Synthesis and Structure of the Polyoxoanion $[Si_2W_{23}O_{77}(OH)]^{9-}$

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Introduction

Two isomers of the Keggin heteropolyanion α-$[XM_{12}O_{40}]^{n-}$ (X = Si, P; M = Mo, W) are known.[1] They are the β- and γ-isomers, and their stability depends on the nature of the metal M and the heteroelement X and on the solvent. The γ-isomer is only known for X = Si and M = W,[2] and it is stable in organic or mixed organic−aqueous solution but not in pure aqueous medium. It is obtained from the divacant γ-$[SiW_{10}O_{36}H]^{7-}$ species,[3] which is stable in aqueous solution, by reaction with tungstate in acidic hydroorganic medium. On the contrary, the β-isomer is obtained when this reaction is performed at pH between 1 and 4 in purely aqueous medium. This paper discusses the compound which is obtained when this reaction is carried out in strongly acidic aqueous solution (pH < 1).

Experimental Section

Synthesis. The potassium salt of the γ-decatungstosilicate (12 g, 4 mmol) was stirred with 30 mL of water and 2.75 mL of 10 M perchloric acid for 30 min. Solid potassium perchlorate was removed by filtration. A 1 M sodium tungstate solution (4 mL, 4 mmol) was added to the filtrate, which was strongly stirred in order to avoid local increase of the pH. This solution was kept for 1 h at room temperature. Addition of about 4 g of rubidium chloride led to the crude product, which was isolated by filtration with a sintered-glass funnel (yield about 75%). This solid was dissolved in a solution of lukewarm 2 M hydrochloric acid (25 mL). A small amount of insoluble material was removed by filtration, and the polyanion was precipitated again by addition of rubidium chloride (6 g). The final yield was about 50%. Anal. Calcd for $Rb_6H_3[Si_2W_{23}O_{77}(OH)]\cdot 12H_2O$: Si, 0.9; W, 67.5; Rb, 8.2. Found: Si, 1.3; W, 66.2; Rb, 8.6.

X-ray Crystallography. A crystal suitable for X-ray diffraction was mounted on a glass fiber. All data were collected at room temperature with an Enraf-Nonius CAD4 diffractometer using Mo Kα (λ = 0.710 69 Å) radiation. The cell dimensions were determined by least-squares procedures from the setting angles of 25 centered reflections. Three standard reflections were measured every 90 min and remained constant throughout data collection. Crystallographic data and other information are summarized in Table 1. All data were corrected for Lorentz and polarization effects, and absorption correction was performed using the DIFABS program.[4] Computations were performed by using the PC version of CRYSTALS.[5] Scattering factors were taken from ref 6. The structure was solved by direct methods using SHELXS 86[7] and successive Fourier difference syntheses. As sometimes observed in structural determinations of heteropolyanions, not all cations had an occupancy equal to 1. Three rubidium cations could unambiguously be located with full occupancy. An attempt to locate the remaining three Rb^+ ions (according to analytical data) was performed by geometrical considerations on the final highest peaks of Fourier syntheses. For these rubidium cations, isotropic thermal parameters were constrained to have the same value which was refined with the occupancies, the sum of the latter being fixed to 3. The result obtained should be considered with limited confidence. Finally, all non-oxygen atoms were anisitropically refined (refinements were carried out in eight blocks).

Table 1. Crystallographic Data for $Rb_6H_3[Si_2W_{23}O_{78}H]\cdot 12H_2O$

a	17.215(3) Å	fw	6265.66
b	13.791(2) Å	space group	$P\bar{1}$ (No. 2)
c	19.753(4) Å	*T*	22 °C
α	94.88(2)°	λ	0.710 73 Å
β	110.60(2)°	ρ_{calcd}	4.77 g cm^{-3}
γ	91.80(2)°	μ(Mo Kα)	342.37 cm^{-1}
V	4364 Å^3	R^a	0.034
Z	2	$R_w{}^b$	0.0386

