

# Condensation of Keggin Anions Containing Chromium(III) and Aluminum(III), Respectively. 1. Synthesis and X-ray Structural Determination of $[\{A-\alpha\text{-SiO}_4\text{W}_9\text{O}_{30}(\text{OH})_3\text{Cr}_3\}_2(\text{OH})_3]^{11-}$

Knut Wassermann,<sup>†</sup> Rosemarie Palm,<sup>‡</sup> Hans-Joachim Lunk,<sup>\*,†,§</sup> Joachim Fuchs,<sup>‡</sup> Norbert Steinfeld,<sup>†</sup> and Reinhard Stösser<sup>†</sup>

Institut für Chemie der Humboldt-Universität zu Berlin, Hessische Strasse 1/2, 10115 Berlin, Germany, and Institut für Anorganische und Analytische Chemie der Freien Universität, Fabeckstrasse 34–36, 14195 Berlin, Germany

Received February 3, 1995<sup>®</sup>

The first example of a "dimerized" Keggin anion,  $[\{A-\alpha\text{-SiO}_4\text{W}_9\text{O}_{30}(\text{OH})_3\text{Cr}_3\}_2(\text{OH})_3]^{11-}$ , containing low-valent heteroelements has been obtained by the condensation of  $[\{A-\alpha\text{-SiO}_4\text{W}_9\text{O}_{30}(\text{OH})_3\text{Cr}_3(\text{OH}_2)_3\}^{4-}]$  in aqueous solution. The reaction between the monomeric units was followed by UV/vis spectroscopy. The single-crystal X-ray structural analysis of  $(\text{NH}_4)_{11}[\{A-\alpha\text{-SiO}_4\text{W}_9\text{O}_{30}(\text{OH})_3\text{Cr}_3\}_2(\text{OH})_3] \cdot 6\text{H}_2\text{O} \cdot 2.5\text{NH}_4\text{Cl}$  ( $P4_2/nmc$ ;  $a, b = 21.778(2)$  Å,  $c = 21.300(2)$  Å;  $Z = 4$ ;  $R = 0.062$  for 2961 observed independent reflections) reveals that the two Keggin anions are linked via three Cr–OH–Cr bridges. Isolation of the new polyoxometalate was accomplished as  $\text{NH}_4^+$  and  $\text{K}^+$  salts, respectively, which were characterized by elemental analysis, IR and ESR spectroscopy. The bond distances and bond angles for the monomeric and dimeric species are discussed in a comparative study. The results from titration experiments of the free acids for mono-, di-, and triple chromium(III) substituted Keggin anions have been used for the description of the "dimer formation".

## Introduction

There is no polyoxo anion which has been more extensively studied in polyoxometalate chemistry than the Keggin anion.<sup>1</sup> Its history of investigation began with Berzelius in 1826, followed by Marignac, Rosenheim, Pauling, and finally Keggin, who described its now well-known structure in 1933, and after whom the anion is rightly named.<sup>2</sup> Since the 1950's the completion with low-valent metals (heteroelements) of lacunary Keggin anions has been of special interest. First undodecatungstosilicates/phosphates were used as precursor anions,<sup>3</sup> which were completed by di- and trivalent metals (3A and 3d elements), respectively.<sup>4</sup> The next step was the successful synthesis and characterization of nona- and decatungstosilicates/phosphates in the late 1970s/early 1980s,<sup>5</sup> which have been used

in the last few years for the preparation of many multiple low-valent substituted Keggin anions.<sup>6</sup>

A characteristic feature of low-valent metal-substituted Keggin anion is a water molecule occupying the terminal oxygen position of the  $\text{M}^{\text{II/III}}\text{O}_6$  octahedra.<sup>7</sup> Consequently the idea of dimerized species generated by condensation was discussed, but until today could not be described structurally neither for mono nor for triply substituted Keggin anions.<sup>6e,8</sup> Recently, the structures for  $[\{A-\alpha\text{-GeO}_4\text{W}_9\text{O}_{33}\text{Ti}_3\}_2\text{O}_3]^{14-}$  and  $[\{A-\beta\text{-SiO}_4\text{W}_9\text{O}_{33}\text{Ti}_3\}_2\text{O}_3]^{14-}$  were reported, both of which reveal the proposed "Keggin dimer".<sup>9</sup> However, both species were not obtained by condensation reaction of monomeric precursors. On

<sup>†</sup> Humboldt-Universität zu Berlin.

<sup>‡</sup> Freie Universität Berlin.

<sup>§</sup> Present address: OSRAM SYLVANIA INC., Hawes Street, Towanda, PA 18848.

<sup>®</sup> Abstract published in *Advance ACS Abstracts*, September 1, 1995.

- (1) (a) Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer Verlag: Berlin, 1983. (b) Pope, M. T.; Müller, A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 34. (c) Pope, M. T.; Müller, A. *Polyoxometalates: from Platonic Solids to Anti-retroviral activity*; Kluwer Acad. Pub.: Dordrecht, The Netherlands, 1994.
- (2) (a) Marignac, C. C. R. *Acad. Sci.* **1862**, *55*, 888. (b) Rosenheim, A.; Jaenicke, H. Z. *Anorg. Chem.* **1917**, *100*, 304. (c) Pauling, L. C. *J. Am. Chem. Soc.* **1929**, *51*, 2868. (d) Keggin, J. F. *Nature* **1933**, *131*, 908; *Proc. R. Soc. London, A.* **1934**, *144*, 75.
- (3) (a) Souchay, P.; Tézé, A.; Hervé, G. C. R. *Acad. Sci., Ser. C* **1972**, *275*, 1013. (b) Matsumoto, K. Y.; Sasaki, Y. *Bull. Chem. Soc. Jpn.* **1976**, *156*, 156. (c) Hervé, G.; Tézé, A. *J. Inorg. Nucl. Chem.* **1977**, *39*, 2151.
- (4) (a) Baker, L. C. W.; Simmons, V. E. *J. Am. Chem. Soc.* **1959**, *81*, 4744. (b) Simmons, V. E. Ph.D. Thesis, Boston University, 1963. (c) Malik, S. A.; Weakley, T. J. R. *J. Chem. Soc. A* **1968**, 2647. (d) Tourné, C. M.; Tourné, G. F. C. R. *Acad. Sci., Ser. C* **1968**, 266. (e) Tourné, C. M.; Tourné, G. F.; Malik, S. A.; Weakley, T. J. R. *J. Inorg. Nucl. Chem.* **1970**, *32*, 3875. (f) Spitsyn, V. I.; Kollí, I. D.; Bogatyreva, T. I. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1974**, *19*, 1036; **1975**, *20*, 1255. (g) Zonnevillie, F.; Tourné, C. M.; Tourné, G. F. *Inorg. Chem.* **1982**, *21*, 2742; *ibid.*, 2751.
- (5) (a) Tourné, C. M.; Revel, A.; Tourné, G. F.; Vencrell, M. C. R. *Acad. Sci., Ser. C* **1973**, *277*, 643. (b) Contant, R.; Fruchart, J. M.; Hervé, G.; Tézé, A. C. R. *Acad. Sci., Ser. C* **1974**, *278*, 199. (c) Massart, R.; Contant, R.; Fruchart, J. M.; Ciabrini, J. P.; Fournier, M. *Inorg. Chem.* **1977**, *16*, 2916. (d) Hervé, G.; Tézé, A. *Inorg. Chem.* **1977**, *16*, 2115. (e) Robert, F.; Tézé, A., *Acta Crystallogr.* **1983**, *B37*, 318. (f) Canny, J.; Tézé, A.; Thouvenot, R.; Hervé, G. *Inorg. Chem.*, **1986**, *25*, 2114. (g) Qu, L.; Zhang, B.; Peng, J.; Liu, J. *Transition Met. Chem.* **1988**, *13*, 183. (h) Peng, J.; Qu, L.; Zhang, B.; Chen, Y. *Chem. J. Chin. Univ. (Engl. Ed.)* **1990**, *6*, 1. (i) Peng, J.; Qu, L.; Chen, Y. *Inorg. Chim. Acta* **1991**, *183*, 157. (j) Qu, L.; Chen, Y.; Peng, J.; Lin, Y.; Yu, Z. *Chem. J. Chin. Univ.* **1991**, *12*, 1009. (k) Liu, J.; Ortéga, F.; Sethuraman, P.; Katsoulis, D. E.; Costello, C. E.; Pope, M. T. *J. Chem. Soc., Dalton Trans.* **1992**, 1901. (l) Gómez-García, C. J.; Coronado, E.; Gómez-Romero, P.; Casañ-Pastor, N. *Inorg. Chem.* **1993**, *32*, 89. (m) Wassermann, K.; Lunk, H.-J.; Palm, R.; Fuchs, J., *Acta Crystallogr.* **1994**, *C50*, 348. (n) Zhang, X.; Liu, J.; Jameson, G. B.; Pope, M. T. Presented at the National Meeting of the American Chemical Society, Washington, DC, 1994.
- (6) (a) Baker, L. C. W.; Figgis, J. S. *J. Am. Chem. Soc.* **1970**, *92*, 3794. (b) Weakley, T. J. R., *J. Chem. Soc., Dalton Trans.* **1973**, 341. (c) Katsoulis, D. E.; Tausch, V. S.; Pope, M. T. *Inorg. Chem.* **1987**, *26*, 215.
- (7) (a) Tézé, A.; Souchay, P. C. R. *Acad. Sci., Ser. C* **1973**, *276*, 1525. (b) Zonnevillie, F.; Tourné, C. M.; Tourné, G. F. *Inorg. Chem.* **1982**, *21*, 2751. (c) Wang, Z.; Wu, N.; Fang, J. *Chem. J. Chin. Univ.* **1992**, *13*, 249.
- (8) (a) Yamase, T.; Ozeki, T.; Sakamoto, H.; Nishiya, S.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 103. (b) Lin, Y.; Weakley, J. R.; Rapko, B.; Finke, R. G. *Inorg. Chem.* **1993**, *32*, 5095.

the contrary the anion  $[\{A-\alpha\text{-SiO}_4\text{W}_9\text{O}_{30}\text{Nb}_3\}_2\text{O}_3]^{8-}$  containing  $\text{Nb}^V$  was synthesized from the monomeric anions.<sup>10</sup>

In the forthcoming paper we shall report the synthesis and characterization of  $[\{A-\alpha\text{-SiO}_4\text{W}_9\text{O}_{30}(\text{OH})_3\text{Cr}_3\}_2(\text{OH})_3]^{11-}$ , which is the first example of a successful condensation reaction between low-valent substituted Keggin anions. The X-ray structural analysis reveals that two Keggin units have been linked via three Cr—OH—Cr bridging groups.

