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Syntheses and Characterization of γ-$[SiW_{10}M_2S_2O_{38}]^{6-}$ ($M = Mo^{V}, W^{V}$). Two Keggin Oxothio Heteropolyanions with a Metal−Metal Bond

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The oxothio polyanions γ-$[SiW_{10}M_2S_2O_{38}]^{6-}$ ($M = Mo^{V}, W^{V}$) were obtained through stereospecific addition of the dication $[M_2S_2O_2]^{2+}$ (M = Mo, W) to the divacant γ-$[SiW_{10}O_{36}]^{8-}$ anion in dimethylformamide. These compounds were isolated as crystals and are stable in usual organic solvents and in aqueous medium from pH = 1 to pH = 7. $NEt_4Cs_3H_2[SiW_{10}Mo_2S_2O_{38}]\cdot 6H_2O$ (a γ-isomer derived from the α Keggin structure capped by the $[Mo_2S_2O_2]^{2+}$ fragment containing a metal−metal bond) crystallizes in the triclinic space group $P\bar{1}$ with a = 12.050(3) Å, b = 12.695(2) Å, c = 20.111(4) Å, α = 74.35(2)°, β = 86.83(2)°, γ = 63.50(2)°, Z = 2. $NEt_4Cs_5[SiW_{12}S_2O_{38}]\cdot 7H_2O$ is isostructural and crystallizes in the triclinic space group $P\bar{1}$ with a = 12.197(4) Å, b = 12.714(3) Å, c = 20.298(3) Å, α = 74.75(1) Å, β = 86.48(2)°, γ = 61.80(2)°, Z = 2. ^{183}W NMR spectra of Li^+ salts in aqueous solution agree with the solid state structures and reveal 100% purity for both anions. Polarographic, infrared and UV−vis data are also given.

Introduction

Relevance of metal−sulfur compounds to bioinorganic chemistry[1] and catalysis[2] has provoked extensive study of the syntheses and characterizations of molybdenum and tungsten containing compounds in sulfur environments.[3] Binary M−S anions, M = Mo, W, are of particular interest for showing an unusually wide range of stoichiometries, coordination geometries, oxidation states, and solid state dimensionalities. Those compounds containing the $M_2S_4^{2+}$ core were particularly investigated for their implications in reactions based on electron-transfer processes.[4] Also, discrete metal−chalcogenide compounds were proven to be functional analogues of active surface species of MoS_2 based catalyst in the HDS process.[5] Heteropolyoxometalates are present in a large field of applications in catalysis, medicine, and materials[6] and were also considered as soluble metal oxide analogues and used as heterogenous catalysts for acidic or oxidation processes.[7] So far, only two oxothioanions based on the Linquist and Keggin structure are known, $[NbW_5SO_{18}]^{3-}$ [8] and α-$[PNbW_{11}SO_{39}]^{4-}$,[9] respectively, in which a sulfur atom is located in the apical position of the NbO_5S octahedron. In order to obtain a mimetic example of a

Table 1. Crystallographic details for $Cs_5NEt_4[SiW_{12}S_2O_{38}]\cdot 7H_2O$ (**4**) and $Cs_3H_2NEt_4[SiW_{10}Mo_2S_2O_{38}]\cdot 6H_2O$ (**5**)

	compd **4**	compd **5**
	$C_8H_{34}O_{45}NS_2Cs_5SiW_{12}$	$C_8H_{34}O_{44}NS_2Cs_3SiMoW_{10}$
fw	3827	3367.61
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
T, °C	25	25
a, Å	12.197(4)	12.050(3)
b, Å	12.714(3)	12.695(2)
c,Å	20.298(3)	20.111(4)
α, deg	74.76(1)	74.35(2)
β, deg	86.48(2)	86.83(2)
γ, deg	61.80(2)	63.50(2)
V, Å^3	2669(40)	2644(30)
Z	2	2
λ, Å	0.710 69	0.710 69
ρ_{calcd}, g cm^{-3}	4.76	4.23
μ, cm^{-1}	298.4	248.01
R^a	0.048	0.059
$R_w{}^b$	0.058	0.072

$^a\ R = \Sigma||F_o - F_c||/\Sigma|F_o|.\ ^b\ R_w = [\Sigma w(|F_o| - |F_c|)^2/F_o{}^2]^{1/2}.$

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Table 2. Fractional Atomic Coordinates for $Cs_5NEt_4[SiW_{12}S_2O_{38}]\cdot 7H_2O$ (**4**)

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(eq)[a]	atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(eq)[a]
W(1)	0.1478(1)	0.6636(1)	0.42392(5)	0.0181	O(68)	0.007(2)	0.621(2)	0.268(1)	0.0221
W(2)	0.3502(1)	0.42334(9)	0.44482(5)	0.0181	O(85)	0.216(2)	0.383(2)	0.2862(9)	0.0191
W(3)	0.1581(1)	0.89274(9)	0.28809(5)	0.0160	O(97)	0.419(2)	0.857(2)	0.1782(8)	0.0060
W(4)	0.58259(9)	0.39511(9)	0.33054(5)	0.0156	O(128)	0.002(2)	0.630(2)	0.136(1)	0.0175
W(5)	0.3945(1)	0.28812(9)	0.30982(5)	0.0168	O(111)	0.430(2)	0.519(2)	0.1133(9)	0.0500
W(6)	−0.03343(9)	0.7912(1)	0.26803(5)	0.0165	O(115)	0.405(2)	0.339(2)	0.209(1)	0.0253
W(7)	0.49079(9)	0.72477(9)	0.26239(5)	0.0155	O(118)	0.185(2)	0.414(2)	0.1543(9)	0.0198
W(8)	0.0826(1)	0.4986(1)	0.22029(6)	0.0177	O(121)	0.203(2)	0.598(2)	0.0651(9)	0.0206
W(9)	0.29813(9)	0.85405(9)	0.12419(5)	0.0152	O(126)	0.004(2)	0.811(2)	0.1711(9)	0.0144
W(10)	0.54033(9)	0.56567(9)	0.14838(5)	0.0155	O(145)	0.374(2)	0.478(2)	0.304(1)	0.0216
W(11)	0.3238(1)	0.44459(9)	0.12582(5)	0.0164	O(136)	0.180(2)	0.706(2)	0.2868(9)	0.0500
W(12)	0.08170(9)	0.73345(9)	0.10194(5)	0.0160	O(410)	0.585(1)	0.438(2)	0.2294(9)	0.0147
Si(1)	0.2850(6)	0.6078(6)	0.2502(4)	0.0158	O(710)	0.597(2)	0.639(2)	0.2021(7)	0.0500
S(1)	0.3571(6)	0.6046(6)	0.4381(4)	0.0227	O(910)	0.438(2)	0.732(2)	0.0903(9)	0.0500
S(2)	0.1414(7)	0.4875(7)	0.4171(4)	0.0261	O(912)	0.190(2)	0.804(2)	0.091(1)	0.0091
O(1)	0.095(2)	0.681(2)	0.500(1)	0.0252	O(917)	0.372(2)	0.669(1)	0.2071(8)	0.0128
O(2)	0.368(2)	0.355(2)	0.531(1)	0.0277	Cs(1)	0.6601(2)	0.2918(2)	0.04505(9)	0.0324
O(3)	0.132(2)	1.036(2)	0.286(1)	0.0214	Cs(2)	0.5307(2)	0.0314(2)	0.1800(1)	0.0429
O(4)	0.742(2)	0.324(2)	0.348(1)	0.0228	Cs(3)	0.8884(2)	0.2657(2)	0.2112(1)	0.0366
O(5)	0.419(2)	0.144(2)	0.313(1)	0.0230	Cs(4)	0.8248(2)	0.5373(2)	0.3691(1)	0.0359
O(6)	−0.193(2)	0.865(2)	0.254(1)	0.0282	Cs(5)	0.1758(2)	0.2740(2)	0.0295(2)	0.0577
O(7)	0.586(2)	0.770(2)	0.293(1)	0.0167	N(1)	0.239(2)	0.036(2)	0.496(1)	0.0182
O(8)	−0.019(2)	0.439(2)	0.232(1)	0.0198	C(1)	0.234(4)	−0.074(3)	0.547(2)	0.0386
O(9)	0.267(2)	0.982(2)	0.0606(9)	0.0194	C(2)	0.116(3)	−0.029(3)	0.588(2)	0.0367
O(10)	0.667(2)	0.508(2)	0.100(1)	0.0234	C(3)	0.224(3)	0.138(3)	0.533(1)	0.0263
O(11)	0.382(2)	0.353(2)	0.069(1)	0.0281	C(4)	0.320(3)	0.076(3)	0.595(2)	0.0271
O(12)	−0.017(2)	0.826(2)	0.0299(9)	0.0136	C(5)	0.129(3)	0.098(3)	0.444(1)	0.0288
O(24)	0.530(2)	0.371(2)	0.4153(9)	0.0221	C(6)	0.125(3)	0.207(3)	0.386(2)	0.0346
O(31)	0.136(2)	0.834(2)	0.3774(9)	0.0157	C(7)	0.365(2)	−0.016(2)	0.464(1)	0.0500
O(37)	0.335(2)	0.804(2)	0.3004(9)	0.0136	C(8)	0.377(3)	−0.095(3)	0.417(2)	0.0317
O(39)	0.185(2)	0.907(1)	0.1892(8)	0.0106	O(100)	0.728(3)	0.761(3)	0.123(2)	0.0771
O(47)	0.544(2)	0.564(2)	0.3201(9)	0.0168	O(101)	0.900(3)	0.440(4)	0.049(3)	0.0910
O(52)	0.379(2)	0.285(2)	0.4005(9)	0.0143	O(102)	0.950(3)	0.110(3)	0.106(1)	0.0573
O(54)	0.562(2)	0.260(1)	0.3170(9)	0.0500	O(103)	0.749(3)	0.013(3)	0.084(1)	0.0585
O(812)	0.218(2)	0.581(2)	0.193(1)	0.0248	O(104)	0.701(2)	0.161(2)	0.207(1)	0.0400
O(61)	−0.016(2)	0.751(2)	0.3610(8)	0.0158	O(105)	0.460(3)	0.121(3)	0.013(2)	0.0713
O(63)	−0.003(2)	0.926(2)	0.2609(6)	0.0500	O(106)	0.235(3)	0.160(3)	0.184(2)	0.0586

