Polyoxoanions Derived from [γ-$SiO_4W_{10}O_{32}$]$^{8-}$-Containing Oxo-Centered Dinuclear Chromium(III) Carboxylato Complexes: Synthesis and Single-Crystal Structural Determination of [γ-$SiO_4W_{10}O_{32}(OH)Cr_2(OOCCH_3)_2(OH_2)_2$]$^{5-}$

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The previously unknown heteropolyoxometalates [γ-$SiO_4W_{10}O_{32}(OH)Cr_2(OOCR)_2(OH_2)_2$]$^{5-}$ (R = H, CH_3) have been prepared by the reaction of [γ-$SiO_4W_{10}O_{32}$]$^{8-}$ with [$Cr(OH_2)_6$]$^{3+}$ in formate or acetate buffer solution. Isolation of these new Cr^{III}-substituted polyoxometalates was accomplished both as Cs^+ salts and as the Bu_4N^+ salt for the acetate-containing anion. The compounds were characterized by elemental analysis, UV/vis, IR, and ESR spectroscopy, and cyclic voltammetry. The single-crystal X-ray structural analysis of $(Bu_4N)_3H_2$[γ-$SiO_4W_{10}O_{32}(OH)Cr_2(OOCCH_3)_2(OH_2)_2$]$\cdot 3H_2O$ [$P2_12_12_1$; $a = 17.608(12)$, $b = 20.992(13)$, $c = 24.464(11)$ Å; $Z = 4$; $R = 0.057$ for 6549 observed independent reflections] reveals that the two corner-linked CrO_6 octahedra are additionally bridged by two acetate groups, demonstrating the relationship to the well-studied oxo-centered trinuclear carboxylato complexes of Cr^{III}.

Introduction

Polyoxoanions are an important class of compounds that are of both practical and theoretical interest.[1] Current strategies for the synthesis of new substances include the use of lacunary derivatives of Keggin or Wells−Dawson anions as precursors to obtain a variety of metal-substituted heteropolyoxoanions.[2−7]

The successful substitution of low-valent metals $M^{II/III}$ (heteroelements) for tungsten in these well-studied anions depends on the stability of the precursor anion as well as on the reaction affinity of the low-valent heteroelement.[4] Furthermore, it should be considered whether two or more $M^{II/III}$ octahedra should be linked by a common edge or corner. As the literature shows, the corner linking is favored, and in these cases the formation of complete Keggin anions is possible.[3c,d] However, when the $M^{II/III}O_6$ octahedra should be edge-linked, as a result of the structure of the precursor anion, the formation of new types of polyoxoanions has been observed.[5] For the anion [α-$PO_4W_{10}O_{34}$-$Cu_2(OH_2)_2$]$^{7-}$ a mixture of two isomers with corner- or edge-shared $Cu^{II}O_6$ octahedra was found.[6] The first example of a complete Keggin anion containing only edge-linked $M^{II/III}O_6$ octahedra was documented by the recently published structure of [γ-$SiO_4W_{10}O_{32}Mn_2(OH)_2(OH_2)_2$]$^{4-}$.[7]

Herein, we report the synthesis and characterization of [γ-$SiO_4W_{10}O_{32}(OH)Cr_2(OH_2)_2(OOCR)_2$]$^{5-}$ (R = H, CH_3; γ-$SiW_{10}Cr_2Fo_2$, γ-$SiW_{10}Cr_2Ac_2$), which were formed in formate and acetate solution, respectively. The single-crystal X-ray structural analysis of $(Bu_4N)_3H_2$[γ-$SiO_4W_{10}O_{32}(OH)Cr_2(OH_2)_2$-$(OOCCH_3)_2$]$\cdot 3H_2O$ reveals that the two corner-linked CrO_6 octahedra are additionally bridged by two acetate groups. As proven by data obtained, the formate group bridges in the same way, which demonstrates the connection to the well-studied oxo-centered trinuclear carboxylato complexes of Cr^{III}.[8,9]

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Experimental Section

Instrumentation and Analytical Procedures. Potentiometric measurements were carried out with a pH 96 pH meter (WTW, Weilheim, Germany). The electronic spectra were obtained with a UNICAM PU 8735 (Philips, Cambridge, U.K.). IR spectra were recorded on a Perkin-Elmer IR 580 B, with a KBr disk. The ESR measurements were carried out on the ERS 300 X-band CW-spectrometer (Zentrum für wissenschaftlichen Gerätebau, Berlin, Germany). The elemental content was determined with an ICP Spectro Flame (Si, Cr, Cs, W) and the Leco CHNS 932 (Leco Corp., St. Joseph, MI) elemental analyzer (C, H, N). The water content was determined by thermogravimetric analysis with a Netzsch STA 429 simultaneous thermoanalyzer (Selb, Germany). The electrochemical studies were performed with the Autolab electrochemical measuring system (Eco Chemie BV, Utrecht, The Netherlands) in conjunction with the VA 663 electrode stand (Metrohm, Herisau, Switzerland) and a personal computer. The reference electrode was a Ag/AgCl electrode (Metrohm, Herisau, Switzerland) with 3 M KCl ($E = 0.208$ V vs NHE).

Materials. All compounds were of reagent grade and were used as supplied. $Cr(NO_3)_3{\cdot}9H_2O$ was recrystallized before use from 1 M HNO_3 at 40 °C. $K_8[\gamma\text{-}SiO_4W_{10}O_{32}]{\cdot}12H_2O$ was synthesized according to the literature,[10] and its purity was checked by IR spectroscopy and polarography.

Preparation of $Cs_5[\gamma\text{-}SiO_4W_{10}O_{32}(OH)Cr_2(OOCCH_3)_2(OH_2)_2]{\cdot}13H_2O$ (I). A 5 g (1.67 mmol) amount of $K_8[\gamma\text{-}SiO_4W_{10}O_{32}]{\cdot}12H_2O$ was dissolved in 50 mL of heated (80 °C) 1 M KAc/HAc buffer solution (pH 4.80) containing 570 mg (3.38 mmol) of CsCl. Next, 7.5 mL of a 0.5 M Cr^{3+} solution (1.6 g of $Cr(NO_3){\cdot}9H_2O$ in 7.5 mL of H_2O) was poured into the stirred solution. After 8−10 min the color changed from bluish green to green. The rapidly stirred solution was heated for 20 more minutes and then cooled to room temperature. The addition of 4.0 g of CsCl gave a white precipitate (<0.5 g, Cs^+ salt of γ-SiW_{10}). An additional 6.0 g of CsCl led at −16 °C to a bluish precipitate contaminated with some dark green oil, which was recrystallized in 20 mL of warm water (40 °C). The resulting precipitate was separated and suspended in 10 mL of water to dissolve the Cs^+ salt of α-SiW_{11}-Cr (byproduct) and was finally filtered. Recrystallization from 10 mL of water (pH 4.7, 40 °C) gave bluish green small tiles. Yield: 1.0 g (18%). For quantities larger than 5.0 g of the title compound we recommend combining 5−8 starting solutions after the 30 min heating.