## Experimental Section

**Instrumentation and Analytical Procedures.** The electronic spectra were obtained with a PU 8735 UNICAM (Philips Cambridge, U.K.). Conductivity and potentiometry measurements were carried out with a Konduktometer CG855 (Schott, Hofheim, Germany) and pH-meter pH 96 (WTW, Weinheim, Germany). IR spectra were recorded on a Perkin-Elmer IR 580 B, KBr disk. The ESR measurements were carried out on the X-band cw-spectrometer ERS 300 (Zentrum für wissenschaftlichen Gerätebau, Berlin, Germany). The freeze drying was carried out by means of LDC-1 (Christ, Osterode, Germany). The elemental content was determined with an ICP SPECTRO FLAME (Si, K, Al, Cr, Mo) and the Elementar Analysator C H N S 932 LECO (N). The tungsten content was obtained by calculating the difference between the sum of all non-tungsten oxides and 100%. The overall sum of all oxides present was ascertained by means of the ignition residue resulting from thermal analysis. For chloride, Schöniger's method was used followed by titration with  $\text{Hg}(\text{ClO}_4)_2$ . The water content was determined by weight loss at 600 °C ( $\text{H}_2\text{O} + \text{NH}_3$ ).

**Materials.** All compounds were of reagent grade and were used as supplied.  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  was recrystallized before use from 1M  $\text{HNO}_3$  at 40 °C.  $\text{Na}_{10}[\text{A}-\alpha\text{-SiO}_4\text{W}_9\text{O}_{30}] \cdot n\text{H}_2\text{O}$  and  $\text{K}_8[\alpha\text{-SiO}_4\text{W}_{11}\text{O}_{35}] \cdot 13\text{H}_2\text{O}$  were synthesized according to the literature<sup>11</sup> and their purity, as well as the purity of the later described compounds, were checked by IR spectroscopy, polarography, and powder diffractometry.

**Preparation of  $\text{K}_4[\text{A}-\alpha\text{-SiO}_4\text{W}_9\text{O}_{30}(\text{OH})_3\text{Cr}_3(\text{OH}_2)_3] \cdot 13\text{H}_2\text{O}$ .** The synthesis described in the literature<sup>6c</sup> was modified in our group by the use of an ultrasonic bath. A 10 g (3.6 mmol) sample of  $\text{K}_8[\text{A}-\alpha\text{-SiO}_4\text{W}_9\text{O}_{30}] \cdot n\text{H}_2\text{O}$  was added to 80 mL of cold water (10 °C). The beaker containing the white suspension was placed in an ultrasonic bath and the suspension was stirred occasionally. After 3 min a dilute solution of  $\text{Cr}^{3+}$  (4.6 g of  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , 1.15 mmol, in 20 mL of water) was poured into the beaker in the ultrasonic bath, the solution being stirred vigorously (5–10 °C, pH 5.0). Next, the resulting green suspension was heated in a water bath at 85 °C for 30 min. The cooled concentrated solution (pH 1.7) was filtered, and the pH was adjusted to between 3.5 and 4.0 by addition of 2 M KOH. The addition of 12.5 g (166.6 mmol) of KCl yielded a light green precipitate, which was collected after few hours. The crude product was stirred at room temperature in 1 mL of water to dissolve the readily soluble impurities ( $\text{NO}_3^-$ ,  $[\alpha\text{-SiO}_4\text{W}_{11}\text{O}_{35}\text{Cr}(\text{OH}_2)]^{5-}$ ). The green salt desired was isolated and recrystallized twice from hot water. Yield: 1.5 g (15%). For larger amounts of the title compound, it is useful to proceed as described before and unite all the cooled concentrated solutions before the addition of KOH.

Anal. Calcd for  $\text{K}_4[\text{A}-\alpha\text{-SiO}_4\text{W}_9\text{O}_{30}(\text{OH})_3\text{Cr}_3(\text{OH}_2)_3] \cdot 13\text{H}_2\text{O}$ : K, 5.43; Si, 0.97; W, 57.48; Cr, 5.42;  $\text{H}_2\text{O}$ , 10.95. Found: K, 5.78; Si, 0.95; W, 56.90; Cr, 5.41;  $\text{H}_2\text{O}$ , 10.78. IR ( $\text{cm}^{-1}$ , KBr disk, polyoxo anion region): 1073 (sh, br), 1006 (m), 957 (s), 913 (vs), 883 (sh), 787 (vs), 724 (vs), 670 (sh, br), 508 (m), 425 (sh), 366 (s), 320 (m). Electronic absorption spectra in water (pH = 5.0):  $\epsilon_{\text{max}(630 \text{ nm})} = 57 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ .

**Preparation of  $(\text{NH}_4)_{11}[\text{A}-\alpha\text{-SiO}_4\text{W}_9\text{O}_{30}(\text{OH})_3\text{Cr}_3(\text{OH}_2)_3] \cdot 23\text{H}_2\text{O}$ .** A 3 g (1.0 mmol) sample of  $\text{K}_4[\text{A}-\alpha\text{-SiO}_4\text{W}_9\text{O}_{30}(\text{OH})_3\text{Cr}_3(\text{OH}_2)_3] \cdot 13\text{H}_2\text{O}$  was added to 20 mL of a stirred mixture of bidistilled water and 10 mL of a strong acid cation exchanger in  $\text{H}^+$  form (Lewatit S100). After

15 min the deep green solution was passed through a column containing another 10 mL of exchanger to complete the cation exchange. To the eluate (30 mL, pH 1.7) 1 M NaOH was added (ca. 4.5 mL) to raise the pH to 7.5. Then it was subjected to refluxing for 1 h. The decreased pH (~4.0) was raised to 7.5 with a few drops of 1 M NaOH (350  $\mu\text{L}$ ) and the solution was refluxed for another hour. To the cooled solution (pH ~4.3) were added a few drops of 1 M NaOH (400  $\mu\text{L}$ ) (pH 7.5). After 2 h of refluxing (pH ~4.5), again 1 M NaOH was added (300  $\mu\text{L}$ , pH 7.5) and the refluxing was continued for 2 h more. To the cooled solution (pH 5.5) was added 3.5 g (66.0 mmol) of  $\text{NH}_4\text{Cl}$ , which immediately resulted in tiny needles of the title compound. The crystals were isolated and recrystallized twice from warm water (60 °C). Yield: 1.1 g (34%).

Anal. Calcd for the bulk material  $(\text{NH}_4)_{11}[\text{A}-\alpha\text{-SiO}_4\text{W}_9\text{O}_{30}(\text{OH})_3\text{Cr}_3] \cdot 23\text{H}_2\text{O}$ : N, 2.78; H, 1.79; Si, 1.01; W, 59.83; Cr, 5.64;  $\text{H}_2\text{O} + \text{NH}_3$ , 14.11. Found: N, 2.82; H, 1.89; Si, 0.95; W, 59.23; Cr, 4.92;  $\text{H}_2\text{O} + \text{NH}_3$ , 14.23. For the single crystals only the N, H, and Cl content was determined. Anal. Calcd for  $(\text{NH}_4)_{11}[\text{A}-\alpha\text{-SiO}_4\text{W}_9\text{O}_{30}(\text{OH})_3\text{Cr}_3] \cdot 6\text{H}_2\text{O} \cdot 2.5\text{NH}_4\text{Cl}$ : N, 3.53; H, 1.41; Cl, 1.65. Found: N, 3.45; H, 2.20; Cl 2.17. IR ( $\text{cm}^{-1}$ , KBr disk, polyoxo anion region): 1160 (w), 999 (m), 957 (s), 906 (vs), 868 (sh), 800 (sh), 774 (vs), 682 (m), 595 (w), 547 (sh), 508 (s), 437 (w), 368 (s), 330 (sh).

**Preparation of  $\text{K}_{11}[\text{A}-\alpha\text{-SiO}_4\text{W}_9\text{O}_{30}(\text{OH})_3\text{Cr}_3] \cdot 14\text{H}_2\text{O}$ .** The preparation is identical to that for the ammonium salt, and instead of  $\text{NH}_4\text{Cl}$ , 7.5 g (0.1 mol) of KCl was used to precipitate the desired potassium salt. Crude products were filtered and twice recrystallized from warm water (60 °C). Yield: 1.5 g (49%).

Anal. Calcd for  $\text{K}_{11}[\text{A}-\alpha\text{-SiO}_4\text{W}_9\text{O}_{30}(\text{OH})_3\text{Cr}_3] \cdot 14\text{H}_2\text{O}$ : K, 7.68; Si, 1.00; W, 59.09; Cr, 5.57;  $\text{H}_2\text{O}$ , 9.95. Found: K, 7.29; Si, 0.92; W, 58.50; Cr, 5.19;  $\text{H}_2\text{O}$ , 9.85. IR ( $\text{cm}^{-1}$ , KBr disk, polyoxo anion region): 1163 (w), 999 (m), 970 (sh), 953 (s), 907 (vs), 875 (sh), 800 (sh), 778 (vs), 739 (vs), 675 (sh, br), 597 (w), 547 (sh), 503 (s), 430 (sh), 366 (s), 330 (sh). Electronic absorption spectra in water (pH = 6.2):  $\epsilon_{\text{max}(621 \text{ nm})} = 120 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ .

**Preparation of  $\text{K}_5[\text{A}-\alpha\text{-SiO}_4\text{W}_{11}\text{O}_{35}\text{Cr}(\text{OH}_2)] \cdot 9\text{H}_2\text{O}$ .** The compound was prepared using a new method developed by us, based on the stabilization effect of  $\text{Li}^+$  for monovacant Keggin anions<sup>5f</sup>. A 36 g (11.2 mmol) sample of  $\text{K}_8[\alpha\text{-SiO}_4\text{W}_{11}\text{O}_{35}] \cdot 13\text{H}_2\text{O}$  was dissolved in 350 mL of 1 M LiCl solution at 80 °C. In a separate beaker, 5.1 g (12.75 mmol) of  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  was dissolved in 100 mL of water, and the pH was adjusted to between 3.5 and 4.0. Then 10 mL of this solution was added slowly to the stirred hot polyoxometalate solution. The resultant precipitate was removed, and then the slow addition of the chromium solution was continued (ca. 1 h). The green solution was stirred for another hour at 80 °C before 40 g (536.5 mmol) of KCl was added. The cooled solution was filtered (pH 4.0), and twice its volume of the MeOH/EtOH (1:1) mixture was poured into the filtrate. The resulting precipitate was recrystallized as described for  $\text{K}_5[\text{A}-\alpha\text{-SiO}_4\text{W}_{11}\text{O}_{35}\text{Fe}(\text{OH}_2)] \cdot 14\text{H}_2\text{O}$ .<sup>8b</sup> Yield: 15.0 g of light green needles (43%).

Anal. Calcd for  $\text{K}_5[\text{A}-\alpha\text{-SiO}_4\text{W}_{11}\text{O}_{35}\text{Cr}(\text{OH}_2)] \cdot 9\text{H}_2\text{O}$ : K, 6.30; Si, 0.90; W, 65.18; Cr, 1.67;  $\text{H}_2\text{O}$  5.81. Found: K, 5.75; Si, 0.87; W, 64.52; Cr, 1.53;  $\text{H}_2\text{O}$ , 5.82. IR ( $\text{cm}^{-1}$ , KBr disk, polyoxo anion region): 1008 (m), 963 (s), 915 (vs), 874 (sh), 783 (vs), 667 (m), 522 (m), 505 (sh), 480 (sh), 422 (sh), 369 (s), 342 (sh). Electronic absorption spectra in water (pH = 5.9):  $\epsilon_{\text{max}(630 \text{ nm})} = 41 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ .

