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## Preparation and Characterization of Two New Isomorphous Heteropoly Oxofluorotungstate Anions: $[\text{CoW}_{17}\text{O}_{56}\text{F}_6\text{NaH}_4]^{9-}$ and $[\text{FeW}_{17}\text{O}_{56}\text{F}_6\text{NaH}_4]^{8-}$

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The ammonium salts of  $[\text{CoW}_{17}\text{H}_4\text{NaO}_{56}\text{F}_6]^{9-}$  and  $[\text{FeW}_{17}\text{H}_4\text{NaO}_{56}\text{F}_6]^{8-}$  have been isolated in crystalline form. X-ray powder patterns of the two compounds are identical. The crystals of  $(\text{NH}_4)_9(\text{FeW}_{17}\text{O}_{56}\text{F}_6\text{NaH}_4) \cdot 8\text{H}_2\text{O}$  belong to the space group *Pnma*, with  $a = 18.015 \text{ \AA}$ ,  $b = 17.743 \text{ \AA}$ ,  $c = 21.860 \text{ \AA}$ ,  $V = 6987 \text{ \AA}^3$ ,  $Z = 4$ ,  $D(\text{calcd}) = 4.283 \text{ g cm}^{-3}$ , and  $R = 0.113$ . FABMS and MS/MS, analytical, spectroscopic (visible, infrared), and X-ray evidence is presented which strongly indicates that the anions in the two isomorphous compounds have the Dawson structure, wherein one  $\text{Fe}^{3+}$  or  $\text{Co}^{2+}$  replaces one  $\text{W}^{6+}$  in the conventional  $\text{X}_2\text{W}_{18}\text{O}_{70}$  formulation. Polarograms of the new fluorinated anions have multiple electron addition steps with  $E_{1/2}$  for the first electronic addition  $-0.2 \text{ V}$  relative to the standard calomel electrode. Tandem mass spectrometry is shown to be a useful technique for the characterization of large inorganic complexes.

### Introduction

The so-called heteropoly electrolytes are members of a very large class of polynuclear oxo complexes ("isopoly and heteropoly anions") of the transition metals of groups V and VI, especially molybdenum, tungsten, and vanadium.<sup>1-6</sup> The polymerization of vanadate, molybdate, and tungstate ions to form isopoly anions (and heteropoly anions, in the presence of heteroatoms) has received a great deal of attention because of the importance of these compounds as models for electron-transfer mechanisms, as colorimetric reagents in analytical procedures, and as industrial catalysts and, more recently, because of their potential clinical applications.

There are several ways to decrease the overall negative charge on the anion. Among these is the use of heteroatoms of high positive charge. Another way to reduce the negative charge is the replacement of  $\text{W}^{6+}$  with an atom of higher charge or the replacement of oxide ions by fluoride ions (fluoride and oxide ions have approximately the same size).

The replacement of oxide ions by fluoride ions has great structural significance and has been the subject of some recent work. Chauveau et al.<sup>7-10</sup> have reported several fluorine-substituted metatungstates in which oxygen atoms that form the central cavity of the Keggin structure have been partially replaced by fluorine. Baker et al.<sup>11</sup> have reported the preparation and characterization of  $[\text{ZnW}_{17}\text{O}_{56}\text{F}_6\text{NaH}_4]^{9-}$ .

In this paper, we report the preparation and characterization of  $[\text{FeW}_{17}\text{O}_{56}\text{F}_6\text{NaH}_4]^{8-}$  and  $[\text{CoW}_{17}\text{O}_{56}\text{F}_6\text{NaH}_4]^{9-}$  anions in which  $\text{Fe}^{3+}$  or  $\text{Co}^{2+}$  has replaced one  $\text{W}^{6+}$  in the Dawson structure (Figure 1). We also introduce the use of tandem mass spectrometry for the characterization of high molecular weight inorganic compounds.