Anal. Calcd for $Cs_5[\gamma\text{-}SiO_4W_{10}O_{32}(OH)Cr_2(OOCCH_3)_2(OH_2)_2]{\cdot}13H_2O$: Cs, 18.37; Si, 0.78; W, 50.62; Cr, 2.87; C, 1.32; H, 1.02. Found: Cs, 17.35; Si, 0.77; W, 50.11, Cr, 2.75, C, 1.26; H, 1.16. IR (cm^{-1}, KBr disk, polyoxoanion region): 1621 (m), 1572 (s), 1444 (m), 1423 (m), 1350 (w), 1035 (m), 1000 (m), 953 (s), 921 (sh), 891 (s), 802 (vs), 717 (s), 680 (sh), 625 (w), 582 (w), 544 (w), 517 (sh), 490 (w), 457 (w), 405 (sh), 388 (s), 364 (s), 352 (sh), 320 (w). Electronic absorption spectra in water (pH = 4.4): $\epsilon_{max(613\ nm)} = 61\ L{\cdot}mol^{-1}{\cdot}cm^{-1}$.

Preparation of $(Bu_4N)_3H_2[\gamma\text{-}SiO_4W_{10}O_{32}(OH)Cr_2(OOCCH_3)_2(OH_2)_2]{\cdot}3H_2O$ (II). The synthesis follows the procedure for **I** without any addition of CsCl. A 5 g amount of $K_8[\gamma\text{-}SiO_4W_{10}O_{32}]{\cdot}12H_2O$ was dissolved in 50 mL of heated (80 °C) 1 M KAc/HAc buffer solution before 7.5 mL of a 0.5 M Cr^{3+} solution was added. The rapidly stirred solution was heated for 30 min and then cooled to room temperature before 40 mL of a 0.27 M Bu_4N^+ solution (3.0 g of Bu_4NCl in 40 mL of water) was added dropwise over a period of 30 min. The voluminous greenish yellow precipitate was collected on a glass frit suspended several times in warm water and filtered. It was identified as the Bu_4N^+ salt of α-$SiW_{11}Cr$. Yield: 1.5−2.0 g (∼30%). Next, the pH was changed from 5.0 to 3.0 by the slow addition of 6 M HCl. A bluish white precipitate was separated (<0.5 g, Bu_4N^+ salts of α-SiW_{12-x}, $x = 0-2$; contaminated with Cr^{3+} solution). Further addition of 6 M HCl gave bluish precipitates at pH 2.5, 2.0, and 1.5, which were collected on a glass frit, suspended several times in warm water until the filtrate appeared colorless. The air-dried Bu_4N^+ salt (2.0 g) was dissolved in 15 mL of CH_3CN. Then, water and few drops of Bu_4NOH were added until the solution turned cloudy. The next day, bluish green needles were isolated. Yield: 1.2 g (24%).

The formation of bluish green crystals (<0.5 g) was observed in the starting solution at pH 1.5 a few days after isolating the Bu_4N^+ salt of γ-$SiW_{10}Cr_2Ac_2$. The IR analysis revealed the known spectrum[8d] for the complex salt $[Cr_3O(OOCCH_3)_6(OH_2)_3]Cl{\cdot}nH_2O$.

Anal. Calcd for $(Bu_4N)_3H_2[\gamma\text{-}SiO_4W_{10}O_{32}(OH)Cr_2(OOCCH_3)_2(OH_2)_2]{\cdot}3H_2O$: Si, 0.80; W, 52.51; Cr, 2.97; N, 1.20; C, 17.84; H, 3.66. Found: Si, 0.79; W, 51.99; Cr, 2.57; N, 1.31; C, 18.17; H, 3.95. IR (cm^{-1}, KBr disk, polyoxoanion region): 1625 (w), 1572 (s), 1484 (m), 1468 (m), 1440 (m), 1380 (w), 1079 (w), 1026 (s), 1004 (m), 979 (sh), 960 (s), 910 (vs), 894 (sh), 830 (s), 800 (sh), 776 (s), 733 (s), 710 (sh), 675 (m), 665 (sh), 625 (w), 582 (w), 570 (sh), 545 (m), 518 (sh), 460 (w), 445 (w), 400 (sh), 383 (s), 360 (s), 332 (sh), 310 (w). Cell parameters obtained by powder diffraction analysis:[11] $a = 17.461(8)$ Å, $b = 20.977(6)$ Å, $c = 24.518(10)$ Å; $\alpha, \beta, \gamma = 90.00°$.

Preparation of $Cs_5[\gamma\text{-}SiO_4W_{10}O_{32}(OH)Cr_2(OOCH)_2(OH_2)_2]{\cdot}10H_2O$ (III). The preparation followed the synthesis for the corresponding acetate compound **I**. In 50 mL of a rapidly stirred 1 M HCOOK/HCOOH buffer solution (pH 3.85) were dissolved 5.0 g of $K_8[\gamma\text{-}SiO_4W_{10}O_{32}]{\cdot}12H_2O$ (1.67 mmol) and 570 mg (3.38 mmol) of CsCl at 80 °C before 7.5 mL of a 0.5 M Cr^{3+} solution was added. The stirred solution was heated for 30 min and then cooled to room temperature, and the resulting white precipitate (<0.5 g, Cs^+ salt of α-SiW_{12}) was removed. The addition of 5.0 g of CsCl at room temperature, as well as at 5 and −16 °C, gave deep green precipitates which were separated. The crude products were digested by 3 mL of water, isolated after 10 min, and finally recrystallized from 20 mL of water at 40 °C. At higher temperatures, the decomposition of the title polyoxoanion, unlike the acetate-containing polyoxoanion, was observed. Yield: 1.0 g (20%). Anal. Calcd for $Cs_5[\gamma\text{-}SiO_4W_{10}O_{32}(OH)Cr_2(OOCH)_2(OH_2)_2]{\cdot}10H_2O$: Cs, 21.23; Si, 0.75; W, 48.94; Cr, 2.75; C, 0.61; H, 0.95. Found: Cs, 21.37; Si, 0.76; W, 48.45; Cr, 2.57; C, 0.51; H, 0.76. IR (cm^{-1}, KBr disk, polyoxoanion region): 1620 (sh), 1590 (s), 1500 (w), 1462 (m), 1034 (m), 1000 (m), 948 (s), 917 (sh), 888 (s), 800 (vs), 712 (s), 685 (sh), 630 (sh), 579 (w), 538 (w), 510 (sh), 485 (w), 460 (w), 400 (sh), 380 (s), 363 (s), 347 (sh), 330 (sh). Electronic absorption spectra in water (pH = 3.7): $\epsilon_{max(617\ nm)} = 57\ L{\cdot}mol^{-1}{\cdot}cm^{-1}$. Cell parameters obtained by powder diffraction analysis:[11] $a = 18.034(7)$ Å, $b = 20.920(6)$ Å, $c = 24.431(12)$ Å; $\alpha, \beta, \gamma = 90.00°$.