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

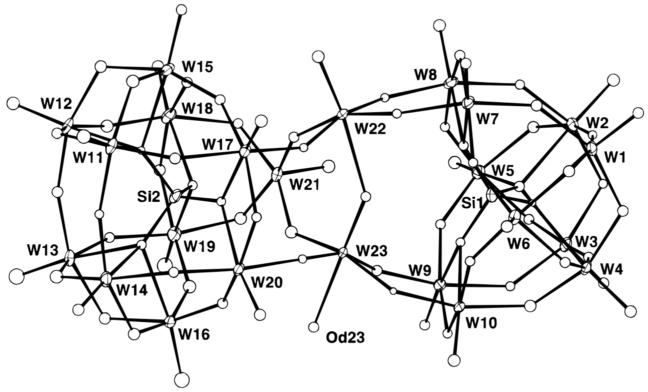

Figure 1. View of the polyoxoanion $[Si_2W_{23}O_{77}(OH)]^{9-}$ (drawing with 50% probability ellipsoids) giving the numbering scheme of silicon and tungsten atoms. Od(23) is probably the oxygen atom of the OH group of the anion.

The anion is shown in Figure 1; the atomic coordinates are given in Table 2, and selected bond lengths and angles, in Table 3. The tungsten atoms are numbered from 1 to 10 and from 11 to 21 for the two moieties around the two silicon atoms Si(1) and Si(2), respectively. The two tungsten atoms W(22) and W(23) link the two subunits. Different types of oxygen atoms are distinguished in the polyanion as usual: Oa oxygens are linked to the silicon atoms, Ob and Oc oxygens link WO_6 octahedra by vertices and edges, respectively, and Od oxygens are terminal (linked to only one tungsten atom). The numbers in parentheses indicate the tungsten atoms to which the oxygens are linked.

Characterization. Silicon 29 and ^{183}W-NMR spectra were recorded on a Bruker AC 300 spectrometer operating at 59.7 and 12.6 MHz, respectively. Concentrated solutions of the heteropolyanion were obtained by dissolution of the rubidium salt in lithium perchlorate and perchloric acid solutions. IR spectra were recorded on a Nicolet 550 spectrometer as KBr pellets. Polarograms and cyclic voltammograms were obtained from mixed 1/1 ethanol/water (containing 0.5 M HCl and 0.5 M NaCl) solutions.

Results and Discussion

Description of the Structure. The polyanion $[Si_2W_{23}O_{77}(OH)]^{9-}$ is formed by two subunits linked by a (μ-oxo)ditungstic group. One of these subunits is the γ-decatungstosilicate anion $[SiW_{10}O_{36}]^{8-}$, and the other one is the γ-undecatungstosilicate anion $[SiW_{11}O_{39}]^{8-}$. The bridging ditungstic group (W(22) and W(23)) is composed of two corner-shared WO_6 octahedra. The bond lengths along Od(22)−W(22)−Ob(22−23)−W(23)−Od(23), involving terminal and μ-oxo oxygen

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Table 2. Fractional Atomic Coordinates for $Rb_6H_3[Si_2W_{23}O_{78}H]\cdot 12H_2O$

