report on a further possibility to incorporate sulfur atoms in a Keggin anion when the size of the thio fragment and that of the cavity of the lacunary oxo precursor are not geometrically complementary with the result that sandwich-type compounds are formed.[2,11]

Experimental Section

Syntheses. All chemicals were of reagent grade and generally used as received. Potassium 9-tungstophosphate $K_9[\alpha\text{-}PW_9O_{34}]\cdot 16H_2O$ was prepared by usual methods and checked by polarography[12] and IR spectroscopy. $[NMe_4]_2[Mo_2O_2S_6]$ has been synthesized by a method derived from that described by A. Müller et al.,[13] who obtained this complex through a two-step reaction resulting first in $[Mo_3S_{13}]^{2-}$ and finally in $[Mo_2O_2S_6]^{2-}$. According to this method, $[Mo_2O_2S_6]^{2-}$ has been isolated through a one-step reaction which ensures a better conversion of starting materials and more convenience in carrying out the different syntheses.

Microanalyses were performed by Service Central d'Analyses du CNRS, Solaize, France.

$[NMe_4]_2[Mo_2O_2S_6]$ (1). A polysulfide solution was prepared by bubbling H_2S until saturation into a suspension of S_8 (8 g; 125 mmol) in 50 mL of 20% commercial ammonia at room temperature. $[NH_4]_6[Mo_7O_{24}]\cdot 4H_2O$ (20 g; 16.16 mmol) was dissolved in 300 mL of a boiling solution of 20% commercial ammonia. The polysulfide solution was added to the molybdate solution, and the resultant mixture was

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heated with stirring at 90−95 °C for 90 min. Addition of solid $[NMe_4]Cl$ (10 g; 90 mmol) to the solution gave an orange solid, which was collected by filtration, washed with a minimum of ethanol (the solid is slightly soluble), dried with ether, and then washed with CS_2 (yield: about 30 g of crude product).

Anal. Calcd for $C_8H_{24}O_2N_2S_6Mo_2$: C, 17.02; H, 4.96; N, 4.25; S, 34.04; Mo, 34.04. Found: C, 19.04; H, 4.75; N, 5.55; S, 34.25; Mo, 32.88. IR (KBr, cm^{-1}): 3018 (m), 1483 (s), 1446 (m), 1281 (w), 948 (s), 945 (s), 927 (s), 514 (m), 468 (m), 358 (m), 322 (w).

$[NMe_4]_2[W_2O_2S_{10}]$ (2). $[NH_4]_2[WS_4]$ (3.2 g; 9.20 mmol) and S_8 (1.18 g; 4.60 mmol) were suspended in 50 mL of DMF and heated at 110 °C for 2 h under a nitrogen atmosphere. The resulting deep-brown solution was evaporated at 70 °C under vacuum, leaving an oily orange-red solid. Ethanol (50 mL) and 5 mL of water were added to the oily residue. The excess of sulfur was filtered off and volatiles were removed at 60 °C under vacuum. The residue was dissolved in 10 mL of ethanol and slowly added to 50 mL of an aqueous solution of tetramethylammonium chloride (2 g; 14 mmol). After 15 min, with moderate stirring, the orange-red precipitate was filtered off and washed with ethanol (caution, the solid is slightly soluble in ethanol), ether, and CS_2. (yield, 80%). Anal. Calcd for $C_8H_{24}N_2O_2S_{10}W_2$: C, 11.06; H, 2.76; N, 3.22; S, 36.87; W, 42.39. Found: C, 11.43; H, 3.04; N, 3.41; S, 34.84; W, 39.86. IR (KBr, cm^{-1}): 3015 (w), 1480 (s), 1444 (w), 1403 (w), 1285 (w), 950 (s), 510 (s), 439 (w), 328 (w).

$K_{12}[P_2W_{18}Mo_6S_6O_{74}(H_2O)_6]\cdot 26H_2O$ (3). I_2 (1.19 g, 4.75 mmol) was dissolved in 15 mL of an aqueous solution of 0.7 mol L^{-1} NaI. $[NMe_4]_2[Mo_2O_2S_6]$ (1.35 g, 2.40 mmol) was suspended in a 15 mL solution of NaI (0.27 g, 1.80 mmol) to which subsequently an iodine solution was slowly added. The mixture was heated at 50 °C for 15 min and filtered to eliminate solid sulfur and tetramethylammonium iodide. The solution was cooled at 0 °C to complete the precipitation of $[NMe_4]I$ as a white insoluble solid which was eliminated. Then, solid α-$K_9[PW_9O_{34}]\cdot 16H_2O$ (2.30 g; 0.89 mmol) was added to the orange filtrate, resulting in a wine-red solution. After addition of solid potassium chloride (2.50 g; 33.3 mmol), the precipitate was filtered off, washed with ethanol, and dried with diethyl ether (yield: 75%). Anal. Calcd for $H_{64}K_{12}P_2O_{106}S_6Mo_6W_{18}$: K, 7.35; P, 0.97; S, 3.01; Mo, 9.04; W, 51.99. Found: K, 7.41; P, 1.17; S, 2.85; Mo, 8.64; W, 50.40. Crystals suitable for X-ray determination were obtained by a slow evaporation of a solution of **3** (0.20 g in 5 mL of water) maintained at 4 °C for several days.