Preparation of $[Cr_3O(OOCCH_3)_6(OH_2)_3]Cl{\cdot}nH_2O$ (IV). The compound was prepared as described elsewhere and characterized by IR spectroscopy.[8d]

X-ray Structural Analysis of II. The crystal, which was stable on air, had approximate dimensions of 0.40 × 0.15 × 0.15 mm and was picked after the first recrystallization of the crude product in the acetonitrile/water mixture. The bluish green needle was mounted on a STOE-4 diffractometer equipped with a graphite monochromator (Mo Kα radiation). The orientation matrix and cell constants were obtained from the setting of 43 reflections. During data collection by ω-scan, three standard reflections were measured every 90 min. Negative intensities were set positive with a value of $0.25\sigma_I$. Any slight decay of intensity was corrected using the intensity of the standard reflections. A summary of crystal data is given in Table 1. The structure was solved

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Table 1. Crystallographic Data for $(\text{Bu}_4\text{N})_3\text{H}_2[\gamma\text{-SiO}_4\text{W}_{10}\text{O}_{32}(\text{OH})\text{Cr}_2(\text{OH}_2)_2(\text{OOCCH}_3)_2]\cdot 3\text{H}_2\text{O}$

M_r	3501.1	no. of params	510
cryst system	orthorhombic	θ	2−25°
space group	$P2_12_12_1$	h	$-24 \rightarrow 0$
a	17.608(12) Å	k	$0 \rightarrow 25$
b	20.992(13) Å	l	$0 \rightarrow 29$
c	24.464(11) Å	measd reflcns	8602
V	9043(15) Å^3	independ reflcns	8587
d_{calc}	1.549 g·cm^{-3}	obsd reflcns [$I > 2\sigma(I)$]	6549
R_w	0.057	μ	82.7 cm^{-1}
T	19 °C	$\Delta\rho_{\max}$	3.5 e Å^3
λ(Mo Kα)	0.710 69 Å	$\Delta\rho_{\min}$	−4.1 e Å^3

by direct methods through the use of SHELXS-86.[12] All calculations (refinement on F) were performed on a VAX computer on the basis of XTAL 3.0.[13] An empirical absorption correction DIFABS[14] based on the isotropically-refined structure was applied. The atomic scattering factors were taken from ref 15.

Results and Discussion

Synthesis. The reaction of $[\gamma\text{-SiO}_4\text{W}_{10}\text{O}_{32}]^{8-}$ (γ-SiW$_{10}$) with $[\text{Cr(OH}_2)_6]^{3+}$, in formate or acetate buffer solution, provided the new Cr$^{\text{III}}$-substituted polyoxometalate $[\gamma\text{-SiO}_4\text{W}_{10}\text{O}_{32}(\text{OH})\text{Cr}_2(\text{OOCR})_2(\text{OH}_2)_2]^{5-}$ which can be isolated as its water-soluble Cs$^+$ salt (R = H, CH$_3$) or the organic solvent-soluble Bu$_4$N$^+$ salt (R = CH$_3$).

On the basis of the limited stability of the precursor polyoxoanion γ-SiW$_{10}$ at pH < 9 and the starting "Cr(OH)$_3$" formation at pH > 4, the synthesis required further additives to "open a reaction window".[16] The use of a 1 M potassium formate or potassium acetate buffer solution and additional amounts of CsCl (to realize the reported[17] γ-SiW$_{10}$ stabilization by Cs$^+$) in a 3:1:2 molar ratio for Cr^{3+}:γ-SiW$_{10}$:Cs$^+$ gave yields between 18 and 28% of the title anions. However, the main product was the mono-Cr$^{\text{III}}$-substituted Keggin anion $[\alpha\text{-SiO}_4\text{W}_{11}\text{O}_{35}\text{Cr(OH}_2)]^{5-}$ (α-SiW$_{11}$Cr) in a 30−35% yield.[18]

In an alternative procedure, the corresponding *sodium* acetate buffer solution was used instead of the *potassium* acetate buffer solution to investigate the influence of the alkali metal ions on the synthesis. The experiments gave only oily precipitates containing α-SiW$_{11}$Cr as the only identifiable polyoxoanion, which indicated that the decomposition of γ-SiW$_{10}$ had occurred more rapidly in this case. These results confirm impressively that γ-SiW$_{10}$ can be stabilized in aqueous solution by K$^+$ and Cs$^+$, as was reported earlier.[17]

As known, Cr$^{\text{III}}$ is complexed by acetate or similar carboxylato acids and forms the well-studied oxo-centered trinuclear carboxylato complex cations, like $[\text{Cr}_3\text{O(OOCCH}_3)_6(\text{OH}_2)_3]^+$.[8] The formation of the complete complex cation is slow enough that fragments of it can react with γ-SiW$_{10}$ to form γ-SiW$_{10}$Cr$_2$Ac$_2$.

The optimization experiments show that the use of a 50% Cr^{3+} excess gave the best results. Further studies using $[\text{Cr}_3\text{O(OOCCH}_3)_6(\text{OH}_2)_3]^+$ (Cr$_3$Ac$_3$) as the Cr$^{\text{III}}$ source did not lead to any Cr$^{\text{III}}$-substituted polyoxoanions, which documents the stability of the oxo-centered trinuclear carboxylato complex at pH 4.80.

Characterization in Solution. Electrochemistry. The polyoxoanions γ-SiW$_{10}$Cr$_2$Ac$_2$ and γ-SiW$_{10}$Cr$_2$Fo$_2$ show entirely identical behavior in 1 M NaAc/HAc buffer solution in the potential range from −0.5 to −1.0 V Ag/AgCl with two reversible anodic and cathodic waves. Furthermore, the recorded cyclic voltammograms for these anions are identical with the one obtained for γ-SiW$_{10}$, which was reported earlier.[17] We observed only a slight shift in the peak potentials for the Cr$^{\text{III}}$-substituted anions relative to the precursor anion (DPP: −0.666, −0.783 V for γ-SiW$_{10}$Cr$_2$Ac$_2$ and −0.687, −0.796 V for γ-SiW$_{10}$). Both redox processes were characterized by coulometric measurements as two-electron processes. The results confirm that the redox properties of polyoxotungstate in the investigated potential range has not been affected substantially by the Cr$^{\text{III}}$ substitution.

Reaction Behavior. In further experiments we used dicarboxylic acids (citric, oxalic, terephthalic acid) instead of acetic and formic acid in the synthesis. The purpose of these studies was the possible linking of Cr$^{\text{III}}$-substituted γ-Keggin anions on the basis of the acid's bifunctionality. However, citric as well as oxalic acid formed complexes with Cr$^{\text{III}}$ which were too stable for further reactions with the lacunary polyoxoanion γ-SiW$_{10}$. In the case of terephthalic acid the formation of α-SiW$_{11}$Cr was observed.

In additional studies, the possible substitution of oxalate ligands in γ-SiW$_{10}$Cr$_2$Ac$_2$ for acetate ligands was investigated. Therefore, solid potassium oxalate or oxalic acid was added in a 1:1 molar ratio relative to Cr$^{\text{III}}$ to a 0.02 M solution of **I**. The experiments were followed by UV/vis spectroscopy.[19] No reaction was observed for either one of the oxalate compounds at room temperature. By the heating of the system to 80 °C for 5 min after each addition, no changes in the UV/vis region were observed for potassium oxalate; however, a change was observed for oxalic acid. After the addition of 4−5 equiv of H$_2$C$_2$O$_4$, the characteristic absorption at 258 nm for α-Keggin anions had increased. The complete decomposition of γ-SiW$_{10}$Cr$_2$Ac$_2$ was observed after adding 6 equiv of H$_2$C$_2$O$_4$ (formation of α-SiW$_{11}$Cr and a white precipitate at pH 2.0 Cs$^+$ salt of α-SiW$_{12}$). So far there is no indication of a successful ligand exchange raction.