[a] $U(eq) = (U_1U_2U_3)^{1/3}$; *U*1, *U*2, *U*3 are the principal axes of the thermal ellipsoids.

thio compound fixed on an oxide surface, we have chosen to stereospecifically introduce sulfur, via a dinuclear thiometalate, in a divacant decatungstosilicate. The γ-isomer $[SiW_{10}O_{36}]^{8-}$ was choosen for displaying four terminal oxygen atoms in the same plane and for its good stability with respect to other tungsten heteropolyanions.[10]

Experimental Section

Materials. All commercial compounds were of reagent grade and were used as supplied unless indicated otherwise. The Keggin precursor γ-$K_8[SiW_{10}O_{36}]\cdot 12H_2O$, was prepared on the basis of literature procedure,[10] and its purity was checked by IR spectroscopy, polarography, and ^{183}W NMR measurements.

Preparation of γ-$(NBu_4)_4H_4[SiW_{10}O_{36}]$. γ-$K_8[SiW_{10}O_{36}]\cdot 12H_2O$ (4 g, 1.32 mmol) and NBu_4Br (7 g, 21.5 mmol) were dissolved in 50 mL of distilled water, and 50 mL of 1 M acetic buffer was added to precipitate the corresponding protonated salt γ-$(NBu_4)_4H_4[SiW_{10}O_{36}]$; yield, 73%. Anal. Calcd for $C_{64}H_{148}N_4SiW_{10}O_{36}$: C, 22.5; H, 4,35; N, 1,6; Si, 0.85; W, 53.8. Found: C, 22.3; H, 4.35; N, 1.6; Si, 1.0, W, 54.2.

Preparations of $(NEt_4)_2[M_2S_{10}O_2]$ (M = W, Mo). Proved syntheses of $(NEt_4)_2[M_2S_{12}]$ are described in the literature.[4,11] We have chosen to slightly modify the procedure reported by E. I. Stiefel and co-workers: 5 mL of distilled water were added at the begining of the procedure to induce the substitution of the two terminal sulfur atoms in $(NEt_4)_2[M_2S_{12}]$ by two oxygen atoms. The resulting $(NEt_4)_2$-$[M_2S_{10}O_2]$ precursors were obtained as an orange-red solid for M = W and a brown powder for M = Mo. IR: $(NEt_4)_2[W_2S_{10}O_2]$, 955.5 (s), 790 (s), 519 (m), 499 (m), 460 (w), 430 (m) cm^{-1}; $(NEt_4)_2$-$[Mo_2S_{10}O_2]$, 946 (s), 789 (s), 529 (m), 456 (m), 421 (w), 355 (w), 322 (w), 304 (vw) cm^{-1}.

Preparation of γ-$(NEt_4)_6[SiW_{10}Mo_2S_2O_{38}]$ (1). $(NEt_4)_2[Mo_2S_{10}O_2]$ (1 g, 3.5 mmol) was dissolved in a degassed mixture of 125 mL of dimethylformamide (DMF) and 50 mL of distilled water. After addition of γ-$(NBu_4)_4H_4[SiW_{10}O_{36}]$ (10 g, 3.0 mmol), 100 mL of a solution of I_2 (1.8 g, 7 mmol) in DMF was rapidly added, while the mixture was heated at 50 °C for 30 min. The solution was then cooled to room temperature and filtered to eliminate the solid sulfur formed. The filtrate was evaporated to dryness and the resultant residue redissolved in 200 mL of CH_3CN, leaving an insoluble material which was filtered off. The procedure was repeated until the formation of insoluble material ceased. The final red residue was recovered and redissolved in 100 mL of CH_3CN prior to addition of NEt_4Cl (10g, 60 mmol). Solid γ-$(NEt_4)_6[SiW_{10}Mo_2S_2O_{38}]$ was obtained by slow precipitation at 0 °C. The crude product was collected by filtration and washed with ethanol, carbon disulfide, and ether (total yield, 7.5 g). Anal. Calcd for $C_{48}H_{120}N_6SiW_{10}Mo_2S_2O_{38}$ (**1**): C, 16.4; H, 3,4; N, 2.39; Si, 0.84; W, 52.3; Mo, 5.5; S, 1.8. Found: C, 15.2; H, 3.5; N, 2.15; Si, 1.0; W, 51.5; Mo, 5.2; S, 2.2.

Recrystallizations to obtain crystals of **1** suitable for X-ray determinations failed, which led us, in order to improve the crystallographic quality of crystals, to partly exchange tetraethylammonium cations by cesium.

Preparation of $Cs_6[SiW_{10}Mo_2S_2O_{38}]$ (2). Compound **1** (0.3 g) was dissolved in 25 mL of distilled water previously heated at 50 °C, and filtered prior solid CsCl (0.5 g) was added. The microcrystalline precipitate was recovered by filtration, washed with ethanol, and dried with ether.