**Preparation of  $\text{K}_5[\text{A}-\alpha\text{-SiO}_4\text{W}_{10}\text{O}_{33}(\text{OH})\text{Cr}_2(\text{OH}_2)_2] \cdot 11\text{H}_2\text{O}$ .** The compound was prepared according to the literature<sup>6b</sup> by the ultrasonic bath method as described above for  $\text{K}_4[\text{A}-\alpha\text{-SiO}_4\text{W}_9\text{O}_{30}(\text{OH})_3\text{Cr}_3(\text{OH}_2)_3] \cdot 13\text{H}_2\text{O}$ . Yield: 2.0 g (18%).

Anal. Calcd for  $\text{K}_5[\text{A}-\alpha\text{-SiO}_4\text{W}_{10}\text{O}_{33}(\text{OH})\text{Cr}_2(\text{OH}_2)_2] \cdot 11\text{H}_2\text{O}$ : K, 6.50; Si, 0.93; W, 61.10; Cr, 3.45;  $\text{H}_2\text{O}$  6.50. Found: K, 6.82; Si, 0.86; W, 60.49; Cr, 3.23;  $\text{H}_2\text{O}$ , 6.82. IR ( $\text{cm}^{-1}$ , KBr disk, polyoxo anion region): 1080 (sh), 1009 (m), 962 (s), 905 (vs), 880 (sh), 780 (vs), 690 (sh), 630 (w), 560 (sh), 499 (s), 468 (sh), 428 (w), 385 (sh), 370 (s), 353 (sh), 327 (w). Electronic absorption spectra in water:  $\epsilon_{\text{max}(619 \text{ nm})} = 78 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ .

**Preparation of  $\text{K}_7[\text{A}-\alpha\text{-SiO}_4\text{W}_9\text{O}_{30}(\text{OH})_3\text{Cr}_3(\text{OH}_2)_3] \cdot 10\text{H}_2\text{O}$ .** A 3 g (1.0 mmol) sample of  $\text{K}_4[\text{A}-\alpha\text{-SiO}_4\text{W}_9\text{O}_{30}(\text{OH})_3\text{Cr}_3(\text{OH}_2)_3] \cdot 13\text{H}_2\text{O}$  were transferred into the solution of the free acid (30 mL, pH 1.7), as described before. Then 7.0 mL of 1 M NaOH were added and the solution was stirred for 5 min more (pH 12). The addition of 20 mL

(10) (a) Finke, R. G.; Droegge, M. W. *J. Am. Chem. Soc.* **1984**, 106, 7274. (b) Finke, R. G.; Droegge, M. W. *J. Mol. Catal.* **1991**, 69, 323.

(11) Tézé, A.; Hervé, G. *Inorg. Synth.* **1990**, 27, 85.

(12) Publication about the synthesis and characterization of  $[\text{A}-\alpha\text{-SiO}_4\text{W}_9\text{Mo}_2\text{O}_{35}\text{Cr}(\text{OH}_2)]^{5-}$ ,  $[\text{A}-\alpha\text{-SiO}_4\text{W}_6\text{MoO}_{33}(\text{OH})\text{Cr}_2(\text{OH}_2)_2]^{5-}$ , and  $[\text{A}-\alpha\text{-SiO}_4\text{W}_9\text{MoO}_{32}(\text{OH})\text{Cr}_2] \cdot 2\text{O}_2(\text{OH})^{11-}$  is in preparation. For X-ray data see ref 20.

**Table 1.** Crystallographic Data for  $(\text{NH}_4)_{11}[\{\text{A}-\alpha\text{-SiO}_4\text{W}_9\text{O}_{30}(\text{OH})_3\text{Cr}_3\}_2(\text{OH})_3]\cdot 6\text{H}_2\text{O}\cdot 2.5\text{NH}_4\text{Cl}$ 

$M = 5358.8 \text{ g mol}^{-1}$	$\theta = 2-24^\circ$
cryst syst: tetragonal	$h = 0-24$
space group: $P4_2/nmc$	$k = 0-24$
$a, b = 21.780(2) \text{ \AA}$	$l = 0-24$
$c = 21.300(2) \text{ \AA}$	no. of measd reflns 8145
$V = 10104(3) \text{ \AA}^3$	no. of indep reflns 4162
$Z = 4$	no. of obsd reflns [ $I > 2\sigma(I)$ ]:
$d_{\text{calc}} = 3.523 \text{ g cm}^{-3}$	2961
$R_w = 0.062$	$\mu = 223.9 \text{ cm}^{-1}$
$T = 19^\circ\text{C}$	$\Delta\rho_{\text{max}} = 3.9 \text{ e \AA}^{-3}$
$\lambda(\text{Mo K}\alpha) = 0.71069 \text{ \AA}$	$\Delta\rho_{\text{min}} = -4.7 \text{ e \AA}^{-3}$
no. of params: 182	

of a 3 M KCl solution yielded a light green precipitate which was washed several times with warm water and finally dried on air. Yield: 2.0 g (69%).

Anal. Calcd for  $\text{K}_7[\text{A}-\alpha\text{-SiO}_4\text{W}_9\text{O}_{30}(\text{OH})_3\text{Cr}_3(\text{OH})_3]\cdot 10\text{H}_2\text{O}$ : K, 9.32; Si, 0.96; W, 56.31; Cr, 5.31;  $\text{H}_2\text{O}$  7.97. Found: K, 9.90; Si, 0.97; W, 55.75; Cr, 5.12;  $\text{H}_2\text{O}$ , 7.76. IR ( $\text{cm}^{-1}$ , KBr disk, polyoxo anion region): 992 (m), 949 (s), 905 (vs), 875 (sh), 800 (vs), 740 (s), 680 (m), 592 (w), 525 (m), 480 (sh), 455 (sh), 365 (m), 350 (sh), 323 (sh).

**Preparation of the Free Acids.** Preparation is identical for all investigated free acids. A 3 g (1.0 mmol) sample of the corresponding potassium salt were added to 20 mL of a stirred mixture of bidistillate and 10 mL of a strong acid cation exchanger in  $\text{H}^+$  form (Lewatit S100). After 15 min the solution was passed through a column containing another 10 mL of exchanger to complete the cation exchange. The potassium-free eluates of the free acids (pH 1.7–2.0) were frozen and finally freeze-dried. The polycrystalline powders were kept in a desiccator over  $\text{P}_4\text{O}_{10}$  for another day. The substances proved stable in tightly closed tubes.

$\text{H}_5[\text{A}-\alpha\text{-SiO}_4\text{W}_{11}\text{O}_{35}\text{Cr}(\text{OH}_2)]\cdot 5\text{H}_2\text{O}$ , I. Anal. Calcd: Si, 0.98; W, 71.22; Cr, 1.83;  $\text{H}_2\text{O}$ , 5.39. Found: Si, 1.00; W, 70.50; Cr, 1.90;  $\text{H}_2\text{O}$ , 5.20.

$\text{H}_5[\text{A}-\alpha\text{-SiO}_4\text{W}_9\text{Mo}_2\text{O}_{35}\text{Cr}(\text{OH}_2)]\cdot 4\text{H}_2\text{O}$ ,<sup>12</sup> II. Anal. Calcd: Si, 1.06; W, 62.55; Mo, 7.25; Cr, 1.97;  $\text{H}_2\text{O}$ , 5.11. Found: Si, 1.12; W, 61.92; Mo, 7.55; Cr, 1.98;  $\text{H}_2\text{O}$ , 5.40.

$\text{H}_5[\text{A}-\alpha\text{-SiO}_4\text{W}_{11}\text{O}_{35}\text{Al}(\text{OH}_2)]\cdot 5\text{H}_2\text{O}$ ,<sup>4b</sup> III. Anal. Calcd: Si, 1.00; W, 71.85; Al, 0.96;  $\text{H}_2\text{O}$ , 5.44. Found: Si, 1.02; W, 71.13; Al, 0.96;  $\text{H}_2\text{O}$ , 5.20.

$\text{H}_5[\text{A}-\alpha\text{-SiO}_4\text{W}_{10}\text{O}_{33}(\text{OH})\text{Cr}_2(\text{OH}_2)_2]\cdot 5\text{H}_2\text{O}$ , IV. Anal. Calcd: Si, 1.04; W, 67.82; Cr, 3.84;  $\text{H}_2\text{O}$ , 6.40. Found: Si, 0.98; W, 67.14; Cr, 3.76;  $\text{H}_2\text{O}$ , 6.64.

$\text{H}_5[\text{A}-\alpha\text{-SiO}_4\text{W}_9\text{MoO}_3(\text{OH})\text{Cr}_2(\text{OH}_2)_2]\cdot 3\text{H}_2\text{O}$ ,<sup>12</sup> V. Anal. Calcd: Si, 1.08; W, 63.97; Mo, 3.32; Cr, 4.02;  $\text{H}_2\text{O}$ , 5.57. Found: Si, 1.08; W, 63.33; Mo, 3.71; Cr, 3.96;  $\text{H}_2\text{O}$ , 5.80.

$\text{H}_4[\text{A}-\alpha\text{-SiO}_4\text{W}_9\text{O}_{30}(\text{OH})_3\text{Cr}_3(\text{OH}_2)_3]\cdot 3\text{H}_2\text{O}$ , VI. Anal. Calcd: Si, 1.11; W, 65.45; Cr, 6.17;  $\text{H}_2\text{O}$ , 6.06. Found: Si, 1.07; W, 64.80; Cr, 6.05;  $\text{H}_2\text{O}$ , 6.20.

$\text{H}_4[\text{A}-\alpha\text{-SiO}_4\text{W}_9\text{O}_{30}(\text{OH})_3\text{Al}_3(\text{OH}_2)_3]\cdot 3\text{H}_2\text{O}$ ,<sup>6e</sup> VII. Anal. Calcd: Si, 1.14; W, 66.97; Al, 3.28;  $\text{H}_2\text{O}$ , 6.93. Found: Si, 1.04; W, 66.30; Al, 3.04;  $\text{H}_2\text{O}$ , 6.87.

**X-ray Structural Analysis.** Although  $\text{K}^+$ ,  $\text{Cs}^+$ ,  $\text{TMA}^+$ ,  $\text{TEA}^+$  and  $\text{NH}_4^+$  have combined with the new anion to form well-shaped crystals, it has taken a long time to obtain single crystals suitable for X-ray structural analysis. For  $\text{K}^+$ ,  $\text{Cs}^+$ ,  $\text{TMA}^+$ , and  $\text{TEA}^+$  large unit cells were found with  $c$ -axes between 35 and 40 Å. Finally, the use of  $\text{NH}_4^+$  yielded valuable nondisordered single crystals, which might be attributed to the nature of  $\text{NH}_4^+$  (high tendency to form hydrogen bonds). A crystal having approximate dimensions of  $0.10 \times 0.25 \times 0.70 \text{ mm}^3$  was picked from the filtrate of the crude product. The green needle was mounted on a STOE-4 diffractometer equipped with a graphite monochromator (Mo K $\alpha$  radiation). The orientation matrix and cell constants were obtained from the setting of 171 reflections. During data collection,  $\omega$ -scan, three standard reflections were measured for 90 min each. A summary of crystal data is given in Table 1. The structure was solved by direct methods by the use of SHELXS-86.<sup>13</sup>

(13) Sheldrick, G. M., *SHELXS-86. Program for the Solution of Crystal Structures*, University of Göttingen: Göttingen, Germany, 1985.