### Experimental Section

**Preparation of  $(\text{NH}_4)_9(\text{FeW}_{17}\text{O}_{56}\text{F}_6\text{NaH}_4) \cdot 8\text{H}_2\text{O}$ .** A solution of 56 g (170 mmol) of sodium tungstate,  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ , in 250 mL of 1 M hydrofluoric acid in a Teflon-coated beaker was heated to 80 °C. Then a solution of 9 g (22 mmol) of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in 60 mL of distilled water was combined with 15 mL of a saturated sodium acetate solution. The resulting solution containing  $\text{Fe}^{3+}$  was added dropwise to the hot tungstate solution. When the addition was complete, the solution was heated for 30 min and left to cool to room temperature. After filtration, 10 g (187 mmol) of  $\text{NH}_4\text{Cl}$  was added to the filtrate. Immediately a precipitate formed and was removed by filtration. The filtrate was left to crystallize; a mixture of crystals appeared overnight, one type of which were the green  $(\text{NH}_4)_8(\text{FeW}_{17}\text{O}_{56}\text{F}_6\text{NaH}_4) \cdot 8\text{H}_2\text{O}$  crystals. Yield: 5%, based on sodium tungstate. Anal. Calcd for  $(\text{NH}_4)_8(\text{FeW}_{17}\text{O}_{56}\text{F}_6\text{NaH}_4) \cdot 8\text{H}_2\text{O}$ : N, 2.49; F, 2.53; Fe, 1.24; W, 69.35. Found: N, 2.25; F, 2.38; Fe, 1.05; W, 62.92.

Table I. Crystallographic Data for  $(\text{NH}_4)_8(\text{FeW}_{17}\text{O}_{56}\text{F}_6\text{NaH}_4) \cdot 8\text{H}_2\text{O}$

formula	$\text{FeW}_{17}\text{O}_{56}\text{F}_6\text{Na}_8\text{H}_{52}$	Z	4
fw	4506.70	T	23 °C
$D(\text{calcd})$	4.283 g $\text{cm}^{-3}$	$\lambda$	0.71073 Å (Mo K $\alpha$ )
space group	<i>Pnma</i>	$\mu$	313.1 $\text{cm}^{-1}$
a	18.015 (10) Å	max/min transm	6/1
b	17.743 (6) Å	R(R)	0.113
c	21.860 (8) Å	$R_w(F)$	0.113
V	6987 (5) Å <sup>3</sup>		

**Preparation of  $(\text{NH}_4)_9(\text{CoW}_{17}\text{O}_{56}\text{F}_6\text{NaH}_4) \cdot 9\text{H}_2\text{O}$ .** A solution of 56 g (170 mmol) of sodium tungstate,  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ , in 250 mL of 1 M hydrofluoric acid in a Teflon-coated beaker was heated to 80 °C. Then a solution of 6 g (24 mmol) of  $(\text{CH}_3\text{COO})_2\text{Co} \cdot 4\text{H}_2\text{O}$  in 100 mL of distilled water was added dropwise to the hot tungstate solution. After completion of the addition, the solution was heated for 25 min and left to cool to room temperature. The cooled blue-green solution was processed through a column of Sephadex LH-20 resin (Pharmacia Fine Chemicals, Pharmacia Inc., Piscataway, NJ) and separated into two colors, green and brown. Two grams (37 mmol) of  $\text{NH}_4\text{Cl}$  was added to both the green and brown solutions, and they were left to crystallize. Each solution yielded first green cubic crystals and then brown  $(\text{NH}_4)_9(\text{CoW}_{17}\text{O}_{56}\text{F}_6\text{NaH}_4) \cdot 9\text{H}_2\text{O}$  crystals. Yield: 5%, based on sodium tungstate. Anal. Calcd for  $(\text{NH}_4)_9(\text{CoW}_{17}\text{O}_{56}\text{F}_6\text{NaH}_4) \cdot 9\text{H}_2\text{O}$ : N, 2.77; Co, 1.30; W, 68.75; F, 2.51. Found: N, 2.47; Co, 1.45; W, 66.37; F, 2.65. FABMS of the green cubic crystals indicated a molecular weight around 3000 Da, and analysis showed a Co:W:F:N atomic ratio of 2:11:1:7 to suggest a preliminary formulation of  $\text{Co}_2\text{W}_{11}\text{O}_{39}\text{FH}_2 \cdot \text{XH}_2\text{O}$  and a distorted Keggin structure.

**Analytical Methods.** The visible spectrum of the  $[\text{CoW}_{17}\text{O}_{56}\text{F}_6\text{NaH}_4]^{9-}$  anion in water was recorded on a Perkin-Elmer Lambda 3B spectrophotometer in the range 400–900 nm.