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Table 3. Fractional Atomic Coordinates for $Cs_3H_2NEt_4[SiW_{10}Mo_2S_2O_{38}]\cdot 6H_2O$ (**5**)

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(eq)[a]	atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(eq)[a]
Mo(1)	0.1475(2)	0.6586(2)	0.42509(9)	0.0276	O(68)	0.012(1)	0.609(1)	0.2677(7)	0.0280
Mo(2)	0.3515(2)	0.4232(2)	0.44764(9)	0.0271	O(85)	0.217(1)	0.377(1)	0.2890(7)	0.0290
W(3)	0.15629(7)	0.88917(7)	0.28568(4)	0.0256	O(97)	0.419(1)	0.858(1)	0.1764(9)	0.0281
W(4)	0.58338(7)	0.40119(7)	0.33132(4)	0.0243	O(128)	0.009(1)	0.612(1)	0.1372(7)	0.0256
W(5)	0.39616(7)	0.28771(7)	0.31226(4)	0.0258	O(111)	0.438(1)	0.513(1)	0.1118(7)	0.0270
W(6)	−0.03048(7)	0.77753(7)	0.26661(4)	0.0255	O(115)	0.409(1)	0.337(1)	0.2085(8)	0.0337
W(7)	0.48798(7)	0.73101(7)	0.26182(4)	0.0251	O(118)	0.189(1)	0.405(1)	0.1573(7)	0.0325
W(8)	0.08580(7)	0.48651(8)	0.22110(5)	0.0276	O(121)	0.202(1)	0.591(1)	0.0629(8)	0.0330
W(9)	0.30031(7)	0.84999(7)	0.12074(4)	0.0258	O(126)	0.009(1)	0.798(1)	0.1668(7)	0.0306
W(10)	0.54094(7)	0.56737(7)	0.14535(4)	0.0258	O(145)	0.374(1)	0.478(1)	0.3074(7)	0.0200
W(11)	0.32551(7)	0.43954(8)	0.12505(4)	0.0266	O(136)	0.180(1)	0.703(1)	0.2829(7)	0.0205
W(12)	0.08494(7)	0.72199(8)	0.09930(4)	0.0259	O(410)	0.584(1)	0.445(1)	0.2269(7)	0.0218
Si(1)	0.2874(4)	0.6050(5)	0.2484(3)	0.0205	O(710)	0.604(1)	0.651(1)	0.1980(7)	0.0308
S(1)	0.3550(4)	0.6064(5)	0.4378(3)	0.0296	O(910)	0.443(1)	0.734(1)	0.0865(7)	0.0289
S(2)	0.1448(5)	0.4802(5)	0.4207(3)	0.0347	O(912)	0.199(1)	0.790(1)	0.0882(7)	0.0258
O(1)	0.096(2)	0.675(2)	0.502(1)	0.0443	O(917)	0.375(1)	0.665(1)	0.2058(6)	0.0231
O(2)	0.371(1)	0.358(1)	0.5342(8)	0.0371	Cs(1)[b]	0.6655(2)	0.2912(2)	0.0492(1)	0.0423
O(3)	0.130(1)	1.034(1)	0.2850(9)	0.0329	Cs(2)[b]	0.5319(2)	0.0378(2)	0.1862(1)	0.0477
O(4)	0.741(1)	0.338(1)	0.3463(7)	0.0305	Cs(3)[b]	0.8861(4)	0.2669(4)	0.2051(3)	0.0490
O(5)	0.423(1)	0.144(1)	0.3135(9)	0.0390	Cs(4)[b]	0.8229(1)	0.5406(1)	0.36304(8)	0.0403
O(6)	−0.190(1)	0.840(1)	0.2545(7)	0.0281	Cs(5)[b]	0.1904(9)	0.273(1)	0.0231(7)	0.0465
O(7)	0.581(1)	0.780(1)	0.2925(8)	0.0336	N(1)	0.234(1)	0.034(2)	0.502(1)	0.0321
O(8)	−0.016(1)	0.423(2)	0.2371(9)	0.0450	C(1)	0.229(3)	−0.075(3)	0.554(2)	0.0621
O(9)	0.267(1)	0.979(1)	0.0547(8)	0.0276	C(2)	0.124(2)	−0.044(2)	0.601(1)	0.0391
O(10)	0.666(1)	0.517(1)	0.0956(7)	0.0160	C(3)	0.228(3)	0.132(3)	0.533(2)	0.0670
O(11)	0.384(2)	0.345(2)	0.0694(9)	0.0480	C(4)	0.318(2)	0.087(2)	0.599(1)	0.0376
O(12)	−0.018(1)	0.811(1)	0.0292(7)	0.0327	C(5)	0.122(3)	0.092(3)	0.446(2)	0.0590
O(24)	0.531(1)	0.378(1)	0.419(1)	0.0420	C(6)	0.116(3)	0.198(2)	0.388(1)	0.0539
O(31)	0.138(1)	0.830(1)	0.3763(8)	0.0318	C(7)	0.353(3)	−0.011(2)	0.466(1)	0.0409
O(37)	0.339(1)	0.807(1)	0.2995(7)	0.0217	C(8)	0.373(3)	−0.092(2)	0.422(1)	0.0477
O(39)	0.187(1)	0.899(1)	0.1839(6)	0.0082	O(100)	0.732(2)	0.761(3)	0.123(2)	0.0979
O(47)	0.545(1)	0.571(1)	0.3205(7)	0.0235	O(101)	0.910(2)	0.499(3)	0.0430(9)	0.0137
O(52)	0.382(1)	0.285(1)	0.4036(7)	0.0276	O(102)	0.935(2)	0.088(2)	0.105(1)	0.0614
O(54)	0.566(1)	0.264(1)	0.3172(7)	0.0231	O(103)	0.748(2)	−0.002(2)	0.092(1)	0.0672
O(812)	0.221(1)	0.575(1)	0.1926(8)	0.0313	O(104)	0.704(2)	0.158(2)	0.211(1)	0.0716
O(61)	−0.012(1)	0.737(1)	0.3604(6)	0.0154	O(105)	0.464(3)	0.101(3)	0.021(2)	0.0986
O(63)	−0.008(1)	0.920(1)	0.2573(8)	0.0315	O(106)	0.261(3)	0.150(2)	0.179(1)	0.0718

[a] $U(eq) = (U_1U_2U_3)^{1/3}$; U_1, U_2, U_3 are the principal axes of the thermal ellipsoids. [b] Cesium atoms are introduced with various occupancy factors. Their sum is 3.

Preparation of γ-$(NEt_4)_6[SiW_{12}S_2O_{38}]$ (3). The preparation of **3** was carried out by using a procedure strictly similar to that used for **1**.

Preparation of $(NEt_4)Cs_5[SiW_{12}S_2O_{38}]\cdot 7H_2O$ (4). $Cs_6[SiW_{12}S_2O_{38}]$ (**2**) (0.15 g) and $(NEt_4)_6[SiW_{12}S_2O_{38}]$ (**1**) (0.03 g) were dissolved in 20 mL of distilled water. The mixture was allowed to stand several days at room temperature after which red-brown well-shaped crystals suitable for X-ray determinations were collected and washed with ethanol and ether.

Preparation of $NEt_4Cs_3H_2[SiW_{10}Mo_2S_2O_{38}]\cdot 6H_2O$ (5). Suitable crystals for X-ray determinations were obtained by using for **5** a procedure similar to that used for **4** except for the crystallization which was performed in 2 M HCl.