atom	*x/a*	*y/b*	*z/c*	*U*(eq),[a] Å^2	occ	atom	*x/a*	*y/b*	*z/c*	*U*(eq),[a] Å^2	occ
W(1)	0.95446(5)	0.24784(7)	−0.04273(5)	0.0211	1.000	W(21)	0.38317(5)	0.14421(6)	−0.30186(5)	0.0199	1.000
W(2)	0.85453(6)	−0.00497(7)	−0.07183(5)	0.0215	1.000	W(22)	0.57085(5)	0.25749(7)	−0.31940(5)	0.0189	1.000
W(3)	0.77957(5)	0.05421(7)	0.06032(5)	0.0198	1.000	W(23)	0.49700(5)	0.32494(6)	−0.15965(4)	0.0160	1.000
W(4)	0.88102(5)	0.30657(7)	0.08993(5)	0.0193	1.000	Si(1)	0.7433(3)	0.2024(4)	−0.0790(3)	0.0167	1.000
W(5)	0.65387(6)	−0.04267(7)	−0.10132(5)	0.0217	1.000	Si(2)	0.2705(3)	0.3547(4)	−0.3871(3)	0.0149	1.000
W(6)	0.84305(5)	0.44072(7)	−0.04786(5)	0.0210	1.000	Rb(1)	0.0427(2)	0.4916(3)	0.2838(2)	0.0684	1.000
W(7)	0.79510(5)	0.28616(7)	−0.21708(5)	0.0212	1.000	Rb(2)	0.3260(2)	0.1586(3)	0.8835(2)	0.0707	1.000
W(8)	0.70706(6)	0.06600(7)	−0.24141(5)	0.0225	1.000	Rb(3)	0.1003(3)	0.8550(3)	0.7250(2)	0.0861	1.000
W(9)	0.58051(5)	0.16407(6)	−0.01858(5)	0.0188	1.000	Rb(4)	0.2750(8)	0.8258(7)	0.4282(5)	0.0791	0.34
W(10)	0.67014(5)	0.38282(6)	0.01085(5)	0.0179	1.000	Rb(5)	0.169(1)	0.8065(7)	0.3963(7)	0.0734	0.26
W(11)	0.25396(6)	0.51781(7)	−0.51820(5)	0.0218	1.000	Rb(6)	0.4372(4)	0.7282(5)	0.5500(4)	0.0788	0.47
W(12)	0.12728(6)	0.31331(7)	−0.56917(5)	0.0228	1.000	Rb(7)	0.1648(7)	0.2743(6)	0.1332(6)	0.0771	0.33
W(13)	0.05498(5)	0.36090(7)	−0.41338(5)	0.0232	1.000	Rb(8)	0.301(1)	0.473(2)	0.290(1)	0.0972	0.19
W(14)	0.17044(6)	0.57122(7)	−0.36901(5)	0.0235	1.000	Rb(9)	0.261(1)	0.749(1)	0.8016(8)	0.0876	0.21
W(15)	0.32845(6)	0.30357(7)	−0.54089(5)	0.0228	1.000	Rb(10)	0.400(1)	0.992(2)	0.8590(9)	0.0819	0.21
W(16)	0.19368(5)	0.41307(7)	−0.24672(5)	0.0208	1.000	Rb(11)	0.362(1)	0.473(2)	0.183(1)	0.0830	0.15
W(17)	0.45469(5)	0.46969(7)	−0.38263(5)	0.0189	1.000	Rb(12)	0.169(2)	0.822(2)	0.529(2)	0.0966	0.15
W(18)	0.23534(6)	0.11393(7)	−0.47142(5)	0.0231	1.000	Rb(13)	0.449(1)	0.367(2)	0.0499(9)	0.0767	0.17
W(19)	0.17769(6)	0.16195(7)	−0.32886(5)	0.0237	1.000	Rb(14)	0.292(2)	0.310(2)	0.094(2)	0.0872	0.15
W(20)	0.38268(5)	0.53059(6)	−0.25240(5)	0.0179	1.000	Rb(15)	0.0181(8)	0.407(1)	0.8400(7)	0.0821	0.38