All calculations were performed on a VAX computer on the basis of XTAL 3.0.<sup>14</sup> An empirical absorption correction DIFABS<sup>15</sup> based on the isotropically-refined structure was applied.

## Results and Discussion

**Synthesis.** The reaction of  $[\text{A}-\alpha\text{-SiO}_4\text{W}_9\text{O}_{30}(\text{OH})_3\text{Cr}_3(\text{OH}_2)_3]^{4-}$  in aqueous solution with the gradual addition of 1 M NaOH and refluxing provides the new  $\text{Cr}^{\text{III}}$  substituted polyoxometalate  $[\{\text{A}-\alpha\text{-SiO}_4\text{W}_9\text{O}_{30}(\text{OH})_3\text{Cr}_3\}_2(\text{OH})_3]^{11-}$ , which can be readily isolated in pure form as its water-soluble  $\text{NH}_4^+$  and  $\text{K}^+$  salt, respectively.

The condensation reaction was followed by UV/vis spectroscopy. In the near UV region will appear both the charge transfer transitions for polyanions ( $\text{O}-\text{W}$ )<sup>1a</sup> and a spin-allowed transition for chromium(III) with  $O_h$  symmetry.<sup>17</sup> In spite of this overlapping, the region 350–500 nm has been sensitive ( ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}$ ) to the structural changes of the chromium environment because of further Cr–OH–Cr bond formations, Figure 1. The shape of the electronic spectra in the near-UV region implies the existence of an isobestic point at 400 nm. This might be possible because the molar absorptivities for the  $\text{O}-\text{W}$  transitions of the monomeric and dimeric species are not likely to have been influenced by the cross-linking reaction. The visible region of the electronic spectra (600–650 nm,  ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}$ ; 680–730 nm,  ${}^4\text{A}_{2g} \rightarrow {}^2\text{E}_g$ ) is only slightly influenced by the cross-linking reaction, and therefore less informative. The addition of the first 1 M NaOH will neutralize approximately four protons of the free acid, Figure 2c, and is accomplished by a slight blue shift in the electronic spectra, which indicates the destruction of the polyanion, possibly via a deprotonation. The refluxing and gradual addition of NaOH lead to the successive linking between the two Keggin anions, which can be concluded from the increasing absorption in the region 350–500 nm, as shown in Figure 1. The “dimerization” is completed for most of the “monomers” after heating for 6 h (yielded crude product >85%).

The synthesis of the new polyoxo anion was further characterized by a few additional experiments which should be briefly described in the following. The immediate addition of the total number of NaOH to the aqueous solution of the free acid (pH 10) has yielded degradation products beside the dimeric anion after refluxing for a short period. The concentration of  $[\text{A}-\alpha\text{-SiO}_4\text{W}_9\text{O}_{30}(\text{OH})_3\text{Cr}_3(\text{OH}_2)_3]^{4-}$  was about 0.033 M, but also for 10-fold diluted solutions, the condensation reaction could be observed. In further experiments the influence of the ion strength was checked. For example, in 5 M NaCl solution the condensation of the Keggin anions takes place more rapidly (4 h). However, the crystallization of the desirable salt has been interfered with by the high percentage of sodium. Furthermore, LiOH was used as hydroxide source, which did not affect the condensation reaction.<sup>18</sup>

**Likely Mechanism Underlying the Formation of  $[\{\text{A}-\alpha\text{-SiO}_4\text{W}_9\text{O}_{30}(\text{OH})_3\text{Cr}_3\}_2(\text{OH})_3]^{11-}$ .** In general, the description

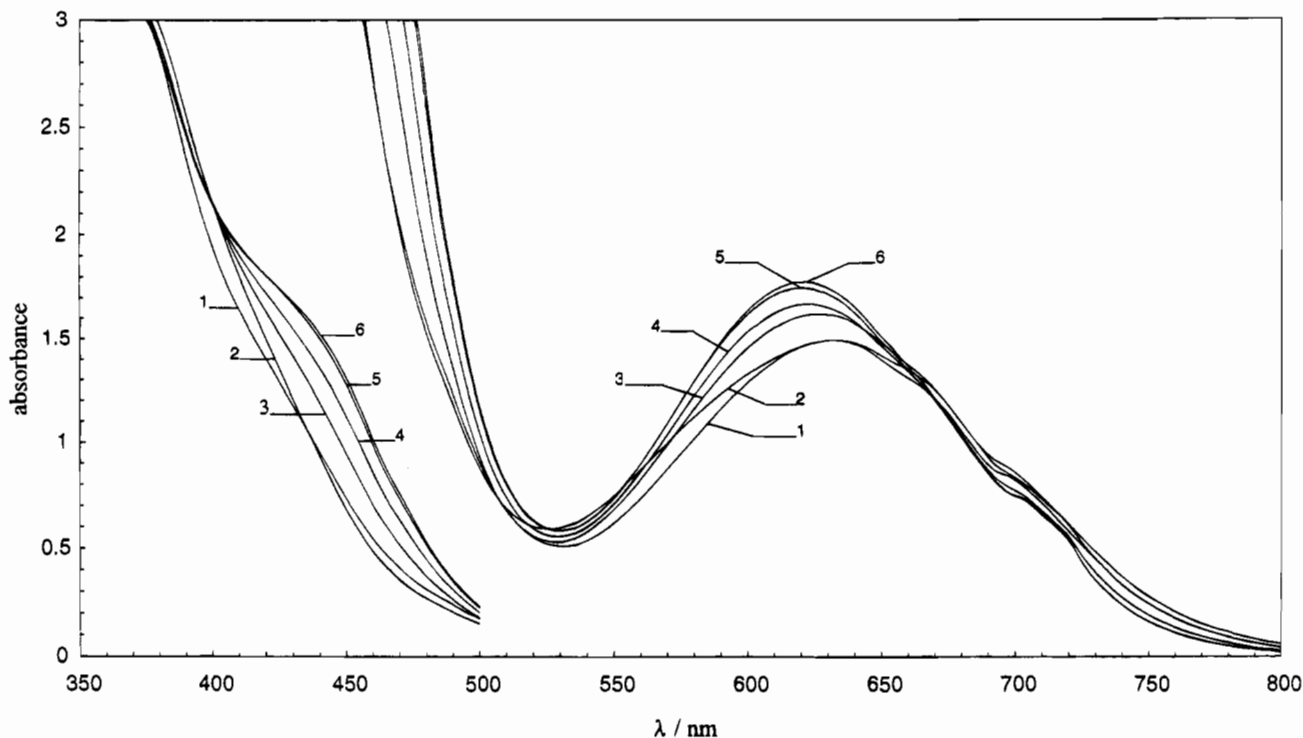
(14) Hall, S. R.; Stewart, J. M. XTAL 3.0. Universities of Western Australia, Australia, and Maryland, 1991.

(15) Walker, N.; Stuart, D., *Acta Crystallogr.* **1983**, A39, 158.

(16) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, UK, 1974; Vol. IV.

(17) Schäfer, H. L.; Gliemann, G. *Einführung in die Ligandenfeldtheorie*; Akad. Verlagsgesellschaft Geest & Portig K.-G.: Leipzig, Germany, 1967.

(18) The stability in acid media has not been studied in detail yet. The results for the time being show that the free acid of the dimer can be obtained by cation exchange and freeze drying (IR, ESR). However, there is no evidence that the sample contains any monomeric units. The <sup>183</sup>W NMR spectra for the analogous aluminum dimer (free acid) reveals the intact anion at room temperature for a long period, but the total decomposition of the anion after a short time of refluxing.



**Figure 1.** Electronic spectra for the formation of  $[\{A-\alpha\text{-SiO}_4\text{W}_9\text{O}_{30}(\text{OH})_3\text{Cr}_3\}_2(\text{OH})_3]^{11-}$  starting with  $[A-\alpha\text{-SiO}_4\text{W}_9\text{O}_{30}(\text{OH})_3\text{Cr}_3(\text{OH}_2)_3]^{4-}$ : ca. 300 mmol W/l; 350–500 nm,  $d = 2$  mm; 450–800 nm,  $d = 10$  mm. Key: (1) aqueous solution of  $\text{H}_4[A-\alpha\text{-SiO}_4\text{W}_9\text{O}_{30}(\text{OH})_3\text{Cr}_3(\text{OH}_2)_3]$ , pH = 1.70; (2) solution + 1 M NaOH, pH = 7.6; (3) solution after 1 h refluxing, pH = 4.00; (4) solution + 1 M NaOH + 1 h refluxing, pH = 4.25; (5) solution + 1 M NaOH + 2 h refluxing, pH = 4.5; (6) solution + 1 M NaOH + 2 h ( $\Sigma$  6 h) refluxing, pH = 5.5.

of mechanisms governing chemical reactions is limited by the experimental scope and our simplistic ideas of structural changes of the species involved. The model proposed for the formation of  $[\{A-\alpha\text{-SiO}_4\text{W}_9\text{O}_{30}(\text{OH})_3\text{Cr}_3\}_2(\text{OH})_3]^{11-}$  is based on the titration experiments of different  $\text{Cr}^{\text{III}}$  and  $\text{Al}^{\text{III}}$ , respectively, substituted Keggin anions and should be discussed first. The following free acids (A- $\alpha$  type) were investigated:  $\text{H}_5[\text{SiW}_{11}\text{-Cr}(\text{OH}_2)]$  (I),  $\text{H}_5[\text{SiW}_9\text{Mo}_2\text{Cr}(\text{OH}_2)]$  (II),  $\text{H}_5[\text{SiW}_{11}\text{Al}(\text{OH}_2)]$  (III),  $\text{H}_5[\text{SiW}_{10}\text{Cr}_2(\text{OH}_2)_2]$  (IV),  $\text{H}_5[\text{SiW}_9\text{MoCr}_2(\text{OH}_2)_2]$  (V),  $\text{H}_4[\text{SiW}_9\text{Cr}_3(\text{OH}_2)_3]$  (VI),  $\text{H}_4[\text{SiW}_9\text{Al}_3(\text{OH}_2)_3]$  (VII); see Figure 2 (I, IV, VI). The titration experiments of the free acids reveal that the Keggin anions, substituted with low-valent metals contain two different types of titratable protons. The first kind of protons as “freely mobile” hydrated ones, whose number was obtained from the potentiometric curve, are not influenced by the Keggin anion. Only for the monosubstituted anions (I, II, III) is this number identical with the anions’ charge (calculated for an anion containing terminal water ligands ( $\text{M}^{\text{III}}$ ) but no further OH groups). For all other anions the estimated number of these freely mobile protons is smaller than the number to be expected theoretically. The difference corresponds to the present corner-bridging oxygens between the  $\text{CrO}_6$  octahedra. We assume that these oxygens are protonated, which is supported by the calculations for cation–oxygen bond valences<sup>19</sup> in the structurally characterized chromium(III)-containing polyoxo anions<sup>6g,20</sup> and the study of hydroxo-bridged  $\text{Cr}^{\text{III}}$  complexes.<sup>21</sup> The protonation of edge-bridging oxygens in  $\text{W}_2\text{CrO}_{13}$  triplets is also possible but less favorable.