Instrumentation and General Procedures. Infrared and UV−vis spectra were recorded on IRFT Magna 550 Nicolet and Perkin-Elmer Lambda 19 spectrophotometers, respectively. Infrared spectra of samples were obtained from KBr pellets and referenced to polystyrene bands. Polarograms were recorded on a Metrohm 626 Polarecord using a drop mercury electrode referenced to a saturated calomel electrode. All electrochemical data were collected at 298 K and are uncorrected for junction potentials. The ^{183}W spectra were recorded for nearly saturated aqueous solutions using 10 mm tubes on a Bruker AC-300 apparatus operating at 12.5 MHz. Chemical shifts were measured with respect to an external 2 M Na_2WO_4 solution in alkaline D_2O, using saturated dodecatungstosilicic acid (D_2O solution) as secondary standard ($\delta = -103.8$ ppm). Elemental analyses were performed by Service Central d'Analyses du CNRS, Solaize, France.

Crystal Structure Determination. Unit cell dimensions for compounds **4** and **5** were obtained from least-squares refinement of the setting angles of 25 reflections. Intensity data were collected at room temperature with a $\theta-2\theta$ scan technique on an Enraf-Nonius CAD4 four-circle diffractometer. Two standard reflections were monitored periodically, they showed no change during data collection. Crystallographic data and pertinent informations are given in Table 1. Corrections for polarization and Lorentz effects were applied. Absorption was corrected by Difabs.[12] Computations were performed by using the Crystals program adapted to a Micro Vax II.[13] Atomic form factors for neutral W, Cs, Si, C, N, O, and S were taken from ref 14. Real and imaginary parts of anomalous dispersion were taken into account. The structure was solved by direct methods using the SHELX-86 program and successive difference Fourier maps.[15] Hydrogen contributions were omitted. Least-squares refinements with approximation in five blocks were carried out by minimizing the function $\Sigma w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factors. Model reached convergence with $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$, having values listed in Table 1. Criteria for a satisfactory, complete analysis were the ratios of the root mean square shift to standard deviation being less than 0.1 and no significant features in the final difference map. The final positional parameters for **4** and **5** are given in Tables 2 and 3, respectively.

Results and Discussion

Synthesis and Characterization. Direct sulfuration of heteropolytungstates or -molybdates generally led to the reduction of the polyanion accompanied with the breaking of the polyanionic framework and substitution of sulfur by oxygen.[16]

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Table 4. Selected Geometric Parameters For γ-[SiW$_{10}$Mo$_2$S$_2$O$_{38}$]$^{6-}$ (**5**)

atoms	dist, Å	atoms	dist, Å	atoms	dist, Å	atoms	dist, Å	mean value, Å
W(4)−O(4)	1.70(1)	W(5)−O(5)	1.70(2)	W(6)−O(6)	1.73(1)	W(3)−O(3)	1.72(1)	1.71
W(4)−O(24)	1.83(2)	W(5)−O(52)	1.83(1)	W(6)−O(61)	1.82(1)	W(3)−O(31)	1.82(1)	1.82
W(4)−O(54)	1.94(1)	W(5)−O(54)	1.93(1)	W(6)−O(63)	1.91(1)	W(3)−O(63)	1.92(1)	1.92
W(4)−O(47)	1.95(1)	W(5)−O(85)	1.95(1)	W(6)−O(68)	1.96(1)	W(3)−O(37)	1.96(1)	1.95
W(4)−O(145)	2.28(1)	W(5)−O(145)	2.29(1)	W(6)−O(136)	2.29(1)	W(3)−O(136)	2.27(1)	2.28
W(4)−O(410)	2.02(1)	W(5)−O(115)	2.03(2)	W(6)−O(126)	2.01(1)	W(3)−O(39)	2.04(2)	2.02
W(9)−O(9)	1.70(1)	W(10)−O(10)	1.73(1)	W(12)−O(12)	1.70(1)	W(11)−O(11)	1.75(2)	1.72
W(9)−O(39)	1.83(1)	W(10)−O(410)	1.83(1)	W(12)−O(126)	1.84(1)	W(11)−O(115)	1.83(1)	1.83
W(9)−O(912)	1.92(1)	W(10)−O(111)	1.89(1)	W(12)−O(912)	1.90(1)	W(11)−O(111)	1.94(1)	1.91
W(9)−O(910)	1.94(1)	W(10)−O(910)	1.96(1)	W(12)−O(121)	1.94(1)	W(11)−O(121)	1.96(1)	1.95
W(9)−O(97)	1.91(1)	W(10)−O(710)	2.06(2)	W(12)−O(812)	1.96(1)	W(11)−O(118)	1.92(1)	1.96
W(9)−O(917)	2.32(1)	W(10)−O(917)	2.31(1)	W(12)−O(812)	2.33(1)	W(11)−O(812)	2.35(2)	2.32
W(7)−O(7)	1.71(1)	W(8)−O(8)	1.72(2)					1.71
W(7)−O(37)	1.86(1)	W(7)−O(47)	1.88(1)	W(8)−O(68)	1.89(1)	W(8)−O(85)	1.88(1)	1.88
W(7)−O(97)	1.92(2)	W(7)−O(710)	1.97(1)	W(8)−O(812)	1.91(2)	W(8)−O(118)	1.91(2)	1.93
W(7)−O(917)	2.35(1)	W(8)−O(812)	2.33(1)					2.34
Mo(2)−O(2)	1.69(1)	Mo(1)−O(1)	1.67(2)					1.68
Mo(2)−O(24)	2.07(2)	Mo(2)−O(52)	2.05(1)	Mo(1)−O(61)	2.06(1)	Mo(1)−O(31)	2.09(2)	2.07
Mo(2)−S(1)	2.300(6)	Mo(2)−S(2)	2.312(5)	Mo(1)−S(1)	2.293(5)	Mo(1)−S(2)	2.305(6)	2.30
Mo(2)−Mo(1)	2.832(1)							

atoms	angle, deg	atoms	angle, deg	atoms	angle, deg	atoms	angle, deg	mean value, deg
W(4)−O(54)−W(5)	114.4(6)	W(3)−O(63)−W(6)	115.3(9)					114.8
W(4)−O(24)−Mo(2)	128.4(9)	W(5)−O(52)−Mo(2)	128.1(7)	W(6)−O(61)−Mo(1)	129.6(6)	W(3)−O(31)−Mo(1)	127.5(8)	128.4
W(4)−O(47)−W(7)	148.0(8)	W(3)−O(37)−W(7)	146.6(8)	W(6)−O(68)−W(8)	146.1(8)	W(5)−O(85)−W(8)	147.6(8)	147.0
W(4)−O(410)−W(10)	147.0(7)	W(6)−O(126)−W(12)	147.0(8)	W(3)−O(39)−W(9)	146.7(7)	W(5)−O(115)−W(11)	145.4(9)	146.5
W(10)−O(710)−W(7)	114.9(6)	W(9)−O(97)−W(7)	117.8(8)	W(12)−O(128)−W(8)	117.4(6)	W(11)−O(118)−W(8)	119.2(8)	117.3
W(9)−O(129)−W(12)	153.6(8)	W(10)−O(111)−W(11)	152.1(8)					152.9
W(12)−O(121)−W(11)	120.5(8)	W(9)−O(109)−W(10)	120.5(7)					120.5
Mo(2)−S(1)−Mo(1)	76.1(2)	Mo(2)−S(2)−Mo(1)	75.6(2)					74.8