$K_{12}[P_2W_{24}S_6O_{74}(H_2O)_6]\cdot nH_2O$ (4). A solution of $[NMe_4]_2[W_2O_2S_{10}]$ (2.32 g, 2.70 mmol) in a mixture of 20 mL of DMF and 5 mL of water was treated with iodine (1.36 g, 5.35 mmol) previously dissolved in 5 mL of DMF. The mixture was heated at 50 °C with stirring for 15 min and filtered to eliminate the solid sulfur formed. To the deep-brown filtrate was added α-$K_9[PW_9O_{34}]\cdot 16H_2O$ (2.30 g, 0.89 mmol), and the mixture was vigorously stirred for 30 min. A brown solid precipitated on addition of 100 mL of ethanol. After filtration, the crude product was washed with ethanol and dried with ether. The solid was subsequently redissolved in 20 mL of water and precipitated on addition of solid potassium chloride (2.30 g, 33.3 mmol). After filtration, the solid was washed with ethanol and ether and analyzed. Found (%): K, 6.31; P, 0.83; S, 2.69; W, 60.81; these values correspond to the molar ratios W/S = 3.93 (calcd: 4), W/P = 12.3(12), W/K = 2.05(2). The number of water molecules was not checked by TGA.

Physical Measurements. Infrared spectra were recorded on an IRFT Magna 550 Nicolet spectrophotometer using pressed KBr pellets. The ^{183}W NMR spectra were recorded at 20 °C from saturated aqueous solutions in 10 mm tubes on a Brucker AC-300 spectrometer operating at 12.5 MHz. Chemical shifts were referenced to an external 2 M Na_2WO_4 solution in alkaline D_2O, and to dodecatungstosilicic acid as secondary standard ($\delta = -103.8$ ppm). Saturated aqueous solution samples were obtained by cationic exchange of **3** and **4** through a Dowex 50W-X2 resin (Li^+ saturated). The eluate was evaporated until dry and redissolved in a minimum of a mixture of H_2O-D_2O (2/3 to 1/3 vv) to obtain a concentration of about 0.8 mol L^{-1}. For $[P_2W_{18}Mo_6S_6O_{74}(H_2O)_6]^{12-}$, the spectral width was 1500 Hz (−90 to −210 ppm), while for $[P_2W_{22}S_6O_{74}(H_2O)_6]^{12-}$, two windows were used to record all the resonances: 3760 Hz (+1100 ppm/+1400 ppm) for the first one to observe the resonances related to the W(V) atoms and 1250 Hz (−100/−195 ppm) for the second one to observe the resonances of W(VI). ^{31}P chemical shifts were referenced to the usual external standard 85% H_3PO_4.

Table 1. Crystallographic Data for $K_{12}[P_2W_{18}Mo_6S_6O_{74}(H_2O)_6]\cdot 26H_2O$

empirical formula	$H_{64}O_{106}P_2S_6K_{12}Mo_6W_{18}$
fw	6370 g mol^{-1}
space group	$Pmn2_1$ (No. 31)
T, °C	−85
a, Å	31.530(6)
b, Å	19.703(4)
c, Å	18.761(4)
V, Å^3	11655
Z	4
ρ_{calcd}, g cm^{-3}	3.63
λ, Å	0.710 69
μ, cm^{-1}	188.49
R^a	0.101
$R_w{}^b$	0.2375

Crystal Structure Determinations. The unit cell of compound **3** was obtained at −85 °C on a Siemens R3m/V diffractometer. Intensities of the three standard reflections measured every 100 reflections remained constant during the data collection. Intensity profile data were processed and subsequently corrected for Lorentz, polarization, and absorption effects. The positions of the heavy atoms were obtained by direct methods, and those of the remaining atoms were taken from successive difference electron density maps. Computations were performed using the SHELX program package.[15] Crystallographic data for compound **3** are listed in Table 1. Final selected non-hydrogen atom positions and equivalent isotropic displacement parameters are provided in Table 2 and selected bond lengths in Table 3. Atomic positions, isotropic and anisotropic displacement parameters, distances, and angles are provided in Tables S1, S2, S3, and S4, respectively.

Results and Discussion

Synthesis. In an ammonium polysulfide solution, the heptamolybdate $[Mo_7O_{24}]^{6-}$ gives the oxothio molybdate $[MoO_2S_2]^{2-}$ through alkaline hydrolysis reactions and successive O/S substitutions. This species represents the simplest monomer involved in the dimer formation. At 90−95 °C, in the presence of polysulfide ions acting as an external oxidizing agent, $[MoO_2S_2]^{2-}$ dimerizes via redox and acidobasic processes formally exemplified in eq 1. For $[NMe_4]_2[W_2O_2S_{10}]$, we have chosen to use in a first step the synthetic method for $(NEt_4)_2[W_2S_{12}]$ reported by E. I. Stiefel and co-workers.[14] Starting from the tetrathiotungstate $[WS_4]^{2-}$, the dinuclear species $[W_2S_{12}]^{2-}$ was obtained quantitatively in DMF at 110 °C in the presence of excess sulfur as oxidizing agent (eq 2).