Characterization in Solid State. X-ray Single-Crystal Structural Analysis of the Bu$_4$N$^+$ Salt. The ball-and-stick and the polyhedral representations of $[\gamma\text{-SiO}_4\text{W}_{10}\text{O}_{32}(\text{OH})\text{Cr}_2(\text{OH}_2)_2(\text{OOCCH}_3)_2]^{5-}$ are shown in Figure 1. The new anion is formed by the γ-SiW$_{10}$ unit and two corner-linked Cr−O octahedra which are additionally bridged via two acetate groups. Atomic coordinates and selected bond lengths are given in Tables 2 and 3. As the comparison of the structural details of γ-SiW$_{10}$Cr$_2$Ac$_2$ and the "pure" γ-SiW$_{10}$ anion[17,20] shows, the W−O and

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(16) The reaction of γ-SiW$_{10}$ and Cr$^{\text{III}}$ in aqueous solution without any further additives gave α-SiW$_{11}$Cr as the only identifiable Cr$^{\text{III}}$-substituted polyoxoanion (final pH 1.5). The compensation of the pH decrease during the Cr^{3+} addition using 2 M KOH led beside the formation of α-SiW$_{11}$Cr to a voluminous precipitate of chromium−tungsten−oxide−hydrate (pH about 4.5).

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(18) The addition of 2 mol of CsCl per polyoxoanion γ-SiW$_{10}$ increased the yield of the new heteropolyanions by 20%. The addition of more CsCl causes the precipitation of the Cs$^+$ salt of γ-SiW$_{10}$. To avoid oils in the gradual precipitation of the Bu$_4$N$^+$ salt of γ-SiW$_{10}$Cr$_2$Ac$_2$ no CsCl was added in this case. For the gradual precipitation of the Bu$_4$N$^+$ salt of γ-SiW$_{10}$Cr$_2$Fo$_2$ the pH was changed from 3.80 to 4.50 using 3 M KOH. However, the anion γ-SiW$_{10}$Cr$_2$Fo$_2$ is no longer stable at the higher pH; among the isolated products only α-SiW$_{11}$Cr could be identified as a Cr$^{\text{III}}$-substituted polyoxoanion.

(19) The UV spectrum for γ-SiW$_{10}$Cr$_2$Ac$_2$ does not show a characteristic absorption in the region of 258 nm as usually observed for α-Keggin anions, as a consequence of the reduced symmetry of the Cr$^{\text{III}}$-substituted polyoxoanion ($T_d \rightarrow C_{2v}$).

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Table 2. Atomic Coordinates and Isotropic (O, N) or Equivalent Isotropic (W, Cr, Si) Thermal Parameters (Å^2)