Table 5. Selected Geometric Parameters for γ-[SiW$_{12}$S$_2$O$_{38}$]$^{6-}$ (**4**)

atoms	dist, Å	atoms	dist, Å	atoms	dist, Å	atoms	dist, Å	mean value, Å
W(4)−O(4)	1.72(2)	W(5)−O(5)	1.70(2)	W(6)−O(6)	1.72(2)	W(3)−O(3)	1.68(2)	1.71
W(4)−O(24)	1.80(2)	W(5)−O(52)	1.83(2)	W(6)−O(61)	1.82(2)	W(3)−O(31)	1.82(2)	1.82
W(4)−O(54)	1.94(2)	W(5)−O(54)	1.91(2)	W(6)−O(63)	1.90(2)	W(3)−O(63)	1.88(2)	1.91
W(4)−O(47)	1.92(2)	W(5)−O(85)	1.94(2)	W(6)−O(68)	1.97(2)	W(3)−O(37)	1.90(2)	1.93
W(4)−O(145)	2.28(2)	W(5)−O(145)	2.27(2)	W(6)−O(136)	2.31(2)	W(3)−O(136)	2.27(2)	2.28
W(4)−O(410)	1.98(2)	W(5)−O(115)	1.99(2)	W(6)−O(126)	1.97(2)	W(3)−O(39)	1.99(2)	1.98
W(9)−O(9)	1.68(2)	W(10)−O(10)	1.74(2)	W(12)−O(12)	1.72(2)	W(11)−O(11)	1.74(2)	1.72
W(9)−O(39)	1.86(2)	W(10)−O(410)	1.87(2)	W(12)−O(126)	1.87(2)	W(11)−O(115)	1.84(2)	1.86
W(9)−O(912)	1.93(2)	W(10)−O(111)	1.94(2)	W(12)−O(912)	1.89(2)	W(11)−O(111)	1.91(2)	1.91
W(9)−O(910)	1.92(2)	W(10)−O(910)	1.95(2)	W(12)−O(121)	1.96(2)	W(11)−O(121)	1.94(2)	1.94
W(9)−O(97)	1.91(2)	W(10)−O(710)	1.94(2)	W(12)−O(812)	1.95(2)	W(11)−O(118)	1.93(2)	1.93
W(9)−O(917)	2.30(2)	W(10)−O(917)	2.31(2)	W(12)−O(812)	2.32(2)	W(11)−O(812)	2.33(2)	2.31
W(7)−O(7)	1.72(2)	W(8)−O(8)	1.71(2)					1.72
W(7)−O(37)	1.91(2)	W(7)−O(47)	1.88(2)	W(8)−O(68)	1.89(2)	W(8)−O(85)	1.89(2)	1.89
W(7)−O(97)	1.95(2)	W(7)−O(710)	1.88(2)	W(8)−O(128)	1.96(2)	W(8)−O(118)	1.95(2)	1.94
W(7)−O(917)	2.34(2)	W(8)−O(812)	2.31(2)					2.32
W(2)−O(2)	1.71(2)	W(1)−O(1)	1.66(2)					1.68
W(2)−O(24)	2.07(2)	W(2)−O(52)	2.05(2)	W(1)−O(61)	2.08(2)	W(1)−O(31)	2.07(2)	2.07
W(2)−S(1)	2.313(7)	W(2)−S(2)	2.333(7)	W(1)−S(1)	2.308(7)	W(1)−S(2)	2.317(7)	2.32
W(2)−W(1)	2.815(1)							

atoms	angle, deg	atoms	angle, deg	atoms	angle, deg	atoms	angle, deg	mean value, deg
W(4)−O(54)−W(5)	116.0(9)	W(3)−O(63)−W(6)	118.4(9)					117.2
W(4)−O(24)−W(2)	128.9(10)	W(5)−O(52)−W(2)	127.7(9)	W(6)−O(61)−W(1)	128.0(10)	W(3)−O(31)−W(1)	127.4(9)	128.0
W(4)−O(47)−W(7)	148.8(10)	W(3)−O(37)−W(7)	148.5(10)	W(6)−O(68)−W(8)	144.5(11)	W(5)−O(85)−W(8)	148.6(10)	147.6
W(4)−O(410)−W(10)	146.3(10)	W(6)−O(126)−W(12)	147.3(10)	W(3)−O(39)−W(9)	146.4(10)	W(5)−O(115)−W(11)	147.2(11)	146.8
W(10)−O(710)−W(7)	120.1(10)	W(9)−O(97)−W(7)	117.2(8)	W(12)−O(128)−W(8)	115.2(9)	W(11)−O(118)−W(8)	116.4(9)	117.2
W(9)−O(129)−W(12)	155.1(11)	W(10)−O(111)−W(11)	152.0(11)					153.5
W(12)−O(121)−W(11)	120.6(9)	W(9)−O(109)−W(10)	121.4(8)					121.0
W(2)−S(1)−W(1)	75.1(2)	W(2)−S(2)−W(1)	74.5(2)					74.8

Nevertheless, polyanionic structures can be stabilized with regard to redox processes induced by sulfur substitution by introducing in the polyanionic framework weakly reducible atoms. Thus, for niobotungstates such as [NbW$_5$O$_{19}$]$^{4-}$ and α-[PW$_{11}$NbO$_{40}$]$^{4-}$,[8,9] isopoly- and heteropolyoxothioanions were generated by using an adequate sulfurizing reagent, both thioniobiates having retained the parent polyanionic arrangements. In both examples, the sulfido ligand is attached to a

Nb(V) atom and is located in the terminal position of a Nb═S double bond. Another original way of synthesis consists in the stereospecific reaction between a preformed thiometallic core and a polyvacant heteropolyanion acting as a specific and adapted receiver. The dinuclear oxothiometallic cation $[M_2S_2O_2]^{2+}$, M = Mo^V, W^V, and the divacant γ-$[SiW_{10}O_{36}]^{8-}$ polyoxoanion represent a quite perfect example of complementary geometries.[10] As shown by Coucouvanis *et al.*,[17] the thiocationic fragment $[Mo_2O_2S_2]^{2+}$ can be obtained from $[(S_4)MoOS_2MoO(S_4)]^{2-}$ through selective oxidation of terminal S_2 or S_4 ligands by 2 equiv of I_2, as represented in eq 1. A similar behavior was obtained with the tungsten homologue $[(S_4)WOS_2WO(S_4)]^{2-}$.

$$[(S_4)MoOS_2MoO(S_4)]^{2-} + 2I_2 \rightarrow [Mo_2S_2O_2]^{2+} + S_8 + 4I^- \qquad (1)$$

In the presence of the divacant heteropolyanion γ-$[SiW_{10}O_{36}]^{8-}$, the $[Mo_2S_2O_2]^{2+}$ thiocation acts as a Lewis acid and rapidly fills the polyoxoanion vacancy to give the metal-saturated γ-$[SiW_{10}Mo_2S_2O_{38}]^{6-}$ (**1**). A similar procedure was applied with the dithiotungstate $[W_2O_2S_{10}]^{2-}$, yielding the expected adduct γ-$[SiW_{12}S_2O_{38}]^{6-}$ (**3**) (eq 2).

$$\gamma\text{-}[SiW_{10}O_{36}]^{8-} + [M_2S_2O_2]^{2+} \rightarrow \gamma\text{-}[SiW_{10}M_2S_2O_{38}]^{6-} \qquad M = Mo, W \quad (2)$$

Structural data obtained by ^{183}W NMR, IR, and UV−vis spectroscopies, together with X-ray determinations, confirm the postulated process of formation of these new heteropolyoxothioanions. Both anions are stable in air, the NEt_4^+ salt being soluble and stable as well in organic solvents, CH_3CN, and DMF as in aqueous solutions in a large range of pH, from pH = 1 to pH = 7.

Structures of γ-$[SiW_{10}M_2S_2O_{38}]^{6-}$ (M = Mo, W). Selected bond distances and angles are given in Tables 4 and 5 for compounds **5** and **4**, respectively.