$$2[MoO_2S_2]^{2-} + H_2S_2 \rightarrow [Mo_2O_2S_6]^{2-} + 2OH^- \qquad (1)$$

$$2[WS_4]^{2-} + {}^6/{}_8S_8 \rightarrow [W_2S_{12}]^{2-} + S_2{}^{2-} \qquad (2)$$

Then, in the presence of water, the terminal sulfur atom can be selectively substituted to give the oxothio precursor $[W_2O_2S_{10}]^{2-}$ (eq 3). The sandwich-like compounds were obtained from reactions that involved the preformed thiometallic core $[M_2S_2O_2]^{2+}$ and the trivacant heteropolyanion α-A-$[PW_9O_{34}]^{9-}$. As reported by Coucouvanis et al., the reactive thiocationic fragment can be obtained selectively and quantitatively from the corresponding anionic parent $[(S_x)MoO(\mu\text{-}S)_2$

$$[W_2S_{12}]^{2-} + 2H_2O \rightarrow [W_2O_2S_{10}]^{2-} + 2H_2S \qquad (3)$$

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Table 2. Selected Fractional Atomic Coordinates ($\times10^4$) and Equivalent Isotropic Displacement Parameters U_{eq} (in 10^{-3} Å^2)

atom	*x*	*y*	*z*	U_{eq}[a]	atom	*x*	*y*	*z*	U_{eq}[a]
W(1)	−31(1)	4125(1)	−460(1)	33(1)	O(21)	−1098(13)	5783(27)	1263(29)	52(12)
W(2)	−31(1)	5528(1)	598(1)	33(1)	O(22)	−864(12)	7100(25)	−135(27)	44(10)
W(3)	−30(1)	5712(1)	−1208(1)	33(1)	O(23)	−1112(13)	6125(28)	−1742(31)	55(12)
W(4)	−997(1)	3500(1)	481(1)	35(1)	O(24)	−843(12)	4247(24)	−2265(27)	43(10)
W(5)	−1007(1)	4888(1)	1504(1)	35(1)	O(25)	−1550(11)	3536(23)	734(25)	40(9)
W(6)	−998(1)	6607(1)	705(1)	35(1)	O(26)	−1565(12)	4655(25)	1527(27)	46(10)
W(7)	−1017(1)	6749(1)	−1070(1)	35(1)	O(27)	−1561(10)	6831(22)	555(24)	35(9)
W(8)	−992(1)	5230(1)	−2242(1)	36(1)	O(28)	−1582(12)	6892(25)	−865(27)	45(10)
W(9)	−1006(1)	3702(1)	−1495(1)	36(1)	O(29)	−1560(11)	5039(23)	−2388(24)	37(9)
W(10)	−32(1)	9488(1)	−4472(1)	32(1)	O(30)	−1561(13)	3798(28)	−1692(30)	55(12)
W(11)	−35(1)	11128(1)	−3877(1)	33(1)	O(31)	−1983(12)	3520(25)	2019(27)	47(11)
W(12)	−48(1)	10789(1)	−5666(1)	32(1)	O(32)	−1967(10)	7897(21)	−116(23)	33(8)
W(13)	−996(1)	9159(1)	−3373(1)	35(1)	O(33)	−1936(10)	3870(21)	−2933(22)	32(8)
W(14)	−1007(1)	10757(1)	−2805(1)	36(1)	O(34)	−2010(17)	4604(35)	278(37)	76(16)
W(15)	−1005(1)	12172(1)	−4116(2)	36(1)	O(35)	−2042(16)	5898(33)	−165(36)	72(15)
W(16)	−1023(1)	11830(1)	−5862(1)	37(1)	O(36)	−2014(16)	4929(30)	−1197(32)	63(14)
W(17)	−1022(1)	10047(1)	−6485(1)	37(1)	O(37)	−442(9)	5112(20)	−387(23)	27(7)
W(18)	−1004(1)	8774(1)	−5314(1)	36(1)	O(38)	−1094(12)	4676(25)	291(26)	41(10)
Mo(1)	−2050(2)	3976(3)	1299(3)	40(1)	O(39)	−1102(10)	5852(23)	−308(25)	36(9)
Mo(2)	−2050(2)	7060(3)	−129(3)	38(1)	O(40)	−1078(9)	4776(20)	−1079(22)	27(8)
Mo(3)	−2055(2)	4476(3)	−1925(3)	43(1)	O(41)	355(10)	8867(22)	−4365(24)	38(9)
Mo(4A)	−2049(4)	12412(6)	−4997(7)	27(3)	O(42)	363(12)	11561(26)	−3408(28)	49(11)
Mo(4B)	−2054(4)	12040(10)	−5003(8)	42(3)	O(43)	293(12)	10977(26)	−6312(27)	49(11)
Mo(5)	−2050(2)	9127(4)	−6193(4)	50(2)	O(44)	−856(12)	8481(25)	2891(28)	47(11)