atom	*x*/*a*	*y*/*b*	*z*/*c*	$U^{a,b}$	atom	*x*/*a*	*y*/*b*	*z*/*c*	$U^{a,b}$
W(1)	−0.0904(1)	0.43187(8)	0.53063(7)	*0.0315	O(1W)	0.206(2)	0.791(2)	0.560(1)	0.050(8)
W(2)	−0.0990(1)	0.41619(8)	0.37820(7)	*0.0325	O(2W)	0.340(2)	0.684(1)	0.431(1)	0.048(8)
W(3)	0.0938(1)	0.40424(8)	0.37591(7)	*0.0323	O(3W)	0.166(6)	0.206(5)	0.462(4)	0.26(5)
W(4)	0.1034(1)	0.42467(8)	0.52791(7)	*0.0317	C(1)	0.107(3)	0.804(2)	0.344(2)	0.04(1)
W(5)	0.01507(9)	0.54422(7)	0.58817(5)	*0.0212	C(2)	0.024(3)	0.851(2)	0.295(2)	0.05(1)
W(6)	−0.14361(9)	0.60947(7)	0.50635(7)	*0.0240	C(3)	0.034(2)	0.817(2)	0.494(2)	0.04(1)
W(7)	−0.14940(9)	0.59349(7)	0.37334(7)	*0.0248	C(4)	0.038(3)	0.870(2)	0.539(2)	0.05(1)
W(8)	0.0042(1)	0.51018(7)	0.29842(5)	*0.0260	N(1)	0.211(2)	0.632(2)	0.727(2)	0.05(1)
W(9)	0.17688(8)	0.59412(7)	0.50129(6)	*0.0225	C(11)	0.199(2)	0.606(2)	0.786(2)	0.035(9)
W(10)	0.17266(9)	0.57421(9)	0.36890(7)	*0.0324	C(111)	0.134(4)	0.549(3)	0.794(3)	0.07(2)
Cr(11)	0.1198(3)	0.7289(3)	0.4214(3)	*0.025	C(112)	0.125(4)	0.537(4)	0.848(3)	0.09(2)
Cr(12)	−0.0775(3)	0.7396(3)	0.4264(3)	*0.026	C(113)	0.081(4)	0.476(3)	0.860(3)	0.09(2)
Si	0.0114(7)	0.5339(5)	0.4429(4)	*0.025	C(12)	0.223(3)	0.571(2)	0.688(2)	0.05(1)
O(910)*	0.088(2)	0.573(1)	0.437(1)	0.033(6)	C(121)	0.282(3)	0.529(3)	0.701(2)	0.06(2)
O(145)	0.009(1)	0.494(1)	0.5025(9)	0.025(5)	C(122)	0.277(4)	0.472(3)	0.665(2)	0.07(2)
O(238)	0.003(1)	0.480(1)	0.3937(8)	0.022(5)	C(123)	0.216(3)	0.424(3)	0.684(2)	0.07(2)
O(67)*	−0.063(1)	0.580(1)	0.441(1)	0.024(6)	C(13)	0.139(2)	0.668(2)	0.713(2)	0.035(9)
O(1)	−0.157(2)	0.380(1)	0.559(1)	0.038(7)	C(131)	0.146(3)	0.701(2)	0.656(2)	0.05(1)
O(14)	0.003(1)	0.3856(9)	0.5399(8)	0.015(4)	C(132)	0.051(4)	0.728(3)	0.639(3)	0.08(2)
O(15)	−0.066(1)	0.484(1)	0.593(1)	0.021(5)	C(133)	0.051(4)	0.785(4)	0.669(3)	0.10(2)
O(16)	−0.155(2)	0.507(1)	0.511(1)	0.043(8)	C(14)	0.283(2)	0.671(2)	0.727(2)	0.04(1)
O(2)	−0.170(2)	0.362(1)	0.363(1)	0.040(7)	C(141)	0.268(3)	0.738(2)	0.760(2)	0.05(1)
O(21)	−0.101(1)	0.407(1)	0.457(1)	0.031(6)	C(142)	0.346(3)	0.772(2)	0.759(2)	0.05(1)
O(23)	−0.004(2)	0.365(1)	0.3758(9)	0.031(6)	C(143)	0.345(4)	0.836(3)	0.788(3)	0.08(2)
O(27)	−0.154(2)	0.495(1)	0.387(1)	0.033(6)	N(2)	−0.192(2)	0.541(2)	0.733(2)	0.05(1)
O(28)	−0.075(2)	0.444(1)	0.307(1)	0.037(7)	C(21)	−0.270(2)	0.527(2)	0.713(2)	0.04(1)
O(3)	0.153(2)	0.343(1)	0.357(1)	0.037(7)	C(211)	−0.270(3)	0.511(3)	0.649(2)	0.07(2)
O(34)	0.100(1)	0.401(1)	0.452(1)	0.030(6)	C(212)	−0.354(4)	0.502(3)	0.632(2)	0.07(2)
O(38)	0.068(2)	0.441(1)	0.306(1)	0.042(7)	C(213)	−0.347(4)	0.486(4)	0.572(3)	0.10(2)
O(310)	0.165(1)	0.477(1)	0.383(1)	0.028(6)	C(22)	−0.169(3)	0.611(3)	0.711(2)	0.06(1)
O(4)	0.166(2)	0.369(1)	0.553(1)	0.037(7)	C(221)	−0.211(4)	0.664(3)	0.722(3)	0.07(2)
O(45)	0.082(1)	0.476(1)	0.593(1)	0.027(6)	C(222)	−0.158(4)	0.717(4)	0.713(3)	0.09(2)
O(49)	0.168(2)	0.494(1)	0.507(1)	0.035(7)	C(223)	−0.207(7)	0.773(6)	0.724(5)	0.16(4)
O(5)	0.016(2)	0.568(1)	0.653(1)	0.048(7)	C(23)	−0.131(3)	0.497(3)	0.717(2)	0.06(1)
O(56)	−0.060(1)	0.595(1)	0.556(1)	0.026(6)	C(231)	−0.143(3)	0.429(3)	0.738(2)	0.06(1)
O(59)	0.093(1)	0.590(1)	0.5544(9)	0.020(5)	C(232)	−0.093(4)	0.377(3)	0.705(3)	0.08(2)
O(6)	−0.221(2)	0.621(1)	0.555(1)	0.044(8)	C(233)	0.001(4)	0.401(3)	0.713(2)	0.07(1)
O(612)	−0.120(1)	0.690(1)	0.4897(9)	0.019(5)	C(24)	−0.204(2)	0.551(2)	0.796(2)	0.04(1)
O(67)	−0.207(1)	0.594(1)	0.444(1)	0.031(6)	C(241)	−0.126(3)	0.574(3)	0.824(2)	0.06(1)
O(7)	−0.230(2)	0.593(1)	0.331(1)	0.042(7)	C(242)	−0.151(8)	0.528(6)	0.894(5)	0.20(6)
O(78)	−0.072(2)	0.568(1)	0.323(1)	0.031(6)	C(243)	−0.081(6)	0.567(5)	0.921(4)	0.15(4)
O(712)	−0.124(1)	0.677(1)	0.376(1)	0.026(6)	N(3)	0.378(3)	0.293(2)	0.528(2)	0.06(1)
O(8)	0.006(2)	0.518(1)	0.229(1)	0.041(7)	C(31)	0.430(4)	0.268(3)	0.489(3)	0.08(2)
O(810)	0.085(1)	0.563(1)	0.323(1)	0.027(6)	C(311)	0.439(7)	0.295(6)	0.433(5)	0.18(5)
O(9)	0.255(1)	0.603(1)	0.545(1)	0.033(6)	C(312)	0.497(4)	0.261(3)	0.395(2)	0.08(2)
O(910)	0.234(1)	0.577(1)	0.435(1)	0.023(5)	C(313)	0.483(6)	0.287(4)	0.340(3)	0.13(3)
O(911)	0.161(1)	0.678(1)	0.483(1)	0.026(6)	C(32)	0.420(3)	0.286(3)	0.580(2)	0.07(2)
O(10)	0.245(2)	0.571(2)	0.323(1)	0.045(8)	C(321)	0.382(3)	0.296(2)	0.635(2)	0.05(1)
O(11)	0.087(2)	0.786(2)	0.360(1)	0.06(1)	C(322)	0.442(7)	0.298(6)	0.683(5)	0.17(5)
O(011)	0.220(2)	0.766(1)	0.414(1)	0.034(7)	C(323)	0.391(5)	0.311(4)	0.732(4)	0.12(3)
O(0011)	0.090(2)	0.796(1)	0.474(1)	0.037(7)	C(33)	0.344(3)	0.359(3)	0.519(2)	0.07(2)
O(1011)	0.155(1)	0.662(1)	0.374(1)	0.022(5)	C(331)	0.414(3)	0.415(3)	0.536(2)	0.07(2)
O(1112)	0.018(2)	0.695(1)	0.428(1)	0.033(6)	C(332)	0.379(4)	0.476(3)	0.522(2)	0.07(2)
O(12)	−0.043(1)	0.793(1)	0.364(1)	0.030(6)	C(333)	0.433(6)	0.518(5)	0.551(4)	0.15(4)
O(012)	−0.179(2)	0.788(1)	0.422(1)	0.036(7)	C(34)	0.269(5)	0.245(5)	0.509(4)	0.12(3)
O(0012)	−0.037(2)	0.806(1)	0.479(1)	0.036(7)					

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}\cdot a_i^*\cdot a_j^*\cdot \mathbf{a}_i\mathbf{a}_j$. [b] Asterisk indicates equivalent isotropic parameter.

Si−O bond lengths and angles are not substantially affected by the Cr^{III} substitution. The observed Cr−O bond lengths in γ-$SiW_{10}Cr_2Ac_2$ are typical for Cr^{III} in an octahedral oxygen coordination and display Cr^{III} in an almost ideal octahedral environment.[3f,i,23] Figure 2 shows the Cr^{III} acetate fragment of γ-$SiW_{10}Cr_2Ac_2$ in detail, with selected bond distances and bond angles as well as the structure of the oxo-centered trinuclear carboxylato complex of Cr^{III}, $[Cr_3O(OOCCH_3)_6(OH_2)_3]^+$($Cr_3$-$Ac_6$).[8b,c]

The bond valence sum (BVS) calculation[24] strongly indicates the location of five protons for the Cr^{III} acetate fragment. The bridging oxygen atom O(1112) between the CrO_6 octahedra has a BVS value of 1.15 and is therefore presumed to be a hydroxo group. The terminal oxygen atoms O(011) and O(012) have much lower BVS values, 0.64 and 0.50, indicating two water ligands. The C−O bonds (Figure 2a) are alternatively short and long, what might be the result of an interaction of the carboxylate oxygen atoms O(11) and O(0012) with the protons of the two water ligands.[8c,25,26] On the basis of the charge balance, two more protons must be present, probably associated with the oxygen atoms of the polyoxoanion. The location of

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(25) On the basis of the alternated C−O bond length in $[Cr_3O(OOCCH_3)_6(OH_2)_3]Cl\cdot 6H_2O$ (Figure 2b) (1.22 Å − 1.31 Å), the authors[8c] formulate $[Cr_3O(HOOCCH_3)_3(OOCCH_3)_3(OH)_3]^+$ and corresponding intermediate states.