The second kind of titratable protons is linked to oxygen atoms of the polyoxo anion. The single deprotonation of terminal water ligands<sup>48</sup> rather than the deprotonation of bridging oxygens within the chromium–oxygen framework during titration should be preferred. This statement has been confirmed both by the congruence of the number of protons titrated and the number of terminal water ligands present and by the largely identical slope of the conductometric curve in this region for all anions investigated.<sup>22</sup>

The titration experiments were carried out by means of polycrystalline powders of the free acids, which were obtained by freeze drying<sup>23</sup> of the corresponding aqueous solutions. The solid samples were dissolved in bidistilled water (0.01 molar) and followed by conductometric and potentiometric titrations with 1 M NaOH. The stability of the Keggin anions in basic media at room temperature was checked by means of UV spectroscopy ( $\epsilon_{\text{max}} = 258$  nm). For the  $\text{Cr}^{\text{III}}$ -substituted anions no degradation reaction was observed. However, for VII the starting decomposition was found a few hours after finishing the titration experiment.

The equations in Scheme 1 illustrate the successive steps of the condensation of the Keggin anions. The neutralization of the freely mobile protons at room temperature is probably followed by the linking between the Keggin anions during the first refluxing. All further linking steps take place in practically neutral medium (pH 7.5) and require only 1 equiv of hydroxide per dimer anion.

**X-ray Single-Crystal Structural Analysis of the  $\text{NH}_4^+$  Salt.** The structure of  $[\{A-\alpha\text{-SiO}_4\text{W}_9\text{O}_{30}(\text{OH})_3\text{Cr}_3\}_2(\text{OH})_3]^{11-}$  is

(19) Brown, I. D.; Wu, K. K. *Acta Crystallogr.* **1975**, *B32*, 1957.

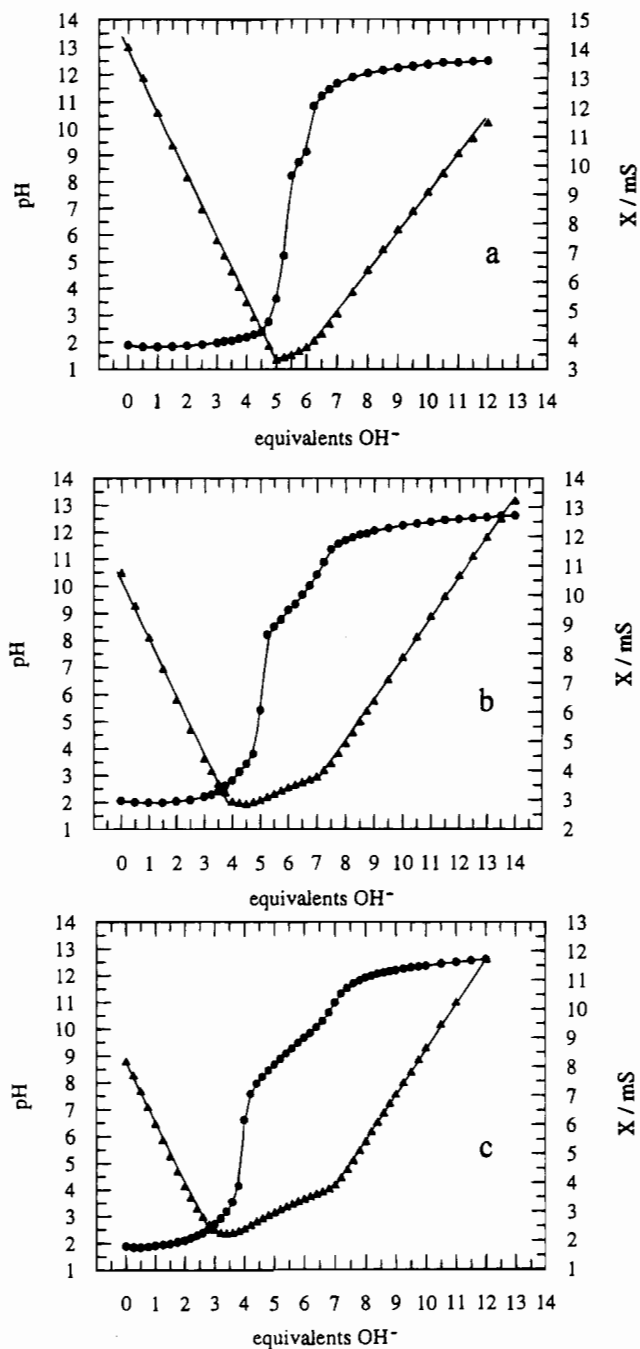
(20) For the range of Cr–O bond distances we have found in  $\text{TBA}_3\text{H}_2[\gamma\text{-SiO}_4\text{W}_{10}\text{O}_{32}(\text{OH})\text{Cr}_2(\text{OOCCH}_3)_2(\text{OH}_2)_2]\cdot 3\text{H}_2\text{O}$  1.91–2.06 Å ( $P2_12_12_1$ ;  $a = 17.608(12)$  Å,  $b = 20.992(13)$  Å,  $c = 24.464(11)$  Å;  $Z = 4$ ;  $R = 0.058$ ) and in  $\text{K}_{5.25}\text{H}_{7.75}[A-\alpha\text{-SiO}_4\text{W}_9\text{MoO}_{33}(\text{OH})\text{Cr}_2(\text{OH})(\text{OH}_2)]\cdot 9\text{H}_2\text{O}$  1.92–2.08 Å ( $I4_1/a$ ;  $a, b = 39.119(4)$  Å,  $c = 11.799(2)$  Å;  $Z = 16$ ;  $R = 0.062$ ).

(21) Springborg, J. *Adv. Inorg. Chem.* **1988**, *32*, 55.

(22) The conductometric and potentiometric titrations of  $\text{H}_{11}[\{A-\alpha\text{-SiO}_4\text{W}_9\text{O}_{30}(\text{OH})_3\text{Cr}_3\}_2(\text{OH})_3]\cdot 8\text{H}_2\text{O}$  reveal only one type of titratable protons. A total of 11 freely mobile protons have been found, which agrees with the assumption of nine bridging hydroxo groups.

(23) Lunk, H.-J.; Salmen, M.; Weiner, H.; Baecker, Ch.; Wilde, W.; Müller, D. Z. *Anorg. Allg. Chem.* **1989**, *568*, 171.

(24) Johnson, C. K., *ORTEP*; Report ORN1–3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.

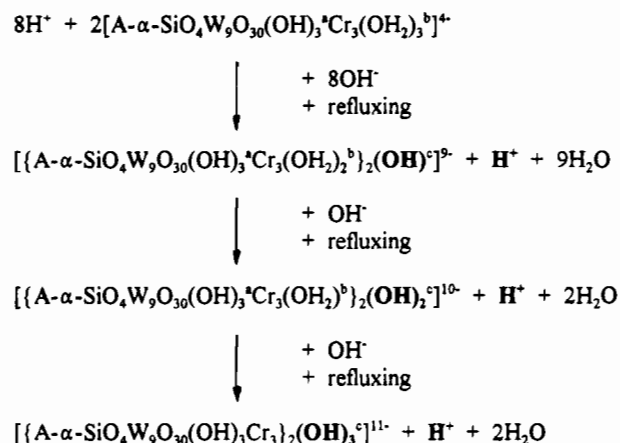


**Figure 2.** Conductometric ( $\blacktriangle$ ) and potentiometric titration ( $\bullet$ ) in 0.01 M aqueous solution: (a)  $H_5[\alpha\text{-SiO}_4W_9O_{30}(\text{OH})_3\text{Cr}_3(\text{OH}_2)_2]\cdot 5\text{H}_2\text{O}$ ; (b)  $H_5[\text{A-}\alpha\text{-SiO}_4W_{10}O_{33}(\text{OH})\text{Cr}_2(\text{OH}_2)_2]\cdot 5\text{H}_2\text{O}$ ; (c)  $H_4[\text{A-}\alpha\text{-SiO}_4W_9O_{30}(\text{OH})_3\text{Cr}_3(\text{OH}_2)_3]\cdot 3\text{H}_2\text{O}$ .

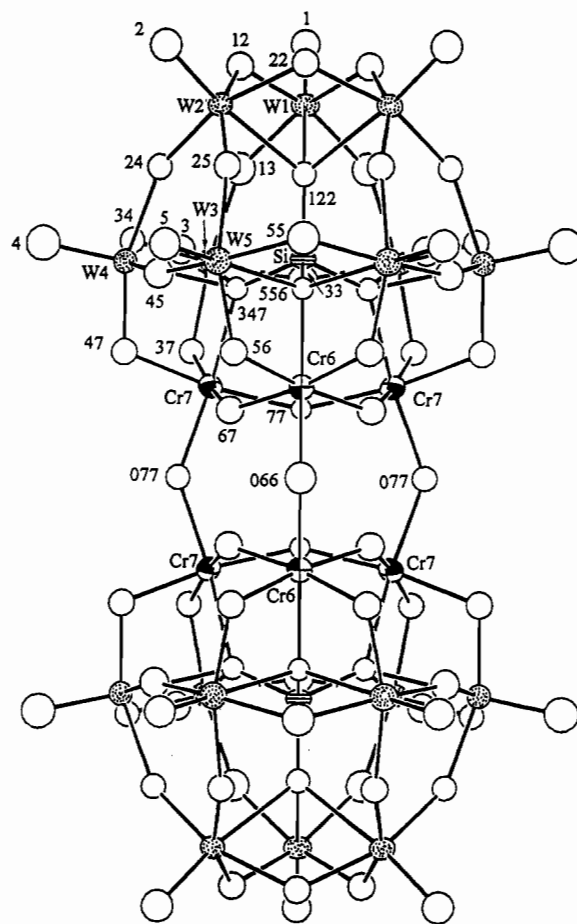
shown in Figure 3. The new anion is formed by two "A- $\alpha$ - $\text{SiO}_4W_9O_{30}(\text{OH})_3\text{Cr}_3$ " units which are linked by three Cr—OH—Cr bridges. Atomic coordinates are given in Table 2. The chemical composition of the ammonium salt was obtained by chemical analysis of single crystals. The positions for the atoms Z(1)—Z(8) correspond to  $\text{H}_2\text{O}$  and  $\text{NH}_4^+$ , respectively. As the comparison with the structural details for the "monomer"<sup>6e</sup> reveals (Table 3), neither the Cr—O(H) and W—O bond lengths and bond angles nor the metal—metal distances are substantially affected by the condensation reaction. The six  $\text{Cr}^{\text{III}}$  form a trigonal prism with Cr—Cr distances of 3.62 Å within the monomer units and 3.61–3.62 Å between the "dimer halves" (Figure 4).<sup>25</sup> The Cr—OH—Cr bond angles in the "dimer

(25) Dowty, E. *Atoms 2.31*; Shape Software, 1993.