Mo(6A)	−2043(4)	9850(7)	−2673(7)	31(3)	O(45)	−880(11)	11066(24)	−2001(25)	40(9)
Mo(6B)	−2054(4)	9886(7)	−3033(9)	35(3)	O(46)	−908(13)	12827(28)	−3706(31)	54(12)
S(1)	−2500	3271(14)	659(15)	49(5)	O(47)	−902(11)	12364(24)	−6525(26)	41(10)
S(2)	−2500	4827(14)	1691(15)	48(5)	O(48)	−898(13)	10062(26)	−7411(27)	48(11)
S(3)	−2500	6901(13)	846(15)	44(5)	O(49)	−875(13)	7939(27)	−5414(30)	52(11)
S(4)	−2500	6922(14)	−1110(15)	46(5)	O(50)	228(10)	10199(21)	−3937(22)	32(8)
S(5)	−2500	5124(13)	−2657(14)	43(5)	O(51)	189(11)	11261(25)	−4840(26)	43(10)
S(6)	−2500	3619(14)	−1503(15)	48(5)	O(52)	187(8)	9963(17)	−5258(19)	20(7)
S(7)	−2500	12373(14)	−4057(15)	47(5)	O(53)	−401(8)	9351(17)	−3734(20)	20(7)
S(8)	−2500	12042(16)	−5944(17)	57(6)	O(54)	−403(11)	10795(23)	−3176(25)	39(9)
S(9)	−2500	9886(15)	−6761(16)	53(6)	O(55)	−423(10)	11817(22)	−4059(24)	36(9)
S(10)	−2500	8519(16)	−5433(17)	56(6)	O(56)	−429(10)	11466(21)	−5717(22)	30(8)
S(11)	−2500	8987(14)	−3087(15)	48(5)	O(57)	−449(10)	10214(21)	−6138(23)	31(8)
S(12)	−2500	10757(13)	−2577(14)	41(5)	O(58)	−395(13)	9024(28)	−5119(29)	53(11)
P(1)	−949(4)	5108(10)	−378(11)	37(3)	O(59)	−850(13)	9823(27)	−2681(30)	52(12)
P(2)	−949(4)	10459(10)	−4663(10)	39(3)	O(60)	−1113(11)	11483(24)	−3324(26)	42(10)
O(1)	349(10)	3493(22)	−528(23)	36(9)	O(61)	−856(13)	12444(28)	−5070(29)	53(12)
O(2)	337(12)	5716(26)	1179(28)	49(11)	O(62)	−1119(11)	11005(23)	−6328(24)	37(9)
O(3)	340(13)	6071(29)	−1734(30)	56(12)	O(63)	−870(12)	9133(25)	−6229(27)	45(10)
O(4)	−863(12)	2670(26)	703(28)	48(11)	O(64)	−1086(12)	8864(25)	−4330(27)	45(10)
O(5)	−924(15)	4991(31)	2383(33)	61(13)	O(65)	−1572(14)	12288(30)	−4355(32)	63(13)
O(6)	−888(11)	7174(23)	1354(25)	36(9)	O(66)	−1586(10)	12018(21)	−5697(22)	30(8)
O(7)	−892(13)	7493(27)	−1579(29)	52(11)	O(67)	−1599(12)	9787(24)	−6482(26)	44(10)
O(8)	−863(14)	5475(30)	−3123(32)	60(13)	O(68)	−1549(11)	8794(25)	−5563(25)	42(10)
O(9)	−919(12)	2966(23)	−1927(26)	41(10)	O(69)	−1542(12)	9234(26)	−3121(27)	47(11)
O(10)	206(10)	4677(21)	279(22)	31(8)	O(70)	−1568(11)	10569(25)	−2706(27)	45(10)
O(11)	218(10)	5929(22)	−286(25)	38(9)	O(71)	−1983(12)	13145(25)	−5226(28)	50(11)
O(12)	196(11)	4793(23)	−1066(24)	38(9)	O(72)	−1967(13)	8559(26)	−6874(28)	52(11)
O(13)	−407(10)	3891(21)	−1196(22)	31(8)	O(73)	−1938(11)	9635(24)	−1878(25)	42(10)
O(14)	−407(11)	3730(23)	179(25)	39(9)	O(74)	−2033(12)	11215(26)	−4826(28)	49(11)
O(15)	−410(12)	4995(25)	1200(27)	45(10)	O(75)	−2040(15)	9898(31)	−5282(33)	64(14)
O(16)	−427(12)	6258(24)	574(27)	46(10)	O(76)	−2037(16)	10124(32)	−3895(32)	67(14)
O(17)	−416(8)	6417(19)	−1048(20)	23(7)	O(77)	−463(10)	10421(23)	−4671(24)	36(9)
O(18)	−406(12)	5275(24)	−1893(26)	44(10)	O(78)	−1091(11)	10207(23)	−3930(24)	37(9)
O(19)	−1082(10)	3424(21)	−520(23)	31(8)	O(79)	−1096(12)	11228(26)	−4807(28)	46(11)
O(20)	−836(12)	3931(25)	1329(28)	48(11)	O(80)	−1102(9)	9991(19)	−5230(21)	25(8)

[a] $U_{eq} = (U_{11} + U_{22} + U_{33})/3$.