γ-$NEt_4Cs_3H_2[SiW_{10}Mo_2S_2O_{38}]\cdot 6\ H_2O$ (5). The crystal structure of **5** consists of discrete γ-$[SiW_{10}Mo_2S_2O_{38}]^{6-}$ anions, NEt_4^+ and Cs^+ cations, and protons. The three Cs^+ and two protons of the molecular unit are statistically distributed in five crystallographic sites. The NEt_4^+ cations are of usual geometry, and the structural data for the cations are given in the Supporting Information. A CAMERON[18] view of anion **5** with the atom-labeling scheme is shown in Figure 1. The overall C_{2v} geometry of the anion can be described as a Baker−Figgis γ-isomer derived from the α Keggin structure by the rotation of $\pi/3$ of two trimetallic W_3O_{13} groups.[19] Both rotated triads are linked to the dithiomolybdic fragment $[MoO(\mu{-}S)_2MoO]^{2+}$ by edge sharing. The coordination geometry about the molydenum atoms can be viewed as two square pyramids sharing a common basal edge formed by the two S(1) and S(2) atoms. Each molybdenum atom in **5** is bonded to three oxygen ligands and two sulfur ligands in a distorted square environment with the Mo(2) atom displaced 0.413 Å away from the {S(1), S(2), O(24), O(52)} basal plane (the Mo(1) atom is 0.421 Å away from the {S(1), S(2), O(61), O(31)} plane). The mean value of the Mo(2)−O(145) and Mo(1)−O(136) distances is large enough, 2.77 Å, to be considered as nonbonding. The dihedral angle between the two basal planes is 147.5°. The apical oxygen−molybdenum distances, Mo(2)−O(2) = 1.67(2) Å and Mo(1)−O(1) = 1.69(2) Å, are comparable with those reported for similar dithiomolybdic structures containing terminal oxygen−molybdenum multiple bond, showing that the sulfur−oxygen substitution led to a fully oxygenated site. A short M−M separation 2.832(1) Å is observed in **5** as well as in **4**, 2.815(1) Å. The metal−metal separation is considerably shorter than the nonbonding metal−metal separation observed for W_2Cl_{10} {W···W = 3.814(2) Å}[20−26] and comparable to the M−M distances observed in *syn*-M(V)−M(V) dinuclear compounds showing similar $M_2X_2(\mu{-}S)_2^{2+}$ (X = O, S) cores, as given in Table 6, including the parent precursor.[11] The good agreement observed between the values of the Mo−Mo separations gathered in Table 6 and that observed in **5** confirms that the polyoxoanion core ($SiW_{10}O_{36}$) acts as a tetradentate ligand toward the central $Mo_2S_2O_2$ fragment which has retained the parent structure. These arguments together with the others developed in this paper (see ^{183}W NMR and electronic spectra data) are consistent with the presence of a metal−metal single

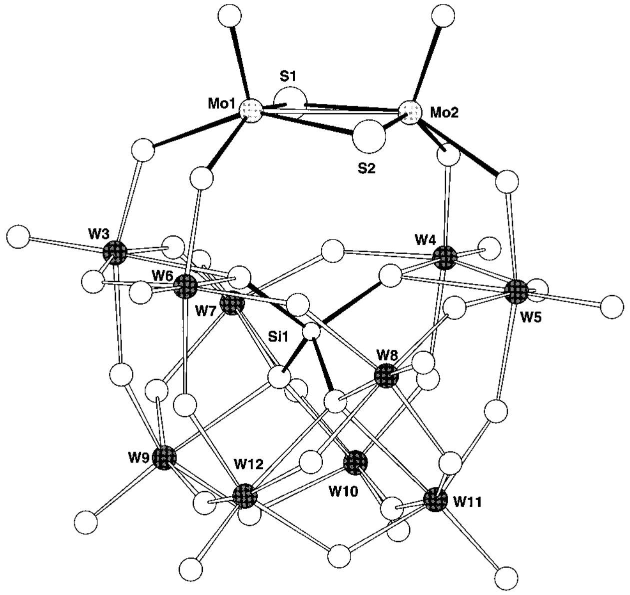

Figure 1. CAMERON view of γ-$[SiW_{10}Mo_2S_2O_{38}]^{6-}$ (**5**). For clarity oxygen numbering was omitted.

Table 6. Structural Data for Selected Anions Containing the $[M_2S_2X_2]^{2+}$ Core, Where M = Mo or W and X = O or S

anion	M−M, Å	ref
$[Mo_2O_2S_2(S_2)_2]^{2-}$	2.825(2)	21
$Mo_2S_4(S_2)_2]^{2-}$	2.821(1)	22
$[Mo_2S_4(S_2)(S_4)]^{2-}$	2.837(1)	23
$[Mo_2O_2S_2(S_2)(S_4)]^{2-}$	2.827(1)	4
γ-$[SiW_{10}Mo_2S_2O_{38}]^{6-}$	2.832(1)	this work
$[W_2S_4(WS_4)_2]^{2-}$	2.912(9)	24
$[W_2S_4(S_4)_2]^{2-}$	2.836(2)	11
$[W_2S_2Cl_2O_2(bpy)_2]$	2.8179(4)	25
γ-$[SiW_{12}S_2O_{38}]^{6-}$	2.815(1)	this work
$[W_2O_2S_2(cys)_2]^{2-}$	2.843(1)	26

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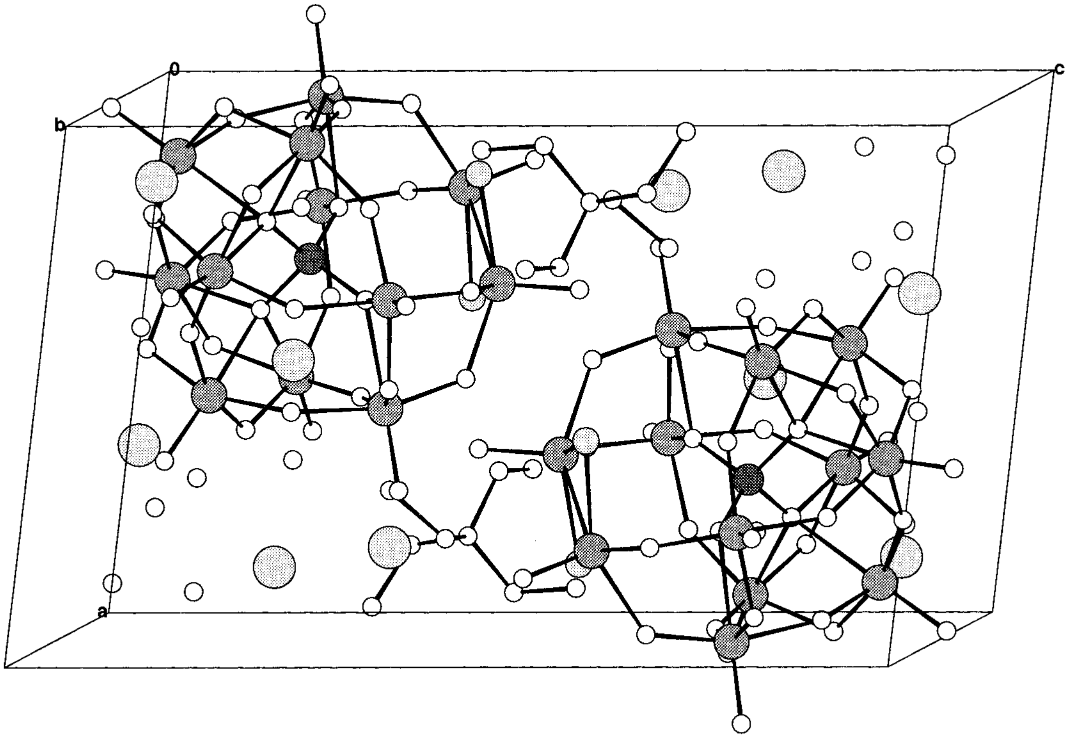

Figure 2. View of the packing of **5** showing the distribution of the various ions and water molecules in the lattice.