**Scheme 1** Course of Reaction for the Successive Steps of the Condensation of the Keggin Anions<sup>a</sup>



<sup>a</sup> Protonated bridging oxygen between corner-linked  $\text{CrO}_6$  octahedra (favored) or edge-linked  $\text{CrO}_6$ — $\text{WO}_6$  octahedra, respectively. <sup>b</sup> Terminal water ligands. <sup>c</sup> Hydroxo bridge between the monomeric units in the "dimer".



**Figure 3.** ORTEP<sup>20</sup> drawing and atomic labeling of  $[\{\text{A-}\alpha\text{-SiO}_4W_9O_{30}(\text{OH})_3\text{Cr}_3\}_2(\text{OH})_3]^{11-}$ .

halves" were found to be 135(1)° and between the two  $\alpha$ -Keggin fragments 134(2) and 136(1)° compared to 131(1) and 132(2)° in  $[\text{A-}\alpha\text{-SiO}_4W_9O_{30}(\text{OH})_3\text{Cr}_3(\text{OH}_2)_3]^{4-}$ . The Cr—O bond lengths observed are typical of chromium(III) in an octahedral oxygen coordination, and display  $\text{Cr}^{\text{III}}$  in an almost ideal octahedral environment.<sup>20,21</sup> As pointed out above we expect all nine bridging oxygens between the  $\text{CrO}_6$  octahedra to be protonated. The bond valence calculation<sup>19</sup> for assumed hydroxo bridges reveals values of 2.0–2.1. Furthermore, this statement has been confirmed by chemical analysis (N, K) and IR spectroscopy.

**Table 2.** Atomic Coordinates and Isotropic (Si, O, N) or Equivalent Isotropic (W, Cr, Cl) Thermal Parameters ( $\text{\AA}^2$ )

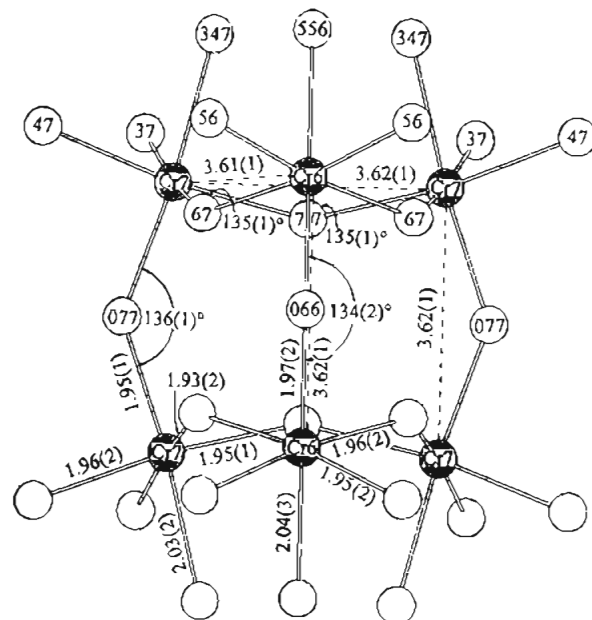
	$x/a$	$y/b$	$z/c$	$U$
W(1)	$1/4$	0.58491(8)	0.51557(8)	0.0268(6) <sup>a</sup>
W(2)	0.32728(6)	0.58522(6)	0.37847(6)	0.0253(4) <sup>a</sup>
W(3)	0.33598(6)	0.44614(6)	0.56565(5)	0.0252(4) <sup>a</sup>
W(4)	0.41338(6)	0.44620(6)	0.42827(6)	0.0252(4) <sup>a</sup>
W(5)	0.32770(6)	0.44714(6)	0.27649(6)	0.0267(4) <sup>a</sup>
Cr(6)	$1/4$	0.3331(3)	0.3255(3)	0.023(2) <sup>a</sup>
Cr(7)	0.1669(2)	0.3331(2)	0.4719(2)	0.023(1) <sup>a</sup>
Si	$1/4$	0.4494(5)	0.4237(6)	0.024(3) <sup>a</sup>
O(1)	$1/4$	0.639(1)	0.571(1)	0.035(8)
O(12)	0.3093(9)	0.6195(9)	0.4604(9)	0.030(5)
O(122)	$1/4$	0.524(1)	0.423(1)	0.024(6)
O(13)	0.309(1)	0.529(1)	0.542(1)	0.040(6)
O(2)	0.378(1)	0.638(1)	0.350(1)	0.042(6)
O(22)	$1/4$	0.623(1)	0.355(1)	0.030(7)
O(24)	0.3823(9)	0.5300(9)	0.4182(9)	0.025(4)
O(25)	0.3200(9)	0.5313(9)	0.3115(9)	0.029(5)
O(3)	0.362(1)	0.457(1)	0.637(1)	0.033(5)
O(33)	$1/4$	0.431(1)	0.581(1)	0.035(8)
O(34)	0.4070(9)	0.4646(9)	0.5163(9)	0.026(5)
O(347)	0.1898(8)	0.4224(8)	0.4581(8)	0.020(4)
O(37)	0.3512(9)	0.3652(9)	0.5564(9)	0.025(5)
O(4)	0.489(1)	0.462(1)	0.414(1)	0.049(7)
O(45)	0.382(1)	0.436(1)	0.344(1)	0.035(5)
O(47)	0.4133(9)	0.3644(9)	0.4448(9)	0.029(5)
O(5)	0.377(1)	0.462(1)	0.217(1)	0.040(6)
O(55)	$1/4$	0.468(2)	0.236(2)	0.043(9)
O(556)	$1/4$	0.423(1)	0.353(1)	0.019(6)
O(56)	0.3121(9)	0.3651(9)	0.2681(9)	0.031(5)
O(66)	$1/4$	$1/4$	0.289(2)	0.04(1)
O(67)	0.185(1)	0.312(1)	0.3858(9)	0.032(5)
O(77)	0.138(1)	$1/4$	0.490(1)	0.025(7)
O(777)	$1/4$	0.313(1)	0.499(1)	0.017(6)
Cl(1)	$1/4$	$3/4$	$1/4$	0.053(8)
Cl(2)	0.4974(7)	$1/4$	0.5647(8)	* 0.062(5)
Z(1)	$1/4$	0.366(2)	0.139(2)	0.06(1)
Z(2)	$1/4$	$3/4$	0.398(3)	0.04(1)
Z(3)	0.499(1)	0.604(1)	0.412(1)	0.043(7)
Z(4)	0.423(2)	0.618(2)	0.532(2)	0.06(1)
Z(5)	0.359(2)	$3/4$	0.480(2)	0.06(1)
Z(6)	$1/4$	0.604(2)	0.213(2)	0.04(1)
Z(7)	$1/4$	$3/4$	$3/4$	1.2(3)
Z(8)	0.441(4)	0.307(4)	0.316(4)	0.22(4)

$$^a U_{eq} = 1/3 \sum_i U_{ij} a_i^* a_j^* a_i a_j$$

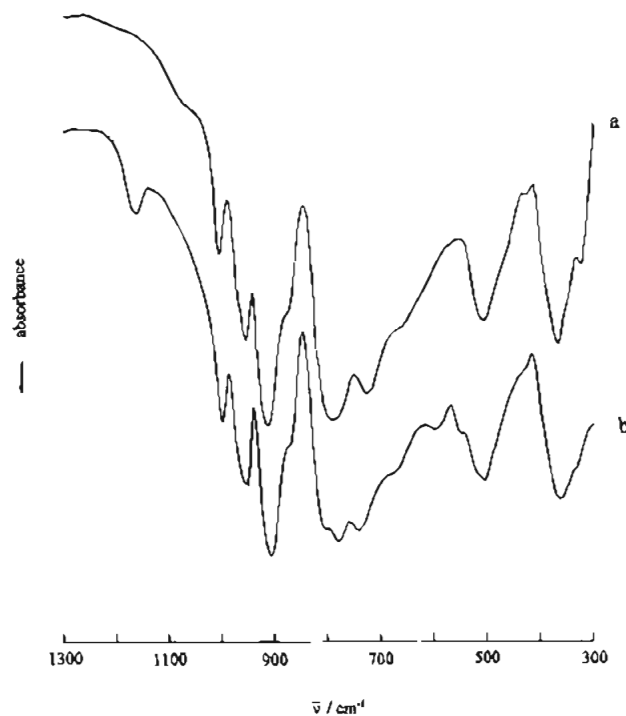
**Characterization in the Solid State. IR Spectroscopy.** The IR spectra of both "monomer" and "dimer" ( $\text{K}^+$  salt) are compared in Figure 5. The main distinguishing feature is the sharp band at  $1163 \text{ cm}^{-1}$  for the bending mode  $\delta(\text{Cr-O-H})$  of the bridging OH groups in the dimer between the  $\text{CrO}_6$  octahedra compared to the monomer, which shows in this region only a weak broad band. Furthermore, the splitting (shoulder) in the region  $810\text{--}770 \text{ cm}^{-1}$ ,  $\nu_{as}(\text{W-O}_c\text{-W})$ , and additional or more intense bands, respectively, for the stretching vibration  $\nu(\text{Cr-O})$  of 739, 675, 597, and  $547 \text{ cm}^{-1}$  confirm the structure of the "Keggin dimer".<sup>26</sup>

**ESR Spectroscopy.** Lacunary Keggin anions allow the substitution with heteroelements in different numbers, various

(26) For the anions  $\{[\text{A-}\alpha\text{-SiO}_4\text{W}_9\text{O}_{30}(\text{OH})_3\text{Al}_3\text{]}_2(\text{OH})_3\}^{11-}$ , VIII,  $\{[\text{A-}\alpha\text{-SiO}_4\text{W}_{10}\text{O}_{32}(\text{OH})\text{Cr}_2\text{]}_2\text{O}_2(\text{OH})\}^{11-}$ , IX,  $\{[\text{A-}\alpha\text{-SiO}_4\text{W}_9\text{MoO}_{32}(\text{OH})\text{Cr}_2\text{]}_2\text{O}_2(\text{OH})\}^{11-}$ , X, we have been able to observe similar structural features. The  $\text{Al}^{\text{III}}$ -containing "dimer" could be regarded as the diamagnetic species analogous to the title anion. The "dimer's"  $^{27}\text{Al}$  MAS NMR spectrum exhibits, in contrast to the monomeric anion  $[\text{A-}\alpha\text{-SiO}_4\text{W}_9\text{O}_{30}(\text{OH})_3\text{Al}_3(\text{OH}_2)_3]^{4-}$ , aluminum(III) in an ideal octahedral oxygen environment. The structural analysis of IX reveals Cr and W disordered in the trigonal prismatic unit. Furthermore, the spectroscopic results (IR, ESR, UV/vis) provide evidence that the linking in IX and X occurs via  $1 \times \text{Cr-Cr}$  and  $2 \times \text{Cr-W}$  or  $2 \times \text{Cr-Mo}$ , respectively. The characterization of these anions will be published in the near future.