$MoO(S_x)]^{2-}$ ($x = 2, 4$) through selective oxidation of the terminal S_2 or S_4 ligands by 2 equiv of I_2 in DMF. We succeeded in transposing the Coucouvanis procedure from DMF medium to the aqueous solution, which allowed us to obtained the hexaaquo dithiocation (eq 4). Then, in the presence of the

$$[Mo_2O_2S_6]^{2-} + 2I_3^- + 6H_2O \rightarrow [(H_2O)_6Mo_2O_2S_2]^{2+} + 6I^- \qquad (4)$$

trivacant heteropolyanion α-A-$[PW_9O_{34}]^{9-}$, the hexaaquo ion acts as an acid and quickly reacts with the most basic terminal oxygen atoms of the defect Keggin anion to give the expected mixed sandwich-type compound (eq 5). With the tungsten-

$$2[PW_9O_{34}]^{9-} + 3[(H_2O)_6Mo_2O_2S_2]^{2+} \rightarrow [(PW_9O_{34})_2(Mo_2O_2S_2)_3(H_2O)_6]^{12-} + 12H_2O \qquad (5)$$

related dianion $[(S_4)_2W_2O_2S_2]^{2-}$, the formation of the dithio-

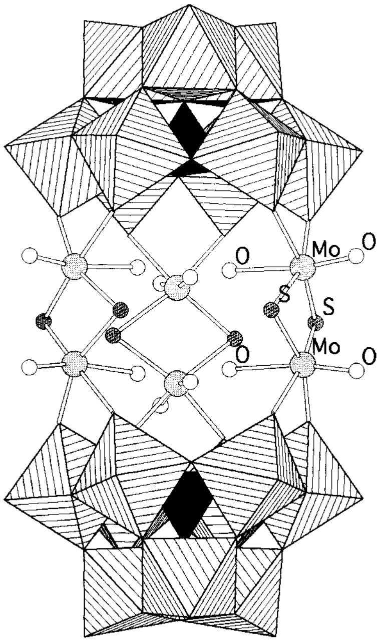

Figure 1. View of $[P_2W_{18}Mo_6S_6O_{74}(H_2O)_6]^{12-}$ showing the $[Mo_2S_2O_2]^{2+}$ fragment sandwiched by two Keggin units.

Table 3. Selected Interatomic Distances (Å) in the $\{Mo_2O_2S_2(H_2O)_2\}$ Central Thio Fragment

Mo(1)−O(31)	1.64(5)	Mo(5)−O(75)	2.29(6)
Mo(1)−O(26)	2.08(4)	Mo(5)−S(9)	2.32(2)
Mo(1)−O(34)	2.28(7)	Mo(6A)−Mo(6B)	0.68(1)
Mo(1)−S(1)	2.32(2)	Mo(6A)−O(73)	1.58(5)
Mo(2)−O(32)	1.67(4)	Mo(6A)−O(70)	2.06(5)
Mo(2)−O(28)	2.05(4)	Mo(6A)−O(69)	2.16(5)
Mo(2)−O(35)	2.29(6)	Mo(6A)−S(12)	2.30(2)
Mo(2)−S(3)	2.34(2)	Mo(6A)−K(7)	3.90(3)
Mo(3)−O(36)	1.64(6)	Mo(6B)−O(76)	1.68(6)
Mo(3)−O(30)	2.10(5)	Mo(6B)−O(69)	2.07(5)
Mo(3)−O(33)	2.27(4)	Mo(6B)−O(73)	2.25(5)
Mo(3)−S(5)	2.34(2)	Mo(6B)−S(11)	2.26(3)
Mo(5)−O(72)	1.72(5)	Mo(6B)−S(12)	2.38(3)
Mo(5)−O(67)	2.00(4)		

cation through the selective oxidation of the terminal S_4 ligand failed in aqueous medium but was nearly quantitative in a mixed DMF−H_2O medium.