atom	*x/a*	*y/b*	*z/c*	*U*(iso), Å^2	atom	*x/a*	*y/b*	*z/c*	*U*(iso), Å^2
Oa(1−4−6)	0.8268(8)	0.273(1)	−0.0351(7)	0.020(3)	Oc(11−12)	0.149(1)	0.445(1)	−0.5792(8)	0.030(4)
Oa(2−3−5)	0.7558(8)	0.092(1)	−0.0552(7)	0.018(3)	Oc(11−15)	0.3054(9)	0.435(1)	−0.5688(8)	0.021(3)
Oa(7−8)	0.7295(8)	0.1979(9)	−0.1635(7)	0.015(3)	Oc(12−15)	0.2131(9)	0.278(1)	−0.6057(8)	0.030(4)
Oa(9−10)	0.6701(8)	0.2440(9)	−0.0549(7)	0.014(3)	Oc(13−14)	0.0668(9)	0.501(1)	−0.4133(8)	0.029(4)
Oa(11−12−15)	0.2496(8)	0.3655(9)	−0.4739(7)	0.015(3)	Oc(13−16)	0.0785(9)	0.383(1)	−0.3122(8)	0.025(3)
Oa(13−14−16)	0.1978(8)	0.406(1)	−0.3640(7)	0.018(3)	Oc(14−16)	0.1708(9)	0.543(1)	−0.2751(8)	0.028(4)
Oa(18−19−21)	0.2702(8)	0.239(1)	−0.3739(7)	0.019(3)	Oc(17−20)	0.4572(9)	0.559(1)	−0.3004(7)	0.020(3)
Oa(17−20)	0.3585(8)	0.412(1)	−0.3416(7)	0.016(3)	Oc(18−19)	0.1709(9)	0.081(1)	−0.4139(8)	0.029(4)
Ob(1−2)	0.9195(9)	0.114(1)	−0.0502(8)	0.022(3)	Oc(18−21)	0.3295(9)	0.075(1)	−0.3937(8)	0.023(3)
Ob(1−7)	0.8919(9)	0.247(1)	−0.1470(8)	0.026(3)	Oc(19−21)	0.2816(9)	0.113(1)	−0.2818(8)	0.027(4)
Ob(2−8)	0.8065(8)	0.028(1)	−0.1715(7)	0.019(3)	Od(1)	1.053(1)	0.240(1)	−0.0406(9)	0.033(4)
Ob(3−4)	0.8480(9)	0.174(1)	0.0892(8)	0.025(3)	Od(2)	0.925(1)	−0.085(1)	−0.0795(8)	0.030(4)
Ob(3−9)	0.6836(8)	0.125(1)	0.0517(7)	0.019(3)	Od(3)	0.8028(9)	0.010(1)	0.1432(8)	0.029(4)
Ob(4−10)	0.7705(9)	0.339(1)	0.0784(8)	0.024(3)	Od(4)	0.9333(9)	0.334(1)	0.1796(8)	0.028(4)
Ob(5−8)	0.6464(9)	0.007(1)	−0.1900(8)	0.025(3)	Od(5)	0.5876(9)	−0.146(1)	−0.1301(8)	0.029(4)
Ob(5−9)	0.5866(8)	0.053(1)	−0.0820(7)	0.020(3)	Od(6)	0.864(1)	0.562(1)	−0.0521(9)	0.035(4)
Ob(6−7)	0.7944(9)	0.392(1)	−0.1478(8)	0.024(3)	Od(7)	0.841(1)	0.343(1)	−0.2689(8)	0.032(4)
Ob(6−10)	0.7385(9)	0.441(1)	−0.0368(8)	0.021(3)	Od(8)	0.697(1)	−0.025(1)	−0.3101(9)	0.037(4)
Ob(7−22)	0.6803(8)	0.313(1)	−0.2741(7)	0.020(3)	Od(9)	0.511(1)	0.117(1)	0.0161(8)	0.031(4)
Ob(8−22)	0.6099(9)	0.136(1)	−0.2910(8)	0.022(3)	Od(10)	0.6592(9)	0.482(1)	0.0633(8)	0.028(4)
Ob(9−23)	0.5052(9)	0.217(1)	−0.0969(8)	0.024(3)	Od(11)	0.249(1)	0.619(1)	−0.5631(9)	0.037(4)
Ob(10−23)	0.5766(8)	0.397(1)	−0.0745(7)	0.018(3)	Od(12)	0.044(1)	0.281(1)	−0.646(1)	0.041(4)