**Figure 4.** Trigonal prismatic bridging unit in  $\{[\text{A-}\alpha\text{-SiO}_4\text{W}_9\text{O}_{30}(\text{OH})_3\text{Cr}_3\text{]}_2(\text{OH})_3\}^{11-}$  with bond lengths, metal-metal distances ( $\text{\AA}$ ), and selected bond angles (deg).<sup>25</sup>



**Figure 5.** IR spectra of  $\text{K}_4[\text{A-}\alpha\text{-SiO}_4\text{W}_9\text{O}_{30}(\text{OH})_3\text{Cr}_3(\text{OH})_3] \cdot 13\text{H}_2\text{O}$  (a) and  $\text{K}_{11}\{[\text{A-}\alpha\text{-SiO}_4\text{W}_9\text{O}_{30}(\text{OH})_3\text{Cr}_3]_2(\text{OH})_3\} \cdot 11\text{H}_2\text{O}$  (b). The newly observed band at  $1163 \text{ cm}^{-1}$  is related to the bending modes of bridging OH groups in the dimer between the  $\text{CrO}_6$  octahedra.

coordination numbers (tetrahedral, octahedral), and ways of linkage (corners, edges). Furthermore, the oxidation state of the metal ions and the electronic structure of the anion can be changed gradually.<sup>1,27</sup> This and especially the weak interactions between the paramagnetic metal ions of different anions make polyoxo anions attractive to spectroscopic investigations, like ESR spectroscopy.<sup>1,28</sup>

For monochromium(III)-substituted Keggin anions the oxidation to  $\text{Cr}^{\text{V}}$  was observed a few years ago.<sup>29</sup> As a part of our

(27) (a) Piepgrass, K.; Pope, M. T. *J. Am. Chem. Soc.* **1987**, *109*, 1586. (b) Casañ-Pastor, N.; Gómez-Romero, P.; Jameson, G. B.; Baker, L. C. W. *J. Am. Chem. Soc.* **1991**, *113*, 5658.

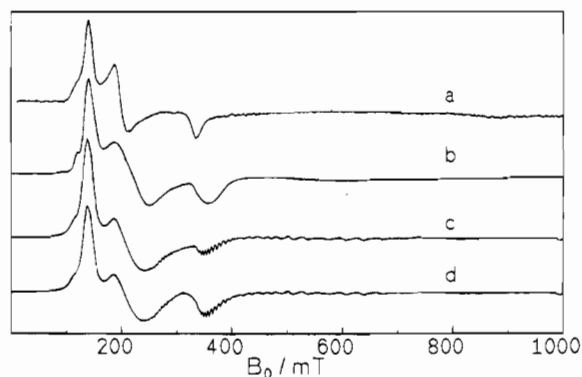
**Table 3.** Comparison of Selected Bond Lengths and Metal–Metal Distances in  $(\text{NH}_4)_3[\text{A}-\alpha\text{-SiO}_4\text{W}_9\text{O}_{30}(\text{OH})_3\text{Cr}_3(\text{OH})_2]\cdot 6\text{H}_2\text{O}\cdot 2.5\text{NH}_4\text{Cl}$  and in  $\text{K}_3\text{H}[\text{A}-\alpha\text{-SiO}_4\text{W}_9\text{O}_{33}(\text{OH})_3\text{Cr}_3(\text{OH})_2]\cdot 11\text{H}_2\text{O}^{6f}$ 

	$[\text{A}-\alpha\text{-SiO}_4\text{W}_9\text{O}_{30}(\text{OH})_3\text{Cr}_3(\text{OH})_2]^{11-}$		$[\text{A}-\alpha\text{-SiO}_4\text{W}_9\text{O}_{30}(\text{OH})_3\text{Cr}_3(\text{OH})_2]^{4-}$	
	M = Cr	M (M') = W	M = Cr	M (M') = W
M–O <sub>i</sub> <sup>a</sup>	2.03(2)–2.04(3)	2.35(2)–2.41(2)	1.98(3)–2.03(2)	2.32(2)–2.42(2)
M–O <sub>c</sub>	1.93(2)–1.97(2)	1.85(2)–1.99(2)	1.96(2)–2.01(3)	1.85(2)–1.99(2)
M–O <sub>e</sub>	1.95(1)–1.97(2)	1.90(2)–1.94(2) <sup>c</sup>	1.95(2)–1.96(2)	1.94(2)–1.96(2) <sup>c</sup>
		1.91(2)–1.96(2) <sup>y</sup>		1.94(3)–1.99(2) <sup>d</sup>
		1.80(2)–1.83(2) <sup>z</sup>		1.79(2)–1.83(2) <sup>e</sup>
M–O <sub>t</sub>		1.65(2)–1.71(2)	1.98(3)–2.00(3)	1.69(3)–1.73(2)
M–M <sub>c</sub> <sup>b</sup>	3.61(1)–3.62(1)	3.71(1)–3.74(1)	3.60(1)–3.64(1)	3.72(1)–3.77(1)
M–M <sub>e</sub>		3.37(1)–3.38(1)		3.37(1)–3.41(1)
M–M' <sub>e</sub>		3.16(1)–3.18(1)		3.15(1)–3.18(1)

<sup>a</sup> O<sub>i</sub>: belonging both to three MO<sub>6</sub> octahedra and the central SiO<sub>4</sub> tetrahedron. O<sub>c</sub>: corner-sharing oxygen. O<sub>e</sub>: edge-sharing oxygen. O<sub>t</sub>: terminal oxygen atom. <sup>b</sup> M–M<sub>c</sub>: corner-sharing MO<sub>6</sub> octahedra. M–M<sub>e</sub>: edge-sharing MO<sub>6</sub> octahedra. <sup>c</sup> W–O<sub>e</sub>–(W) inside a W<sub>3</sub>O<sub>13</sub> group. <sup>y</sup> W–O<sub>e</sub>–(W) inside a W<sub>2</sub>CrO<sub>13</sub> group. <sup>d</sup> W–O<sub>e</sub>–(Cr) inside a W<sub>2</sub>CrO<sub>13</sub> group.

study we have extended the oxidation experiments on  $[\text{A}-\alpha\text{-SiO}_4\text{W}_9\text{Mo}_2\text{O}_{35}\text{Cr}(\text{OH})_2]^{5-}$  and multiple substituted Keggin anions. We have isolated solid samples of intact Keggin anions containing Cr<sup>V</sup> in good yields for the mono- and even for the dichromium-substituted anions, which seems to be a remarkable result for the latter type of anion. The powdered crystalline compounds are stable on air stored at low temperatures (–16 °C) for months. The existence of the triply Cr<sup>V</sup>-substituted anion was proven in acetonitrile solution, but it could not be isolated as solid samples. However, our ESR study has been focused on chromium(III) in Keggin anions to follow the spin resonance behavior for different numbers of incorporated Cr<sup>III</sup> ions yielding various structural arrangements. The Cr<sup>III</sup> centers undergo a diamagnetic dilution in polyoxometalates by tungsten and the counteranions, which offers unique possibilities to study structural details including weak exchange interactions. Within this publication we shall present some new results of the measured series of powdered crystalline samples. It seems to be worthwhile to discuss these findings in more detail.

The experimental and completely simulated<sup>30,31</sup> ESR spectra for  $\text{K}_5[\text{A}-\alpha\text{-SiO}_4\text{W}_{11}\text{O}_{35}\text{Cr}(\text{OH})_2]\cdot 9\text{H}_2\text{O}$  are given in Figure 6b,c. The parameters for the zero field splitting (zfs),  $|D| = 0.916 \text{ cm}^{-1}$ , and  $|E| = 0.108 \text{ cm}^{-1}$ , reveal a rhombohedral distortion of the CrO<sub>6</sub> octahedron. The magnetic dipole–dipole interactions between the Cr<sup>III</sup> ions was represented in all simulations by an appropriate line width. For  $\text{K}_5[\text{A}-\alpha\text{-SiO}_4\text{W}_9\text{Mo}_2\text{O}_{35}\text{Cr}(\text{OH})_2]\cdot 14\text{H}_2\text{O}$  which crystallizes tetragonally<sup>32</sup> like the former compound, we observed the similar spectra given in Figure 6a, with a reduced axial distortion for the CrO<sub>6</sub> octahedron,  $|D| = 0.783 \text{ cm}^{-1}$  and  $|E| = 0.1 \text{ cm}^{-1}$ , respectively. At this time this statement could not be derived from other methods. It should be mentioned that the reproduction of the experimental spectra by simulation required for both systems



**Figure 6.** ESR spectra of  $\text{K}_5[\text{A}-\alpha\text{-SiO}_4\text{W}_9\text{Mo}_2\text{O}_{35}\text{Cr}(\text{OH})_2]\cdot 14\text{H}_2\text{O}$  (a) and  $\text{K}_5[\text{A}-\alpha\text{-SiO}_4\text{W}_{11}\text{O}_{35}\text{Cr}(\text{OH})_2]\cdot 9\text{H}_2\text{O}$  (b) at 77 K. The observed spectrum (b) was simulated with a Gaussian distribution around  $|D| = 0.916 \text{ cm}^{-1}$ ,  $|E| = 0.108 \text{ cm}^{-1}$  (c); superposition of 10% of a single Lorentz line ( $g' = 1.98$ , line width: 250 mT) to the simulated spectrum c gives spectrum d.

not only a distribution of zfs parameters but also the consideration of a small amount of exchange interaction, Figure 6d. The last has also been proved independently by the data obtained from the low temperature magnetic susceptibility for  $\text{K}_5[\text{A}-\alpha\text{-SiO}_4\text{W}_{11}\text{O}_{35}\text{Cr}(\text{OH})_2]\cdot 9\text{H}_2\text{O}$ . From a structural point of view (closest interanionic Cr–Cr approach 5.5–6.0 Å), this is an unexpected effect and shows the sensitivity of the magnetic methods with respect to small structural changes and weak magnetic interactions between the substituted polyoxo anions.

The incorporation of a second Cr<sup>III</sup> into the Keggin anions of  $\text{K}_5[\text{A}-\alpha\text{-SiO}_4\text{W}_{10}\text{O}_{33}(\text{OH})\text{Cr}_2(\text{OH})_2]\cdot 11\text{H}_2\text{O}$  and  $\text{K}_5.5\text{H}_0.5[\text{A}-\alpha\text{-SiO}_4\text{W}_9\text{MoO}_{33}(\text{OH})\text{Cr}_2(\text{OH})(\text{OH})_2]\cdot 11\text{H}_2\text{O}$  has a remarkable effect on the pattern of the ESR spectra, Figure 7a. The magnetic behavior is characterized by dominant exchange coupling between the Cr<sup>III</sup> centers belonging to the same anion, yielding the main signal at  $g' = 1.98$ . Beside these exchange coupled species a weaker low field signal was observed, which might be attributed to less effective coupled Cr<sup>III</sup> ions ( $S = 3/2$ , Figure 7d) or to a system with  $S = 1$ . The obtained spectra for the free acid show such behavior very clearly at different temperatures, Figure 7b–d. The assumption of coexisting paramagnetic species is supported by the temperature dependence of the signals. However, all signals for the Mo-containing anion exhibit a better spectral resolution, which is caused by small symmetry changes in the neighborhood of the chromium(III) ion.