Structure of $K_{12}[P_2Mo_6W_{18}S_6O_{74}(H_2O)_6]\cdot 26H_2O$ (3). The crystal structure of **3** consists of discrete $[P_2Mo_6W_{18}S_6O_{74}(H_2O)_6]^{12-}$ anions and K^+ cations. Using difference Fourier syntheses, the 26 water molecules were located, but only 8.5 of the 12 expected potassium atoms were placed by this way. The missing potassium atoms are probably distributed in disordered positions but not found in the lattice as sometimes observed in that type of macrostructure.[16] Ball and stick and polyhedral views of the anion are shown in Figure 1 and Figure 2, respectively. Each structural unit can be described as being formed by two $\{PW_9\}$ Keggin subunits doubly bridged by three $\{Mo_2S_2O_2\}^{2+}$ fragments in a sandwich-type arrangement. The connections between the Keggin subunit and the thiofragment are provided by Mo−O−W bridges, the Keggin units having retained the original A-α type of the $\{PW_9\}$ precursor. The interatomic distances W(1)−W(2) = 3.40 Å, W(1)−W(3) = 3.43 Å, and W(2)−W(3) = 3.41 Å are typical for the edge-sharing trimetallic $\{W_3O_{13}\}$ fragment, and the six tungsten atoms of the belt show normal coordination. The two $\{PW_9\}$ Keggin units forming the polythioanion are equivalent and are related by the equatorial crystallographic mirror plane containing the six sulfur atoms. Two of the polythioanions in the unit cell are regular while the remaining two exhibit an intramolecular disorder. Atoms in the regular unit are labeled W(1)−W(9), P(1), Mo(1)−Mo(3), S(1)−S(6), respectively, and W(10)−W18), P(2), S(7)−S(12) in the disorderd anion. Two of the three $\{Mo_2S_2O_2\}^{2+}$ fragments are involved in the molecular disorder through the positions of the Mo atoms, Mo(4A), Mo(4B), Mo(6A), and Mo(6B), which are distributed over two sites, namely, A and B, with a 50% occupancy. The molybdenum atoms exhibit distorted octahedral coordination with the four equatorial positions occupied by two oxygen atoms of the Keggin moiety and two bridging sulfur atoms and the two axial positions by two oxygen atoms. The short axial distances Mo(1)−O(31) = 1.64 Å, Mo(2)−O(32) = 1.67 Å, and Mo(3)−O(36) = 1.64 Å agree with values expected for an Mo═O double bond. The other three axial distances are longer, Mo(1)−O(34) = 2.28 Å, Mo(2)−O(35) = 2.29 Å, and Mo(3)−O(33) = 2.27 Å, and are attributed to Mo−OH_2 bonds. In Figure 3a the projection in the Mo(1)Mo(2)Mo(3) plane of the different atoms attached to the central Mo atoms is represented; two water molecules, O(34) and O(35), are directed toward the inner cage defined by the three $\{Mo_2S_2O_2\}$ fragments while the third water molecule linked to Mo(3) is directed out of the cavity. This situation corresponds to the rotation of 180° of the $\{Mo_2S_2O_2\}$ fragment with respect to the two other fragments and is probably due to steric constraints. A similar distribution was evidenced by ^{183}W NMR for $[P_2W_{21}O_{71}]^{6-}$, but the three bridging $\{WO_5(H_2O)\}$ octahedra enclosed two terminal oxygen atoms and only one water molecule.[17] In Figure 3b the projection relating to the disordered molybdenum atoms Mo(4A), Mo(4B), Mo(6A), and Mo(6B) is presented. Distances between the oxo and aquo ligands in the cavity, O(36)−O(35) = 2.72 Å, O(36)−O(34) = 2.84 Å, and O(35)−O(34) = 2.68 Å, are short enough to postulate hydrogen bonding between the terminal oxygen atom bound to Mo(3) and the two water molecules attached to Mo(1) and Mo(2). In the distorted molecular unit the Mo(5) atom was unambiguously placed and the relative positions of the oxo ligand and the water molecule bound to Mo(5) clearly estab-

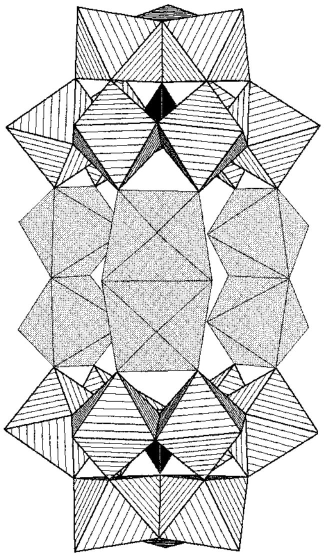

Figure 2. Polyhedral representation of $[P_2W_{18}Mo_6S_6O_{74}(H_2O)_6]^{12-}$. The W octahedra are light gray, and the Mo octahedra are dark gray.

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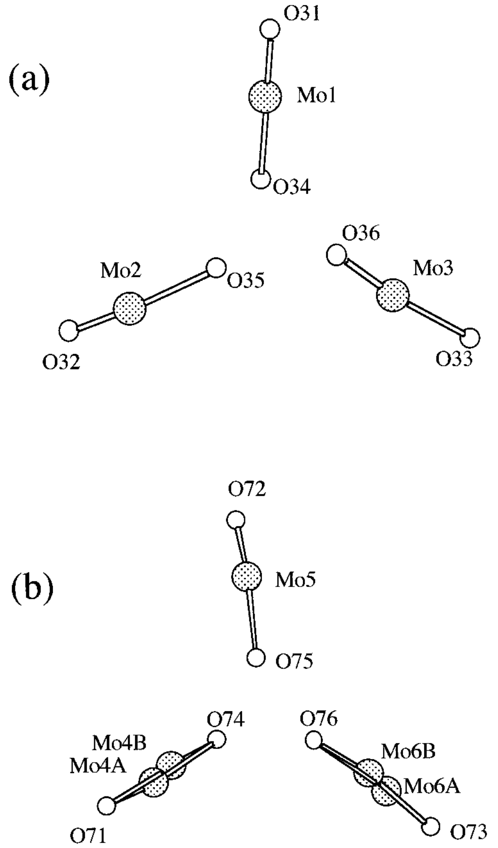

Figure 3. Projection in the equatorial plane showing the distribution of terminal oxygen atoms and water molecules attached to the central Mo centers: (a) nondisordered Mo(1)Mo(2)Mo(3) atoms; (b) disordered Mo(4A)Mo(4B)Mo(6A)Mo(6B).

lished. The water molecule is directed toward the inner cavity so that for the two others attached to Mo(4) and Mo(6), respectively, two orientations are possible as represented in Figure 3b. In the molecular units, the mean Mo−Mo distance in the $\{Mo_2S_2O_2\}$ fragments is 2.83 Å, thus confirming that the metal−metal bond present in the precursor has been retained in the final product.