Table 3. Selected Bond Lengths (Å) for $(\text{Bu}_4\text{N})_3\text{H}_2[\gamma\text{-SiO}_4\text{W}_{10}\text{O}_{32}(\text{OH})\text{Cr}_2(\text{OOCCH}_3)_2(\text{OH}_2)_2]\cdot\text{H}_2\text{O}$

W(1)−O(125)	2.29(2)	W(1)−O(1)	1.74(3)	W(1)−O(14)	1.93(2)
W(1)−O(15)	1.92(2)	W(1)−O(16)	2.00(3)	W(1)−O(21)	1.89(3)
W(2)−O(238)	2.28(2)	W(2)−O(2)	1.73(3)	W(2)−O(21)	1.93(3)
W(2)−O(23)	1.99(3)	W(2)−O(27)	1.92(3)	W(2)−O(28)	1.88(3)
W(3)−O(238)	2.31(2)	W(3)−O(23)	1.91(3)	W(3)−O(3)	1.72(3)
W(3)−O(34)	1.87(3)	W(3)−O(38)	1.94(3)	W(3)−O(310)	1.98(2)
W(4)−O(145)	2.30(2)	W(4)−O(14)	1.97(2)	W(4)−O(34)	1.92(3)
W(4)−O(4)	1.72(3)	W(4)−O(45)	1.95(3)	W(4)−O(49)	1.92(3)
W(5)−O(145)	2.35(2)	W(5)−O(15)	1.92(2)	W(5)−O(45)	1.87(2)
W(5)−O(5)	1.67(3)	W(5)−O(56)	1.88(2)	W(5)−O(59)	1.87(2)
W(6)−O(67)*	2.22(2)	W(6)−O(16)	2.17(3)	W(6)−O(56)	1.93(2)
W(6)−O(6)	1.82(3)	W(6)−O(612)	1.78(2)	W(6)−O(67)	1.91(3)
W(7)−O(67)*	2.27(2)	W(7)−O(27)	2.10(3)	W(7)−O(67)	2.00(3)
W(7)−O(7)	1.76(3)	W(7)−O(78)	1.90(3)	W(7)−O(712)	1.80(2)
W(8)−O(238)	2.41(2)	W(8)−O(28)	1.97(3)	W(8)−O(38)	1.85(3)
W(8)−O(78)	1.91(3)	W(8)−O(8)	1.71(2)	W(8)−O(810)	1.90(3)
W(9)−O(910)*	2.25(3)	W(9)−O(49)	2.11(3)	W(9)−O(59)	1.97(2)
W(9)−O(9)	1.75(3)	W(9)−O(910)	1.95(2)	W(9)−O(911)	1.84(2)
W(10)−O(910)*	2.24(3)	W(10)−O(310)	2.08(2)	W(10)−O(810)	1.93(3)
W(10)−O(910)	1.93(2)	W(10)−O(10)	1.70(3)	W(10)−O(1011)	1.88(2)
Cr(11)−O(911)	1.98(2)	Cr(11)−O(11)	2.02(4)	Cr(11)−O(011)	1.94(3)
Cr(11)−O(0011)	1.98(3)	Cr(11)−O(1011)	1.92(2)	Cr(11)−O(1112)	1.94(3)
Cr(12)−O(612)	2.01(2)	Cr(12)−O(712)	1.99(3)	Cr(12)−O(1112)	1.92(3)
Cr(12)−O(12)	1.98(3)	Cr(12)−O(012)	2.06(3)	Cr(12)−O(0012)	2.02(3)
Si−O(910)*	1.59(3)	Si−O(145)	1.68(2)	Si−O(238)	1.65(2)
Si−O(67)*	1.63(3)	C(1)−O(11)	1.34(6)	C(3)−O(0011)	1.17(5)
C(1)−O(12)	1.18(5)	C(3)−O(0012)	1.33(5)	C(1)−C(2)	1.56(6)
C(3)−C(4)	1.57(6)				

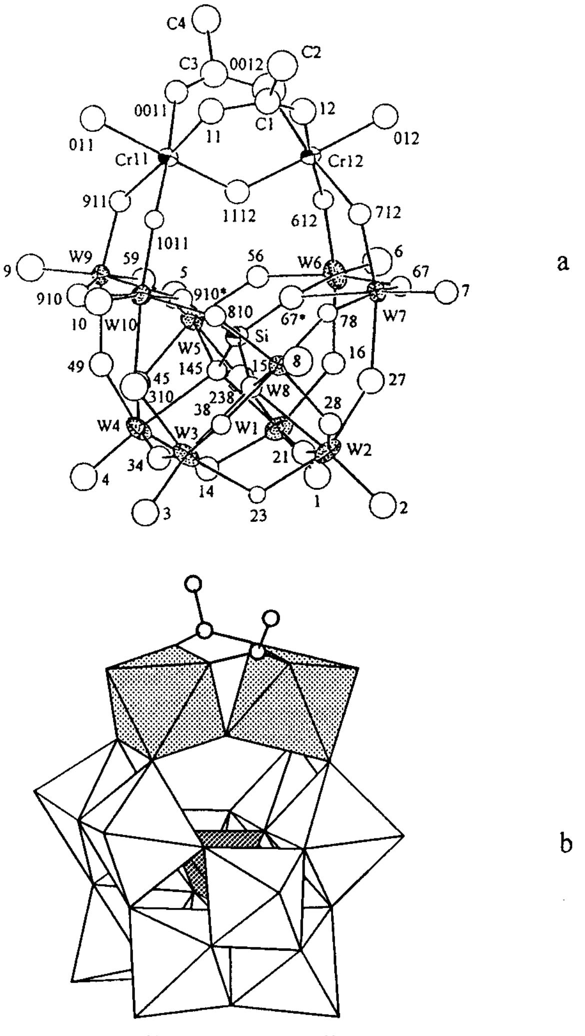

Figure 1. ORTEP[21] (a) and ATOMS[22] (b) plots of $[\gamma\text{-SiO}_4\text{W}_{10}\text{O}_{32}(\text{OH})\text{Cr}_2(\text{OOCCH}_3)_2(\text{OH}_2)_2]^{5-}$.