For the triply chromium(III)-substituted Keggin anion the interesting fact has been observed, that the shape of the spectra is characterized by a strong dependence on the counter ions ( $\text{H}^+$ ,  $\text{K}^+$ ,  $\text{Cs}^+$ ,  $\text{TBA}^+$ ) present, Figure 8. As proved by the

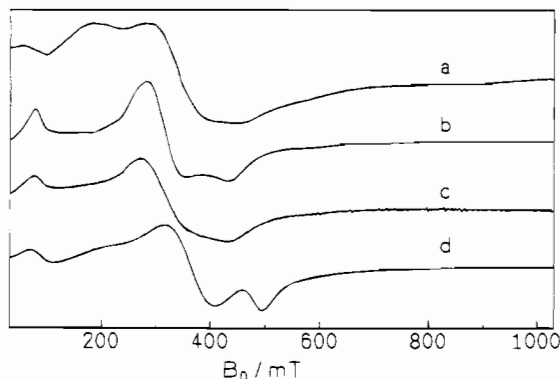
- (28) (a) Harmalkar, S. P.; Pope, M. T. *J. Inorg. Biochem.* **1986**, *28*, 85. (b) Katsoulis, D. E.; Pope, M. T. *J. Chem. Soc., Dalton Trans.* **1989**, 1483. (c) Gómez-García, C. J.; Coronado, E.; Borrás-Almenar, J. J. *Inorg. Chem.* **1992**, *31*, 1667.
- (29) Katsoulis, D. E.; Pope, M. T. *J. Chem. Soc., Chem. Commun.* **1986**, 1186. (b) Khenkin, A. M.; Hill, C. L. *J. Am. Chem. Soc.* **1993**, *115*, 8178.
- (30) The ESR spectra for the chromium(III)-substituted Keggin anions were completely simulated by diagonalization of the following spin Hamiltonian operator:

$$H = g\beta H S + D[S_z^2 - \frac{1}{3}S(S+1)] + E(S_{xz} - S_{yz})$$

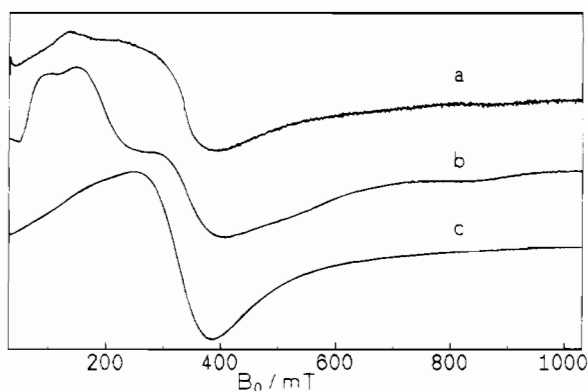
$$S = 3/2; i = x, y, z$$

To reproduce the full pattern of the experimental spectra the use of anisotropic and transition dependent line widths was necessary.

- (31) Pedersen, E.; Toftlund, H. *Inorg. Chem.* **1974**, *13*, 1603.
- (32)  $\text{K}_5[\text{A}-\alpha\text{-SiO}_4\text{W}_9\text{Mo}_2\text{O}_{35}\text{Cr}(\text{OH})_2]\cdot 9\text{H}_2\text{O}$  crystallizes tetragonal in space group *P4nc*. The positions of chromium and molybdenum beside tungsten in the anion could not be refined.



**Figure 7.** ESR spectra of  $K_5[A-\alpha-SiO_4W_9O_{30}(OH)Cr_2(OH_2)_2] \cdot 11H_2O$  at 77 K (a) and  $H_5[A-\alpha-SiO_4W_9O_{30}(OH)Cr_2(OH_2)_2] \cdot 5H_2O$  at 77 K (b) and 297 K (c). For the observed spectra of the free acid a simulated spectrum (d) consisting of two components was generated: 30%  $|D| = 0.200 \text{ cm}^{-1}$ ,  $|E| = 0$  and 70% of a single Lorentz line ( $g' = 1.98$ , line width 50 mT).



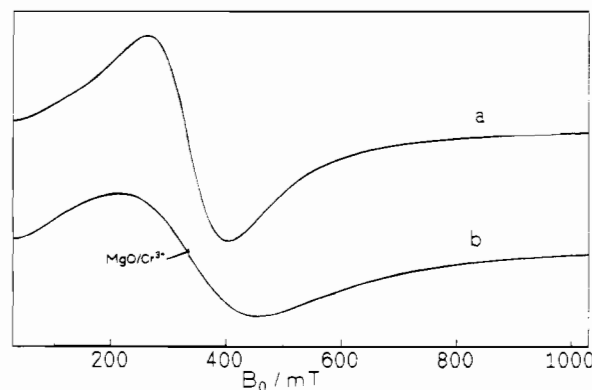
**Figure 8.** Influence of protons, OH groups and potassium content on the ESR spectra of  $H_4[A-\alpha-SiO_4W_9O_{30}(OH)_3Cr_3(OH_2)_3] \cdot 3H_2O$  (a),  $K_4[A-\alpha-SiO_4W_9O_{30}(OH)_3Cr_3(OH_2)_3] \cdot 13H_2O$  (b), and  $K_7[A-\alpha-SiO_4W_9O_{30}(OH)_3Cr_3(OH_2)_3] \cdot 10H_2O$  (c) at 77 K.

analyses of the spectra the effectiveness of the exchange interaction inside and between the anions is sensitively influenced by the number of protons and proton-containing groups like OH, OH<sub>2</sub> and crystal water present. The results revealed that the interanionically mediated interactions of the Cr<sup>III</sup> centers take place via the terminal water molecules and can be forced by their deprotonation,<sup>33</sup> Figure 8c. This means that from a magnetic point of view the crucial structural unit in the anions is similar to that present in the chromium(III)- $\mu$ -hydroxo complexes.<sup>34</sup>

A new dimension of magnetic interaction has been established by the formation of a special "Keggin dimer" with the consequence of a very special arrangement of six corner-bridged CrO<sub>6</sub> octahedra. There is no report in the literature available concerning such a structural arrangement, Figure 4. The ESR spectra of the dimeric species at 77 and 297 K consist of almost isotropic lines (Lorentz shape) with  $g$  values of 1.98, Figure 9. Inspection of all ESR spectra obtained gives evidence for the structurally supported effectiveness of exchange interactions between the Cr<sup>III</sup> centers. For example the free acid shows a more narrow signal with a line width (peak to peak) of 130 mT at 77 K (137 mT at 297 K) than the potassium salt with 230

(33) For  $K_7[A-\alpha-SiO_4W_9O_{30}(OH)_3Cr_3(OH_2)_3] \cdot 10H_2O$  we assume deprotonated terminal water ligands which cause a more effective exchange interactions between the Cr<sup>III</sup> centers shown by a significant line narrowing.

(34) Goodson, P. A.; Glerup, J.; Hodgson, D. J.; Michelsen, K.; Rychlewska, U. *Inorg. Chem.* **1994**, *33*, 359.



**Figure 9.** ESR spectra of  $H_{11}[\{A-\alpha-SiO_4W_9O_{30}(OH)_3Cr_3\}_2(OH)_3] \cdot 8H_2O$  (a) and  $K_{11}[\{A-\alpha-SiO_4W_9O_{30}(OH)_3Cr_3\}_2(OH)_3] \cdot 11H_2O$  (b) at 77 K.

mT (310 mT) and the ammonium salt with 270 mT (310 mT), respectively which can—following the discussion given above—be attributed to the increased anion–anion distance and higher water content of the two salts. The numerical analysis of the temperature dependence of the intensity of the ESR signal reveals an energy difference  $\Delta E$  between the antiferromagnetic ground and the paramagnetic state.<sup>35</sup> In this way a value of  $60 \pm 10 \text{ cm}^{-1}$  results for the potassium salt of the "dimer". For the well-studied chromium sesquioxide Cr<sub>2</sub>O<sub>3</sub>,<sup>36</sup> which shows a Lorentz shaped signal at  $g = 1.978$  and a line width of 48 mT,  $\Delta E$  was determined to  $430 \pm 15 \text{ cm}^{-1}$ .<sup>35</sup> As expected, the exchange interaction in Cr<sub>2</sub>O<sub>3</sub> is more effective. This is caused by the larger number of interacting chromium ions per volume in the sesquioxide and by the different ways of linkage of the CrO<sub>6</sub> octahedra.<sup>37</sup>

Our results confirm a general property of chromium(III) characterized by binding forces in a matrix in a way, allowing effective magnetic interactions between the Cr<sup>III</sup> ions known from the study of oxides<sup>38</sup> and glasses.<sup>39</sup> The well-defined structures of the different chromium(III)-substituted Keggin anions yield the basis for more detailed and chemically relevant studies of the electronic and magnetic effects of Cr<sup>III</sup>–Cr<sup>III</sup> interactions. The change from mono chromium(III) substituted anions to the dimeric species with six Cr<sup>III</sup> via di- and trisubstituted anions, has been characterized by an increase of the exchange interactions, which indicate a gradual and controlled adaptation of structural elements of the Cr<sub>2</sub>O<sub>3</sub> structure.

**Acknowledgment.** This work has been supported by a scholarship of the Studienstiftung des deutschen Volkes for K.W. The authors wish to thank Prof. Michael T. Pope, Georgetown University, Washington, DC, for helpful discussions and Dr. Egbert Feike and Dr. Rainer Bertram for analytical support. Thomas Uhlich deserves credit for recording the electronic spectra.

**Supporting Information Available:** Tables of atomic anisotropic displacement parameters, bond distances, bond angles and contact distances are available (3 pages). Ordering information is given on any current masthead page.

IC950131E

(35) Dräger, K., *Ber. Bunsen-Ges. Phys. Chem.* **1975**, *79*, 996.

(36) Newnham, R. E., de Haan, Y. M. *Z. Kristallogr.* **1962**, *117*, 235.

(37) In Cr<sub>2</sub>O<sub>3</sub> (corundum structure) the linkage between CrO<sub>6</sub> octahedra occurs via common faces (2.65 Å, 82.3°), edges (2.89 Å, 93.1°) and corners (3.43 Å, 121.4°; 3.65 Å, 133.1°), respectively (Cr–Cr distances, Cr–O–Cr angles in parentheses), from ref 36.

(38) Dräger, K. *Z. Naturforsch.* **1988**, *43A*, 262.

(39) (a) Landry, R. J.; Fournier, J. T.; Yang, C. G. *J. Chem. Phys.* **1967**, *46*, 1285. (b) Fournier, J. T.; Landry, R. J.; Bartram, R. H. *J. Chem. Phys.* **1971**, *55*, 2522.