^{31}P NMR Characterizations. ^{31}P NMR spectra were obtained from aqueous solutions of **3** and **4**. In both spectra a single line was observed at −11.89 and −12.13 ppm, respectively. These results suggest that both PW_9 subunits in the sandwich-like arrangement are equivalent in solution.

^{183}W NMR Characterizations. The ^{183}W NMR spectra of $[P_2W_{18}Mo_6S_6O_{74}(H_2O)_6]^{12-}$ and $[P_2W_{24}S_6O_{74}(H_2O)_6]^{12-}$ with the numbering scheme are shown in Figure 4 and Figure 5, respectively and corresponding data are reported in Table 4.

$[P_2W_{18}Mo_6S_6O_{74}(H_2O)_6]^{12-}$. The ^{183}W NMR spectrum of the $Li_{12}[P_2W_{18}Mo_6S_6O_{74}(H_2O)_6]$ solution revealed five resonance lines with 2:1:2:2:2 relative intensities as expected for nine tungsten nuclei involved in a C_s-PW_9 subunit. Chemical shifts in the −100/−200 ppm range are usual values for W(VI) atoms in an octahedral oxo environment. The lowering of the symmetry of the PW_9 subunit from C_{3v} to C_s agrees with the X-ray data discussed above and was attributed to the rotation of the $[Mo_2O_2S_2(H_2O)_2]$ bridging group at an angle of 180° with respect to the other two. On the basis of intensity data, the −151.3 ppm line, which presents one corner coupling constant corresponding to the W_1−O−$W_9(W_8)$ bridge (^2J = 15.0 Hz), was unambiguously assigned to the single tungsten atom W_1.[18] Such a coupling constant was observed as a unique doublet satellite only on the −111.2 ppm line. Thus, the −111.2 ppm line has been attributed to the $W_8(W_9)$ atoms which have only one corner junction. Although the −125.6 and −117.7 ppm lines are mutually coupled (AB system, $^2J_{W-W}$ = 24−25 Hz), the remaining features cannot be assigned because the three remaining inequivalent tungsten groups exhibit the same distribution of connections (two corner-sharing and one edge-sharing). Moreover, the edge coupling constants could not be determined because of the broadness of the lines ($\Delta\nu$ = 7−10 Hz). Only a partial assignment can be proposed on the basis of the observations of the ^{183}W chemical shifts in the trisubstituted mixed compounds derived from the A-α-$[XW_9O_{34}]^{n-}$ (X = P or Si) precursor. For A-α-$[SiW_9M_3(H_2O)O_{37}]^{n-}$ [19] (M = Al^{III}, Ga^{III}, Mn^{II}, Fe^{III}, Co^{II}, Ni^{II}, Cu^{II}) and A-α-$[XW_9Mo_{(3-x)}V_xO_{40}]^{n-}$,[20−21] the six equivalent tungstens of the belt appear deshielded with respect to the three-tungsten cap so that the −151.3, −149.9, and −125.6 peaks can be assigned to the above-mentioned six-tungsten belt, numbered W_4 to W_9, the other two being separated by only 1.4 ppm from the W_{1-3} triad cap.

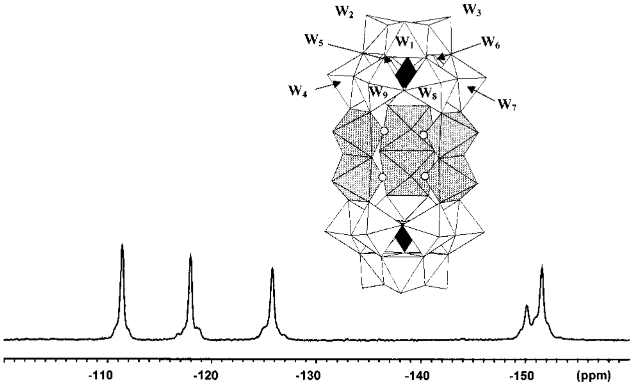

Figure 4. ^{183}W NMR spectra for $[P_2W_{18}Mo_6S_6O_{74}(H_2O)_6]^{12-}$ with the corresponding numbered structure (white spheres = H_2O).

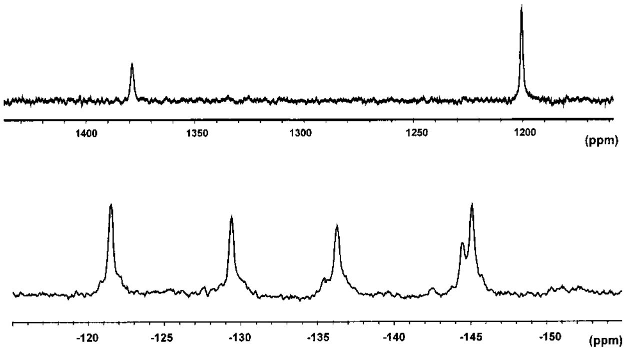

Figure 5. ^{183}W NMR spectra for $[P_2W_{24}S_6O_{74}(H_2O)_6]^{12-}$.