Ob(11−14)	0.1982(8)	0.558(1)	−0.4527(7)	0.019(3)	Od(13)	−0.050(1)	0.340(1)	−0.4416(9)	0.040(4)
Ob(11−17)	0.3556(9)	0.536(1)	−0.4440(8)	0.026(3)	Od(14)	0.145(1)	0.688(1)	−0.3678(9)	0.031(4)
Ob(12−13)	0.0732(9)	0.344(1)	−0.5031(8)	0.027(4)	Od(15)	0.380(1)	0.262(1)	−0.5965(9)	0.032(4)
Ob(12−18)	0.1518(9)	0.190(1)	−0.5240(8)	0.025(3)	Od(16)	0.181(1)	0.423(1)	−0.1654(8)	0.032(4)
Ob(13−19)	0.0936(9)	0.234(1)	−0.3934(8)	0.028(4)	Od(17)	0.522(1)	0.536(1)	−0.4085(9)	0.036(4)
Ob(14−20)	0.2931(9)	0.586(1)	−0.3138(8)	0.020(3)	Od(18)	0.217(1)	0.012(1)	−0.5317(9)	0.034(4)
Ob(15−17)	0.4138(9)	0.363(1)	−0.4593(8)	0.023(3)	Od(19)	0.118(1)	0.093(1)	−0.2961(9)	0.038(4)
Ob(15−18)	0.3140(9)	0.190(1)	−0.4985(8)	0.025(3)	Od(20)	0.4157(9)	0.624(1)	−0.1849(8)	0.028(4)
Ob(16−19)	0.206(1)	0.275(1)	−0.2606(8)	0.031(4)	Od(21)	0.443(1)	0.058(1)	−0.2561(9)	0.035(4)
Ob(16−20)	0.3058(9)	0.452(1)	−0.2221(7)	0.019(3)	Od(22)	0.566(1)	0.241(1)	−0.4083(8)	0.031(4)
Ob(17−22)	0.5275(8)	0.388(1)	−0.3258(7)	0.018(3)	Od(23)	0.4078(9)	0.358(1)	−0.1010(8)	0.022(3)
Ob(20−23)	0.4631(8)	0.438(1)	−0.1994(7)	0.017(3)	Ow(1)	0.027(2)	0.231(2)	0.783(2)	0.12(1)
Ob(21−22)	0.4581(9)	0.207(1)	−0.3344(8)	0.025(3)	Ow(2)	0.174(2)	0.169(2)	0.259(2)	0.12(1)
Ob(21−23)	0.402(1)	0.251(1)	−0.2268(8)	0.029(4)	Ow(3)	0.020(2)	0.073(3)	0.835(2)	0.14(1)
Ob(22−23)	0.5622(9)	0.291(1)	−0.2056(7)	0.021(3)	Ow(4)	0.422(2)	0.030(3)	0.468(2)	0.14(1)
Oc(1−4)	0.9712(9)	0.268(1)	0.0590(8)	0.024(3)	Ow(5)	0.434(3)	0.258(3)	0.274(2)	0.15(1)
Oc(1−6)	0.9447(9)	0.387(1)	−0.0474(8)	0.029(4)	Ow(6)	0.494(3)	0.065(3)	0.371(2)	0.16(2)
Oc(2−3)	0.8626(9)	−0.008(1)	0.0280(8)	0.024(3)	Ow(7)	0.219(3)	0.281(3)	0.946(2)	0.17(2)
Oc(2−5)	0.7591(9)	−0.092(1)	−0.0997(8)	0.028(4)	Ow(8)	0.014(3)	0.084(4)	0.204(3)	0.21(2)
Oc(3−5)	0.7004(9)	−0.051(1)	0.0021(8)	0.022(3)	Ow(9)	0.981(3)	0.090(4)	0.456(3)	0.21(2)
Oc(4−6)	0.8896(9)	0.430(1)	0.0547(8)	0.025(3)	Ow(10)	0.622(3)	0.171(4)	0.239(3)	0.22(2)
Oc(7−8)	0.7711(9)	0.160(1)	−0.2711(8)	0.029(4)	Ow(11)	0.755(4)	0.108(5)	0.325(3)	0.26(3)
Oc(9−10)	0.6034(9)	0.290(1)	0.0379(8)	0.023(3)	Ow(12)	0.142(4)	0.415(5)	0.221(3)	0.25(3)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