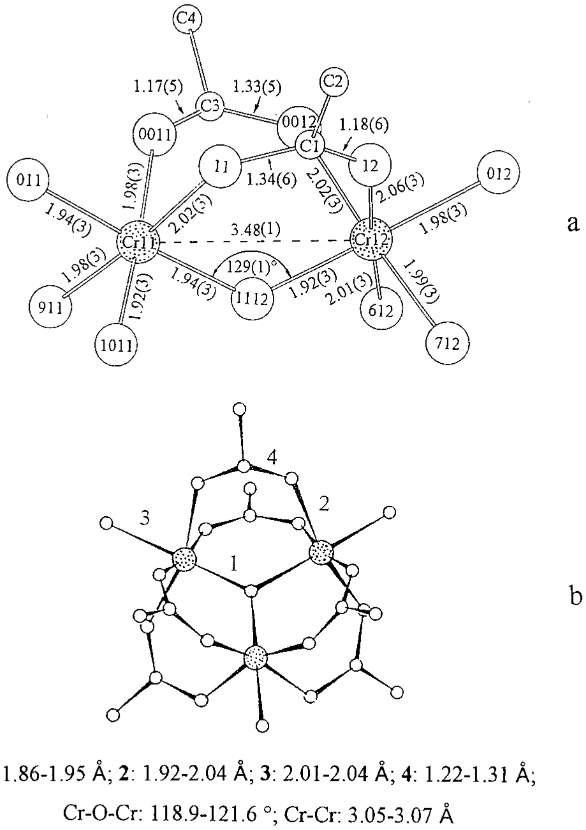

Figure 2. Cr^{III} acetate unit with selected bond distances and bond angles in $[\gamma\text{-SiO}_4\text{W}_{10}\text{O}_{32}(\text{OH})\text{Cr}_2(\text{OOCCH}_3)_2(\text{OH}_2)_2]^{5-}$ (ATOMS[21] drawing) (a) and in $[\text{Cr}_3\text{O}(\text{OOCCH}_3)_6(\text{OH}_2)_3]^+$ (modified drawing[8b]) with crystallographic data[8c] (b).

the two protons is less certain. The BVS calculation for the other oxygen atoms reveals values similar to the lacunary anion γ-SiW$_{10}$ in the octarubidium[17] and octacesium[20] salts. This demonstrates the inadequacy of BVS calculations for the

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(26) The structural analysis of carboxo acids gave the following bond distances and bond angles, respectively (data for formic acid): C=O, 1.20−1.28 Å (1.23 Å); C−OH, 1.25−1.31 Å (1.26 Å); O−C−OH, 122−126° (123.1°). Holtzberg, F.; Post, B.; Fankuchen, I. *Acta Crystallogr.* **1953**, *6*, 127−130.

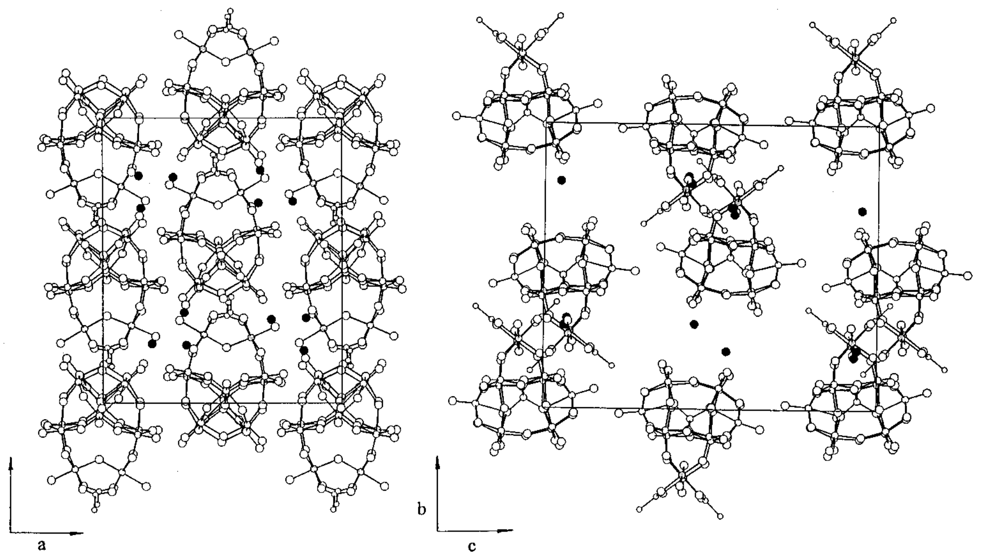

Figure 3. Packing diagrams for $(Bu_4N)_3H_2[\gamma\text{-}SiO_4W_{10}O_{32}(OH)Cr_2(OH_2)_3(OOCCH_3)_2]\cdot 3H_2O$ in the unit cell viewed down the *c* and the *a* axes. The Bu_4N^+ cations are omitted for better clarity; ● indicates water molecules.

detection of protons disordered over several sites of the polyoxoanion.

The packing diagrams for γ-SiW$_{10}$Cr$_2$Ac$_2$ in the unit cells viewed down the *c* and the *a* axes are given in Figure 3; the Bu_4N^+ cations are omitted in this figure for better clarity.[27] The view down the *c* axis shows two differently oriented "anion chains", and the view down the *a* axis reveals the "zigzag" pattern of these chains. The Cr^{III}-substituted sites of γ-SiW$_{10}$Cr$_2$Ac$_2$ are oriented toward each other, indicating the tendency of Cr^{III} for effective interanionic Cr^{III}$-$Cr^{III} interaction despite the influence of hydrogen bridging bonds. The three shortest interanionic Cr^{III}$-$Cr^{III} distances were determined as 6.54(1), 9.65(1), and 12.85(1) Å. The location of the three water molecules is given in Figure 3 by three dark circles (O1W$-$O3W). For the molecules OW1 and OW2, short distances of 2.66 and 2.75 Å were found in relation to the terminal water ligands O012 and O011 of the CrO$_6$ octahedra, indicating the presence of bridging hydrogen bonds.

IR Spectroscopy. The IR spectra for the Cs$^+$ salt of γ-SiW$_{10}$Cr$_2$Ac$_2$ (**I**) and γ-SiW$_{10}$Cr$_2$Fo$_2$ (**III**), respectively, as well as the spectra for the precursor material $K_8[\gamma\text{-}SiO_4W_{10}O_{32}]\cdot 12H_2O$ and the oxo-centered trinuclear carboxylato complex $[Cr_3O(OOCCH_3)_6(OH_2)_3]Cl\cdot nH_2O$ are shown in Figure 4. Formally, the spectrum for **I** could be considered as a combination of the spectra given in Figure 4a,b. The persistence of the γ-structure in γ-SiW$_{10}$Cr$_2$Ac$_2$ and in γ-SiW$_{10}$Cr$_2$Fo$_2$ is indicated through the pattern in the region 300$-$400 cm^{-1}, even with the overlap of the deformation band $\delta_{sym}(Cr_2O)$. The shift for the band $\nu_{as}(W-O_c-W)$ in γ-SiW$_{10}$Cr$_2$Ac$_2$ to higher wavenumbers (740 → 800 cm^{-1}) compared to γ-SiW$_{10}$ is caused by the more compact structure of the Cr^{III}-substituted polyoxoanions.