Table 7. ^{183}W NMR Data of (a) γ-$[SiW_{10}Mo_2S_2O_{38}]^{6-}$ (**5**) and (b) γ-$[SiW_{12}S_2O_{38}]^{6-}$ (**4**)

multiplicity	referenced peak, assignt	A	B	C	D
		(a) For **5**			
1	A (W_7, W_8)	−177.0	4.5	21.6	
2	B (W_9, W_{10}, W_{11}, W_{12})	(a)	−145.4	15.4	
2	C (W_3, W_4, W_5, W_6)	21.6	15.4	−122.9	
		(b) For **4**			
1	A (W_7, W_8)	−184.4	*a*	*a*	
2	B	*a*	−144.6	a	
2	C	*a*	*a*	−121.3	*a*
1	D (W_1, W_2)			*a*	+1041.2

[a] Not measurable. Chemical shifts are on the diagonal (ppm/2 M WO_4^{2-}). The off diagonal values are the coupling constants $^2J_{W-O-W}$ (Hz).

bond between Mo(2) and Mo(1). The mean value 2.06(1) Å found for Mo(1)−O(61), Mo(1)−O(31), Mo(2)−O(24), and Mo(2)−O(52) distances confirm that the capping $[Mo(\mu-S)_2Mo]^{2+}$ fragment is bonded through Mo−O−W bridges to the divacant precursor γ-$[SiW_{10}O_{36}]^{8-}$. Bond lengths and angles listed in Table 4 and Table 5 show that the $SiW_{10}O_{36}$ fragment in **5** has retained the overall geometry of the parent decatungstosilicate γ-$[SiW_{10}O_{36}]^{8-}$.[10] However a noteworthy feature in the structure of the polyoxoanionic fragment in **5** is the high symmetry of the central tetrahedron compared to that of the γ-$[SiW_{10}O_{36}]^{8-}$ precursor. Examples of this high local symmetry are the values of the four Si−O distances, strictly equal in **5** 1.62 ± 0.02 Å but quite different in the parent γ-$[SiW_{10}O_{36}]^{8-}$, 1.54 ± 0.14 Å.[10] A view of the packing of **5** is given in Figure 2, showing the distribution of anions, cations, and water molecules in the lattice.

γ-$NEt_4Cs_5[SiW_{12}S_2O_{38}]\cdot 7\ H_2O$ (4). The structure of **4** is similar to that of **5**, as exemplified by the structural data given in Table 4 and Table 5. The same atom labeling was used for **4** and **5** to make easier the comparison of the main structural features of the two structures. The complete structural data for **4** are given in the Supporting Information.

^{183}W NMR Characterizations

Highly soluble samples **1a** and **3a** were obtained from **1** and **3** by cationic exchange NEt_4^+/Li^+ by using a cationic resin Dowex 50W-X2. The resultant eluate was evaporated to dryness, and the lithium salts **1a** and **3a** were dissolved in water to obtain a concentration of about 0.8 M. For compound **1a** the spectral width was 1400 Hz (about 110 ppm), and for **3a** two spectral ranges +1000 to +1200 and −200 to −100 ppm were scanned to obtain all the expected resonances. The complete assignments of the spectra are based on the examination of the $^2J_{W-O-W}$ coupling constants. The coupling constant values depend on the W−O−W angles and bond lengths. For saturated Keggin anions, tungsten atoms engaged in corner-μ-oxo junctions (angles about 150°) have $^2J_{W-O-W}$ values of about 15−22 Hz, while those participating to edge junctions (angles about 120°) exhibit weaker coupling, generally about 5−7 Hz.[27] The ^{183}W NMR data with the corresponding IUPAC labeling are shown in Table 7 and Figure 3, and the related spectra, in Figure 4.

Table 8. Polarographic Data[a]

compd	pH	$E_{1/2}$ V vs SCE (electron number)
γ-$[SiW_{10}Mo_2S_2O_{38}]^{6-}$	4.2	−0.78(2); −0.89(2)
	5.3	−0.78(1); −0.87(1); −1.02(2)
γ-$[SiW_{12}S_2O_{38}]^{6-}$	4.2	−0.76(2); −0.96(2)
	5.3	−0.76(1); −0.87(1); −1.08(2)

[a] Polarogramms obtained from acetic buffer in the pH 4.2−5.3 range using drop mercury electrode as working electrode.

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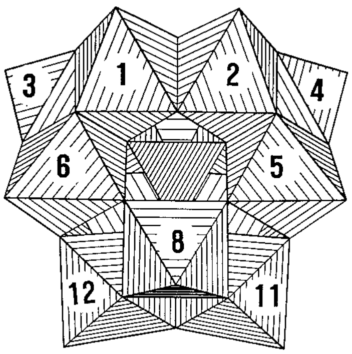

Figure 3. Idealized polyhedral representation of γ-$[XM_{12}O_{40}]^{n-}$ showing the numbering scheme used for ^{183}W NMR attributions.

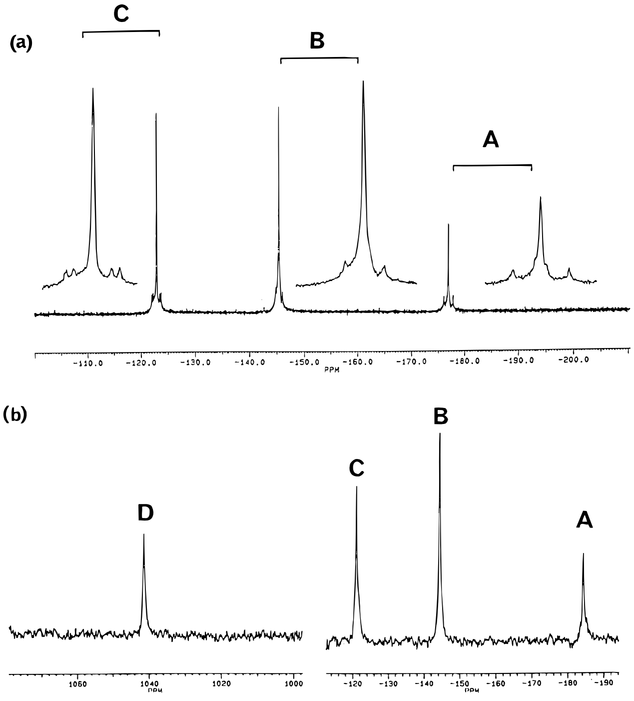

Figure 4. ^{183}W NMR spectra of (a) γ-$[SiW_{10}Mo_2S_2O_{38}]^{6-}$ and (b) γ-$[SiW_{12}S_2O_{38}]^{6-}$.