atoms, are 1.72, 2.31, 1.72, and 2.26 Å, respectively, i.e. alternatively short and long. W(22)−Od(22) has clearly a double-bond character, but Od(23) which is weakly bound to W(23), could belong either to a hydroxyl group or a water molecule. Chemical analysis of rubidium indicates that the structure has four protons which cannot be located by X-ray diffraction; consequently, it is not possible to decide which one of these two hypotheses is correct. However, because of the oxidation state VI of the tungsten atom, an OH group is more probable than a water molecule, and the formula was accord-

Table 3. Selected Bond Lengths (Å) and Angles (deg)

W(20)−Oa(17−20)	2.21(1)	W(20)−Ob(16−20)	1.96(1)
W(20)−Ob(14−20)	1.83(1)	W(20)−Ob(20−23)	1.99(1)
W(20)−Od(20)	1.70(2)	W(20)−Oc(17−20)	1.89(1)
W(21)−Oa(18−19−21)	2.46(1)	W(21)−Ob(21−23)	1.93(2)
W(21)−Ob(21−22)	1.86(1)	W(21)−Oc(19−21)	1.97(1)
W(21)−Oc(18−21)	1.88(1)	W(21)−Od(21)	1.70(2)
W(22)−Ob(21−22)	1.95(1)	W(22)−Ob(17−22)	1.97(1)
W(22)−Ob(8−22)	1.88(1)	W(22)−Ob(7−22)	1.88(1)
W(22)−Od(22)	1.72(2)	W(22)−Ob(22−23)	2.31(1)
W(23)−Ob(21−23)	1.90(2)	W(23)−Ob(20−23)	1.82(1)
W(23)−Ob(9−23)	1.99(1)	W(23)−Ob(10−23)	1.92(1)
W(23)−Od(23)	2.26(1)	W(23)−Ob(22−23)	1.72(1)
Si(1)−Oa(2−3−5)	1.63(1)	Si(1)−Oa(1−4−6)	1.63(1)
Si(1)−Oa(9−10)	1.60(1)	Si(1)−Oa(7−8)	1.60(1)
Si(2)−Oa(18−19−21)	1.63(1)	Si(2)−Oa(13−14−16)	1.64(1)
Si(2)−Oa(17−20)	1.61(1)	Si(2)−Oa(11−12−15)	1.64(1)
W(22)−Ob(22−23)−W(23)	144.6(8)		
Ob(21−22)−W(22)−Od(22)	98.6(7)	Ob(21−23) −W(23)−Od(23)	82.2(6)
Ob(8−22)−W(22)−Od(22)	98.4(7)	Ob(9−23)−W(23)−Od(23)	74.8(5)
Ob(7−22)−W(22)−Od(22)	99.9(7)	Ob(10−23)−W(23)−Od(23)	83.3(5)
Ob(17−22)−W(22)−Od(22)	95.4(6)	Ob(20−23)−W(23)−Od(23)	83.5(6)
Ob(21−22)−W(22)−Ob(22−23)	77.3(5)	Ob(21−23) −W(23)−Ob(22−23)	94.8(7)
Ob(8−22)−W(22)−Ob(22−23)	88.0(5)	Ob(9−23)−W(23)−Ob(22−23)	102.4(6)
Ob(7−22)−W(22)−Ob(22−23)	84.2(5)	Ob(10−23)−W(23)−Ob(22−23)	99.4(6)
Ob(17−22)−W(22)−Ob(22−23)	78.2(5)	Ob(20−23)−W(23)−Ob(22−23)	99.4(6)
Od(22)−W(22)−Ob(22−23)	172.5(6)	Od(23)−W(23)−Ob(22−23)	175.9(6)

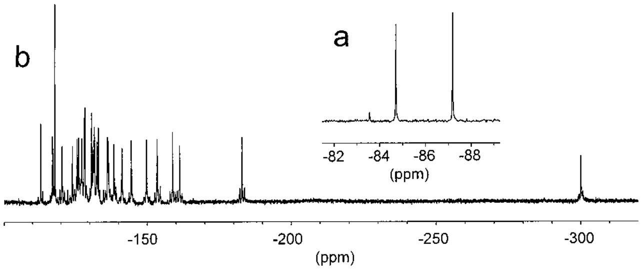

Figure 2. (a) ^{29}Si-NMR spectrum. (b) ^{183}W-NMR spectrum.