The IR spectra were recorded for KBr disks on a Nicolet 20 DX system FTIR spectrometer in the range 4600–400  $\text{cm}^{-1}$ .

Chemical analyses were performed by Galbraith Laboratories, Knoxville, TN 37950-1610.

Powder X-ray patterns were taken for the hydrated ammonium compounds  $(\text{NH}_4)_9(\text{CoW}_{17}\text{O}_{56}\text{F}_6\text{NaH}_4) \cdot 9\text{H}_2\text{O}$  and  $(\text{NH}_4)_8(\text{FeW}_{17}\text{O}_{56}\text{F}_6\text{NaH}_4) \cdot 8\text{H}_2\text{O}$ . Powder patterns were recorded with a Phillips diffractometer employing Cu K $\alpha$  radiation by Peter B. Leavens, Department of Geology,

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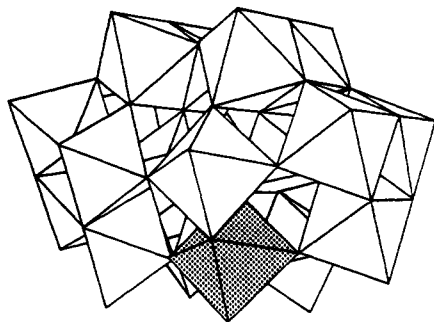


Figure 1. Proposed structure of the  $[XW_{17}H_3O_{56}F_6]^{9-}$  anion.

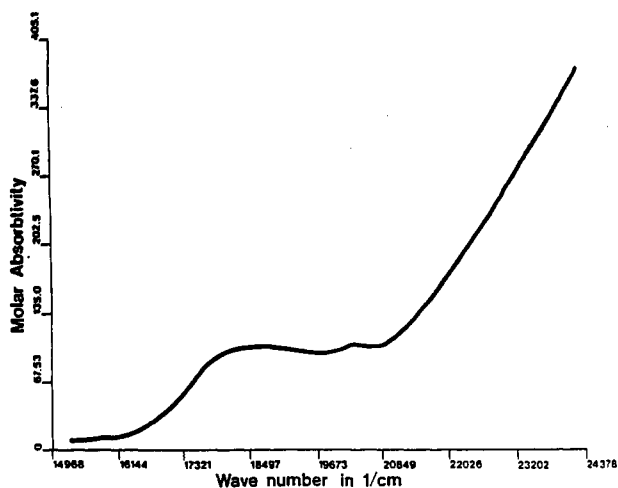


Figure 2. Visible spectrum of  $1.47 \times 10^{-3}$  M  $(NH_4)_9(CoW_{17}O_{56}F_6NaH_4) \cdot H_2O$  in water.

University of Delaware. A Nicolet R3m diffractometer was used for the crystal structure (Table I, Figure 4). Of 5058 data collected, 4723 were independent and 2685 were observed ( $F_o \geq 3\sigma(F_o)$ ). Positional data appear in Table II. All software used is part of the SHELXTL (5.1) library (G. Sheldrick, Nicolet XRD, Madison, WI). Details of both sets of X-ray results are available from the authors upon request.

**Polarographic Studies.** The polarographic behavior of the ammonium salt of the  $[CoW_{17}O_{56}F_6NaH_4]^{9-}$  anion was investigated by using a Sargent-Welch Model 4001 recording polarograph. The dropping mercury electrode assembly consisted of a leveling bulb partially filled with triply distilled mercury connected by rubber tubing to a capillary. Typical capillary characteristics were  $h = 96$  cm from the base,  $t = 3.17$  s/drop, and  $m = 2.626$  mg/s. A standard cell was used. The solution compartment (30-mL volume) was connected to a saturated calomel electrode by a bridge containing a sintered-glass disk and agar gel. Prior to each run, deoxygenation of the solution was accomplished by bubbling nitrogen gas through the cathode chamber for 20 min. The supporting electrolyte was generally 0.9 M  $Na_2SO_4$  solution.