γ-$[SiW_{10}Mo_2S_2O_{38}]^{6-}$ (1a). The ^{183}W NMR spectra of γ-$Li_6[SiW_{10}Mo_2S_2O_{38}]$ in aqueous solution exhibit three well-resolved resonances referenced A, B, and C of relative intensities 1:2:2, respectively, in agreement with ten tungsten atoms involved in the C_{2v} γ-structure described above. The chemical shifts observed between −110 and −180 ppm have the usual values reported for tungsten(VI) in the oxo environment.[28a−c] On the basis of its intensity, the low-frequency A peak at −177.0 ppm is assigned to W_8 (W_7) atoms which are edge coupling with W_9, W_{10} (W_{11}, W_{12}) ($^2J_{W-O-W} = 4.5$ Hz) and corner coupling with W_3, W_4 (W_5, W_6) ($^2J_{W-O-W} = 21.6$ Hz). The C peak located at −122.9 ppm displays a corner coupling constant of 21.6 Hz and then can be assign to W_3, W_4 (W_5, W_6). The second corner constant observed for C and B peaks ($^2J_{W-O-W} = 15.4$ Hz) corresponds to the corner junction between W_3, W_4 (W_5, W_6) and W_9, W_{10} (W_{11}, W_{12}). Thus, the remaining peak at −145.4 ppm can be unambigously attributed to W_9, W_{10} (W_{11}, W_{12}). The edge coupling constant observed at the A peak as poorly resolved satellites ($^2J_{W-O-W} = 4.5$ Hz) is observed as a shoulder on the B line in agreement with the edge junction between W_8 (W_7) and W_9, W_{10} (W_{11}, W_{12}).

γ-$[SiW_{12}S_2O_{38}]^{6-}$ (3a). The ^{183}W NMR spectra of γ-$Li_6[SiW_{12}S_2O_{38}]$ in aqueous solution reveal four resolved resonance lines referenced A, B, C, and D with relative intensities of 1:2:2:1, respectively, in agreement with twelve tungsten atoms involved in the γ-isomer structure. The observed resonances are too broad ($\Delta\nu_{1/2} = 3-4$ Hz) to estimate the coupling constant. Therefore, on the basis of their chemical shift range (−130 ppm, −200 ppm), the A−C lines are attributed to ten tungsten (VI) atoms in an octahedral oxo environment. The A peak at −184.4 ppm with the relative intensity of 1 can be assigned to W_7 (W_8) . Both lines at −144. 6 and −121.3 ppm correspond to the two groups of four equivalent tungsten atoms W_3, W_4 (W_5, W_6) and W_9, W_{10} (W_{11}, W_{12}), but the discrimination between these resonances cannot be established. The D peak corresponding to high frequency observed at +1041.2 ppm with the relative intensity of 1 should be related to the remaining W_1 (W_2) since they are not observed in the spectra of the Mo homologue (**1a**). Moreover such a positive chemical shift is usual for reduced tungsten atom in a sulfur environment and would correspond to the two formal tungsten(V) atoms of the $[W^VO(\mu\text{-}S)_2W^VO]$ core.[11] The sharpness of the overall ^{183}W resonances indicates that the polyoxothioanion is diamagnetic, confirming the paired electrons are localized on the two W(2) and W(1) atoms and participate to the postulated metal−metal bond.

Another and significant feature showing the two paired electrons are localized on the two M(2) and M(1) metallic sites is the absence of the effect of these electrons on the chemical shift of the different types of tungstens of the polyanionic framework, as shown in Table 8.[29]

Electronic Spectra. The electronic spectra of compounds **1** and **3** in water exhibit strong absorptions observed as broad shoulders about 240 nm (ϵ = 22 300 L mol^{-1} cm^{-1}), 280 nm (ϵ =15 000 L mol^{-1} cm^{-1}) assigned to the O(2p) → M(4d, 5d) charge transfer.[30] In the vis region, the electronic spectra of γ-$[SiW_{10}Mo_2S_2O_{38}]^{6-}$ and γ-$[SiW_{12}S_2O_{38}]^{6-}$ exhibit absorptions at 412 nm (ϵ = 1980 L mol^{-1} cm^{-1}) and 476 nm (ϵ = 2050 L mol^{-1} cm^{-1}), respectively. These absorptions can be attributed to the charge transfer S(3p) → M(4d, 5d), M = Mo^V, W^V, in the dithiometallic fragment by comparison with the frequencies reported for the parent and other dinuclear compounds.[4] The absence of intervalence or d−d transition below 500 nm indicates that the two d^1 electrons are strongly trapped on Mo(2) and Mo(1), or W(2) and W(1). These spectral data are also in agreement with the presence of a M(2)−M(1) metal−metal bond.

Infrared Spectra. The main features observed in the IR spectrum of **1** given in Figure 5 are similar to those observed for a saturated $[SiW_{12}O_{40}]^{4-}$ Keggin-type structure, the addition of the dithiometalate fragment in the vacancies shifting the ν_{as}(W−O−W) absorptions from 740 to 790 cm^{-1}. For α, β, and γ Keggin isomers, the expected splittings of the main vibrational modes in the 700−1000 cm^{-1} range related to the lowering of the symmetry from $T_d \rightarrow C_{3v} \rightarrow C_{2v}$ are generally not observed, making this range unsuitable for any assignment. Between 400 and 200 cm^{-1}, absorptions assigned to the "breathing" mode of the anion are known to be sensitive to the symmetry of the anion.[31] For example, the rotation of a trimetallic group W_3O_{13} in α-$[SiW_{12}O_{40}]^{4-}$ to give the β-isomer is accompanied with the splitting of the two well-resolved bands at 334 and 384 cm^{-1}

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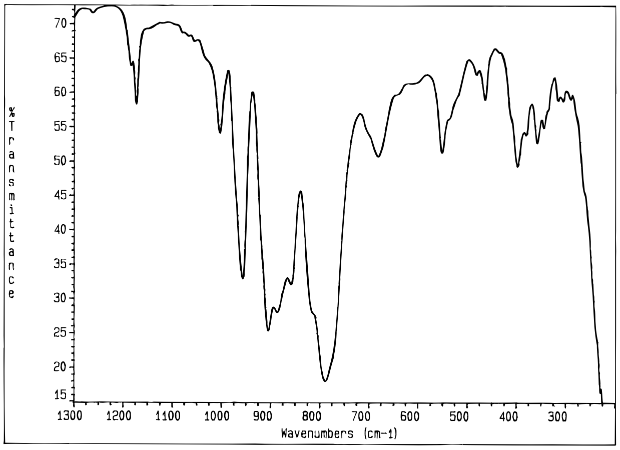

Figure 5. IR spectrum of $(NEt_4)_2[SiW_{12}S_2O_{38}]$ (**3**) as a KBr pellet.

into a set of four well-resolved bands.[31] In agreement with these previous observations, a set of several bands characteristic of the γ-structure is present in this range in the spectra of $[SiW_{10}M_2S_2O_{38}]^{6-}$. In addition, a weak but well-defined absorption is observed at 489.5 cm^{-1} for γ-$[SiW_{10}Mo_2S_2O_{38}]^{6-}$ and 465.0 cm^{-1} for γ-$[SiW_{12}S_2O_{38}]^{6-}$. Such absorptions in thiometalates are characteristic of bridging Mo−S−Mo and W−S−W.[11]

Electrochemical Behavior. Polarographic data are reported in Table 8. The polarograms of γ-$[SiW_{10}Mo_2S_2O_{38}]^{6-}$ and γ-$[SiW_{12}S_2O_{38}]^{6-}$ in 1 M acetic buffer exhibit two waves of two electrons at −0.78, −0.89 V and −0.76, −0.96 V, respectively. The complete electrochemical study will be published elsewhere.

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Supporting Information Available: For **4**, crystal data (Table S1) listings of fractional atomic coordinates (Table S2), interatomic distances (Table S3) and bond angles (Table S4), anisotropic thermal parameters (Table S5) and a figure showing a CAMERON view of the anion of **4**, for **5**, crystal data (Table S6) listings of fractional atomic coordinates (Table S7), interatomic distances (Table S8) and bond angles (Table S9), and anisotropic thermal parameters (Table S10) (19 pages). Ordering information is given on any current masthead page.

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