ESR Spectroscopy. The study of the magnetic behavior of Cr^{III}-substituted polyoxoanions has been of special interest to us.[4] As shown by the former ESR-spectroscopic investigations of mono-, di-, and triply Cr^{III}-substituted α-Keggin anions and dimeric α-Keggin species containing four or six Cr^{3+} ions, respectively, the effectiveness of the exchange interaction between the paramagnetic Cr^{III} centers crucially depends on the type of linkage between the CrO$_6$ octahedra.[3i]

The ESR spectra obtained for a powdered crystalline sample of $(Bu_4N)_3H_2[\gamma\text{-}SiO_4W_{10}O_{32}(OH)Cr_2(OOCCH_3)_2(OH_2)_2]\cdot 3H_2O$ (**II**) are shown in Figures 5 and 6. The shape of the spectra and their temperature dependence contrasts with the spectra obtained for the α-Keggin anions. This has to be attributed to the special linkage between the two CrO$_6$ octahedra which is effected via one oxygen atom and the acetate groups in the salts of the γ-Keggin anion. The pattern of the spectra is characterized by coupling between the paramagnetic Cr^{III} centers. The ESR spectra recorded in the temperature range 77 ≤ T ≤ 300 K (Figure 5) exhibit a pattern which cannot be explained on the basis of individual Cr^{III} centers; the simulations yield large

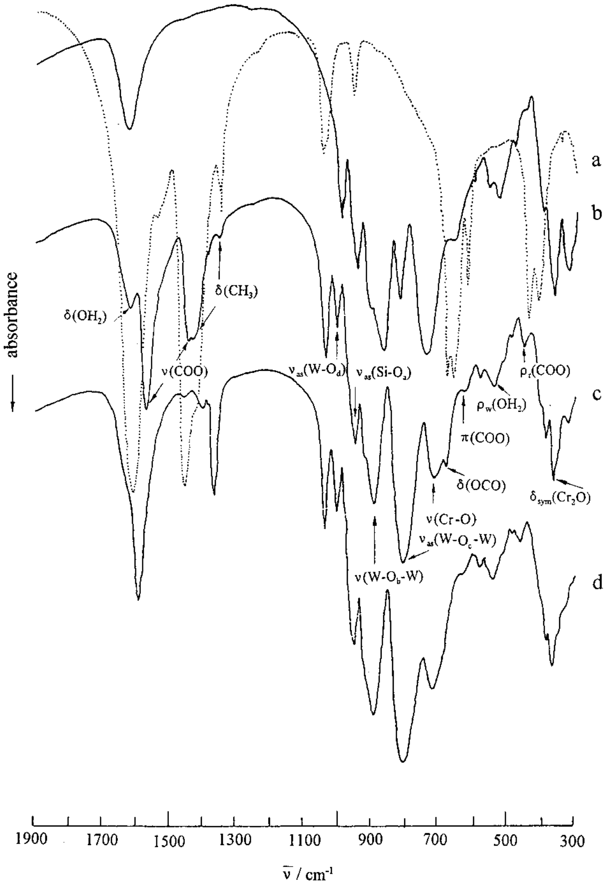

Figure 4. IR spectra of $[Cr_3O(OOCCH_3)_6(OH_2)_3]Cl\cdot nH_2O$ (a), $K_8[\gamma\text{-}SiO_4W_{10}O_{32}]\cdot 12H_2O$ (b), $Cs_5[\gamma\text{-}SiO_4W_{10}O_{30}(OH)Cr_2(OOCCH_3)_2(OH_2)_2]\cdot 13H_2O$ (c), and $Cs_5[\gamma\text{-}SiO_4W_{10}O_{32}(OH)Cr_2(OOCH)_2(OH_2)_2]\cdot 10H_2O$ (d).

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[27] It must be noted that one of the $CH_3-(CH_2)_3-$ chains of the third Bu_4N^+ cation could not be refined.

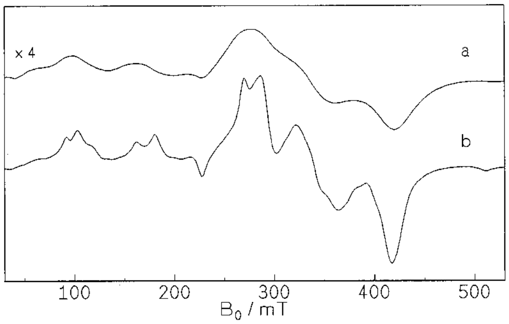

Figure 5. ESR spectra of $(Bu_4N)_3H_2[\gamma\text{-}SiO_4W_{10}O_{32}(OH)Cr_2(OH_2)_3\text{-}(OOCCH_3)_2]\cdot 3H_2O$ at 297 K (a) and 77 K (b).

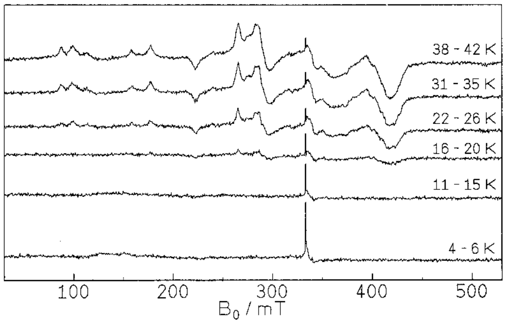

Figure 6. ESR spectra of $(Bu_4N)_3H_2[\gamma\text{-}SiO_4W_{10}O_{32}(OH)Cr_2(OH_2)_3\text{-}(OOCCH_3)_2]\cdot 3H_2O$ in the range from 4 to 42 K.

deviations between the calculated and the experimental spectra. Starting at 77 K and continuing to the region above the thermally induced decoupling and averaging process, the ESR spectra for the magnetically coupled Cr^{III} ions are transferred into broad lines.

The spectra recorded below 20 K provide evidence of antiferromagnetic coupling between the Cr^{III} centers, which influences the magnetic interactions up to 77 K before mainly paramagnetic states dominate (Figure 6). The observed transitions between these states show larger line widths with increasing temperature, caused by fluctuations of the Cr^{III}–acetate units. The narrow signal at $g' \sim 2$ (330 mT) exhibits a typical paramagnetic temperature dependence and is probably caused by an iron (Fe^{III}) impurity. Low-temperature magnetic susceptibility measurements correspond to the results of the ESR spectra and confirm the existence of an antiferromagnetic ground state below a Néel temperature in the region 15–16 K.[28] The concentration of the proposed Fe^{III} impurity is very low as indicated by the integrated intensity and the pronounced saturation behavior for the narrow signal (Figure 6, 4–6 K).

The recorded ESR spectra for the Cs^+ salts of $\gamma\text{-}SiW_{10}Cr_2Ac_2$ (**I**) and $\gamma\text{-}SiW_{10}Cr_2Fo_2$ (**III**) show a similar pattern as observed for the Bu_4N^+ salt of $\gamma\text{-}SiW_{10}Cr_2Ac_2$ (**II**). It should be noted that the antiferromagnetic coupling in these Cr^{III}-substituted polyoxoanions is less effective than the observed coupling in $[Cr_3O(OOCCH_3)_6(OH_2)_3]Cl\cdot nH_2O$ (**IV**) because of the reduced possibilities for superexchange processes. In contrast to **I**–**III**, an intense narrowed exchange line at $g' = 1.98$ was observed for **IV**.

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Supporting Information Available: Tables atomic anisotropic displacement parameters, bond distances, and bond angles (10 pages). Ordering information is given on any current masthead page.

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[28] We thank Prof. Charles O'Connor University of New Orleans for magnetic susceptibility measurements.