$[P_2W_{24}S_6O_{74}(H_2O)_6]^{12-}$. The ^{183}W NMR spectrum of the saturated aqueous solution of $Li_{12}[P_2W_{24}S_6O_{74}(H_2O)_6]$ contains seven resonance lines showing relative intensities of 2:1:2:2:2 for those in the −100 to −150 ppm range and 2:1 for the deshielded resonance at +1376.3 and +1197.0 ppm, respectively. The five low-frequency peaks are in agreement with the presence of nine W^{VI} atoms involved in the two equivalent A-α-$[PW_9O_{34}]^{9-}$ subunits in C_{3v} symmetry. On the basis of its intensity, the peak at −143.1 ppm can be attributed to the unique

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Table 4. ^{183}W NMR Data (ppm and Hz) for $[P_2W_{18}Mo_6S_6O_{74}(H_2O)_6]^{12-}$ and $[P_2W_{24}S_6O_{74}(H_2O)_6]^{12-}$

compound	chemical shift ($^2J_{W-W}$)
$[P_2W_{18}Mo_6S_6O_{74}(H_2O)_6]^{12-}$	−151.3 (15; 15); −149.9 (14); −125.6 (14.5; 25); −117.7 (24.5; 15); −111.2 (15)
$[P_2W_{24}S_6O_{74}(H_2O)_6]^{12-}$	−144.2; −143.1; −133.4; −127.1; −119.4; +1197.0; +1376.3

W_1 atom, but no further assignment could be attempted because overall coupling satellites overlap with the main resonance lines. Therefore, the ^{183}W NMR of the A-α-$[PW_9O_{34}]^{9-}$ subunit involved in both compounds, $[P_2W_{18}Mo_6S_6O_{74}(H_2O)_6]^{12-}$ and $[P_2W_{24}S_6O_{74}(H_2O)_6]^{12-}$, exhibits the same peak pattern. The three high-frequency lines at −119.4, −127.1, and −133.4 ppm have been attributed to the six-tungsten belt and the two closed resonances at −143.1 and −144.2 ppm to the triad cap. The two resonances observed at high frequency were related to the three $\{W^V{}_2O_2S_2\}$ bridging cores. On the basis of the intensity, the peak at +1376.3 ppm ($\Delta\nu = 30$ Hz) was assigned to the $\{W^V{}_2O_2S_2(H_2O)_2\}$ fragment containing the two water molecules directed toward the outer cavity. The remaining line at +1197.0 ppm ($\Delta\nu = 20$ Hz) was then attributed to the two equivalent thio fragments containing water molecules directed toward the inner cavity. Such chemical shifts are usual for reduced tungsten atoms and can be related to a strong paramagnetic effect on the nuclear screening. In a previous paper related to ^{183}W NMR characterization of the oxothio γ-isomers $[XW_{10}(W_2O_2S_2)O_{36}]^{n-}$, we reported a similar chemical shift of +1041.2 ppm for X = Si^{IV} and +1078.0 ppm for X = P^V.[9,10] Pope and co-workers reported another significant example about the ^{183}W NMR features of W(IV) trimers in heteropoly "brown".[22] The three tungsten(IV) atoms are deshielded by about +1500 ppm while the nine tungsten(VI) atoms have a chemical shift very close to that of the fully oxidized parent anion (−103.8 ppm for α-$[SiW_{12}O_{40}]^{4-}$). Pope reported that such a behavior was consistent with a complete localization of the W(IV) and W(VI) valences (class I behavior).

Infrared Characterizations. The infrared spectra of both $\{Mo_2O_2S_2\}$ and $\{W_2O_2S_2\}$ derivatives are very similar to each other and close to the IR spectrum of α-$[PW_{12}O_{40}]^{3-}$. The IR spectra are characterized by four main bands: P−O (1000−1100 cm^{-1}), W−O (terminal) (950−990 cm^{-1}), W−O−W (corner-sharing octahedra) (900−890 cm^{-1}), and W−O−W (edge-sharing octahedra) (820−780 cm^{-1}).[23,24] The asymmetric phosphate stretch represents a good probe for determining the local symmetry of the polyanion. The lowering of the symmetry from ideal T_d removes the degeneracy of the triply degenerated P−O stretch in α-$[PW_{12}O_{40}]^{3-}$ and results in band splitting.[23,24] For α-$[PW_9O_{34}]^{9-}$ (C_{3v} symmetry) two bands are observed at 1056 and 1003 cm^{-1}. $[P_2W_{18}Mo_6S_6O_{74}(H_2O)_6]^{12-}$ (**3**) and $[P_2W_{24}S_6O_{74}(H_2O)_6]^{12-}$ (**4**) IR spectra showed three bands (1087, 1067, 1022 cm^{-1} for **3** and 1091, 1067, 1026 cm^{-1} for **4** suggesting that the significant lowering of the local symmetry of the phosphato groups is due to the arrangement of the three thio fragments. This is in agreement with the X-ray diffraction results and ^{183}W NMR measurements that confirm the distribution of the three dinuclear thio fragments. On the spectrum of **3** and **4**, weak but well-defined bands are observed at 464 and 445 cm^{-1}, respectively. Such absorptions in thiometalates are characteristic for bridging Mo−S−Mo and W−S−W.[25a−d]

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Supporting Information Available: Tables giving fractional atomic coordinates, anisotropic thermal parameters, interatomic distances, and bond angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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