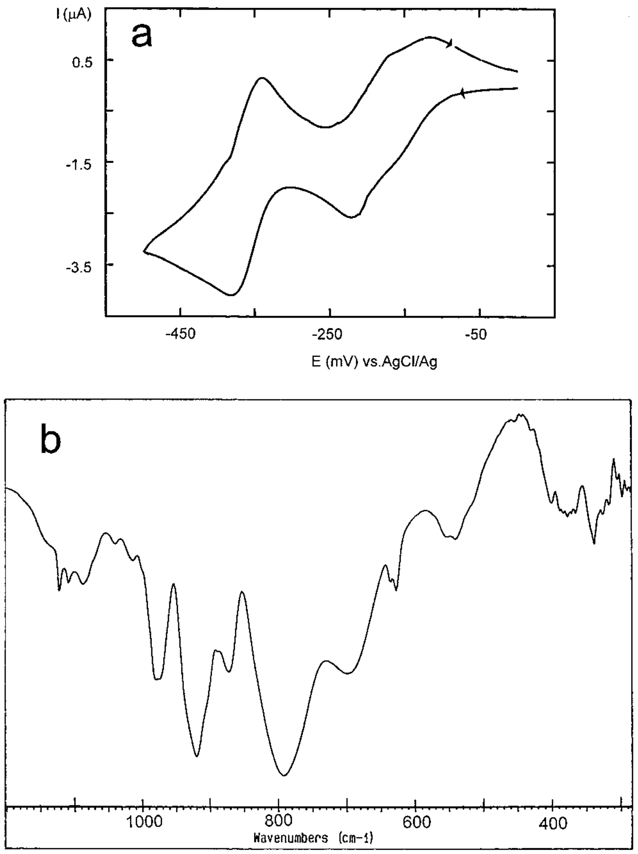

Figure 3. (a) Cyclic voltammogram in acidic water/ethanol solution. (b) IR spectrum.

ingly written. Due to the asymmetry of the bridging group, the whole heteropolyanion has point symmetry C_s.

The decatungstosilicate subunit of the title complex displays structural features similar to those observed for the rubidium salt of γ-[$SiW_{10}O_{36}H$]$^{7-}$.[3] However, in the latter compound, the SiO_4 tetrahedron is significantly distorted: Si−O bonds to triply bridging oxygen atoms are significantly shorter (1.57 Å) than those for quadruply bridging oxygens (1.68 Å). In the title complex, these differences are smaller (Si−O bond lengths 1.60 and 1.63 Å, respectively) presumably due to the influence of the ditungstic bridging group (W(22) and W(23)).

The undecatungstosilicate subunit of the title complex does not display special features. It has not been isolated alone as expected from the Lipscomb rule, since in the free anion, the WO_6 octahedron added to γ-[$SiW_{10}O_{36}H$]$^{7-}$ would have three terminal oxygen atoms.

Isolated deca- and undecatungstosilicate anions would each have a mirror plane, but asymmetry of the junction group leads to significant distortions. For example, octahedra W(17) and W(20) which are corner sharing with junction octahedra W(22) and W(23) have respectively short and long binding with the latter.

Characterization and Stability in Aqueous Solution. The ^{29}Si-NMR spectrum of γ-[$Si_2W_{23}O_{77}(OH)$]$^{8-}$ in solution consists of two signals of equal intensity (Figure 2a), in agreement with the structure in the solid state. The NMR spectrum did not change with time in acid solution (pH $<$ 1) showing that the anion is stable under these conditions. The ^{183}W-NMR spectrum is very complex (Figure 2b), since all 23 tungsten atoms are magnetically inequivalent, leading to 23 signals. Interpretation of this spectrum is virtually impossible because of overlapping resonances and satellites, especially in the downfield region of the spectrum. The title polyanion is not stable in aqueous solutions with pH $>$ 1. It decomposes to β-[$SiW_{12}O_{40}$]$^{4-}$ at pH = 2 (sulfuric buffer), identified by its electrochemical behavior,[2] and to γ-$[SiW_{10}O_{36}H]^{7-}$ at pH > 4. It is feasible, that at 1 < pH < 4, hydrolysis of γ-$[Si_2W_{23}O_{77}(OH)]^{9-}$ leads to free γ-$[SiW_{11}O_{39}H_x)]^{(8-x)-}$ anions, which then slowly isomerize to give the β species.

The polarogram recorded in acidic aqueous solution is poorly defined, but two quasi-reversible waves at −0.30 and −0.48 V/SCE, respectively (Figure 3a), in acidic mixed 1/1 (v/v) water/ethanol solutions are detectable. The IR spectrum is shown in Figure 3b.

Conclusion

Reaction of tungstate with γ-decatungstosilicate in very acidic aqueous solution (pH < 1) does not lead to the γ-isomer of the Keggin structure. A possible reason is that the two μ-oxo bonds between the first two added tungsten atoms are very sensitive to hydrolysis. A complex condensation process then takes place, leading to the new species γ-$[Si_2W_{23}O_{77}(OH)]^{9-}$, which consists of two subunits linked by a ditungstic group in which there is only a single μ-oxo bond between the two tungsten atoms.

Acknowledgment. The authors thank Mr. Francis Robert for help during the X-ray determination.

Supporting Information Available: X-ray crystallographic experimental details (Table S1), anisotropic temperature factors of the tungsten, silicon, and rubidium atoms (Table S2), and interatomic distances (Table S3) and bond angles (Table S4) (9 pages). Ordering information is given on any current masthead page.

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