**Mass Spectrometry.** Positive- and negative-ion fast-atom-bombardment mass spectra were recorded for samples dissolved in 1:1 water/glycerol. The spectra were obtained by using the first two sectors of a JEOL HX110/HX110 tandem mass spectrometer, operated at  $\pm 10$ -kV accelerating voltage, with  $\mp 18.5$ -kV postacceleration at the detector. Xenon atoms (6 keV) were used as the primary beam. The resolution was 1:500. The JEOL DA5000 data system was used for instrument control and data acquisition and processing. Negative-ion collision-induced-decomposition (CID) mass spectra were recorded by using all four sectors of the JEOL HX110/HX110 mass spectrometer, an instrument of  $E_1B_1-E_2B_2$  geometry. CID took place in a collision cell located between MS-1 and MS-2, which was operated at 3 kV below ground potential, so that collision energy was 7 keV. Xenon was used as the collision gas, at a pressure sufficient to reduce the precursor ion abundance to 30% of its initial value. Both MS-1 and MS-2 were operated at 1:500 resolution and were calibrated with  $[(Cs)_nCs]^+$  clusters in the positive-ion mode and  $[(Cs)_nI]^-$  clusters in the negative-ion mode. All experimental and calculated mass values given are average values, since individual isotopic peaks would not be resolved at 1:500 resolution.

## Results and Discussion

**Spectroscopy.** The visible spectrum of the  $[CoW_{17}O_{56}F_6NaH_4]^{9-}$  anion (Figure 2) is similar to that of a

Table II. Atomic Coordinates ( $\times 10^4$ ) and Isotropic Thermal Parameters ( $\text{\AA}^2 \times 10^3$ ) for  $(NH_4)_9(FeW_{17}O_{56}F_6NaH_4) \cdot 8H_2O$

	x	y	z	U
W(1)	3108.7 (25)	7500	-2371.3 (19)	56.7 (14) <sup>a</sup>
W(2)	4438.2 (18)	6575.7 (17)	-1647.4 (15)	61.2 (10) <sup>a</sup>
W(3)	4509.7 (17)	6572.5 (16)	36.0 (15)	56.7 (10) <sup>a</sup>
W(4)	3352.6 (18)	6565.8 (16)	1472.3 (14)	59.6 (10) <sup>a</sup>
W(5)	1451.3 (18)	6582.6 (20)	2078.5 (18)	77.3 (13) <sup>a</sup>
W(6)	114.8 (29)	7500	1371.3 (25)	70.9 (19) <sup>a</sup>
W(7)	549.8 (17)	6467.0 (15)	-47.9 (15)	56.6 (10) <sup>a</sup>
W(8)	1691.5 (17)	6454.8 (15)	-1479.8 (14)	54.1 (10) <sup>a</sup>
W(9)	3026.4 (17)	5528.4 (16)	-761.4 (14)	54.0 (9) <sup>a</sup>
W(10)	1874.3 (17)	5528.4 (16)	672.3 (14)	55.1 (10) <sup>a</sup>
Na	2484 (22)	7500	3 (16)	51 (11) <sup>a</sup>
F(1)	2553 (20)	6682 (19)	-763 (15)	49 (8)
F(2)	3752 (29)	7500	-176 (23)	49 (12)
F(3)	2795 (30)	7500	982 (24)	53 (13)
F(4)	1677 (17)	6678 (15)	322 (14)	37 (7)
O(1)	2900 (40)	7500	-3083 (32)	59 (17)
O(2)	2489 (29)	6784 (26)	-2095 (23)	64 (12)
O(3)	3666 (27)	7500	-1494 (21)	25 (10)
O(4)	3857 (24)	6752 (21)	-2396 (18)	46 (10)
O(5)	4919 (56)	7500	-1841 (44)	96 (27)
O(6)	3724 (25)	5873 (22)	-1420 (20)	51 (11)
O(7)	5045 (31)	5912 (29)	-1931 (24)	72 (14)
O(8)	4675 (33)	6641 (30)	-808 (27)	79 (15)
O(9)	3735 (31)	5911 (28)	-165 (23)	70 (14)
O(10)	5091 (52)	7500	222 (40)	87 (24)
O(11)	5118 (27)	6012 (24)	172 (20)	56 (12)
O(12)	4094 (29)	6613 (25)	820 (22)	64 (12)
O(13)	3675 (46)	7500	1814 (36)	73 (21)
O(14)	3801 (32)	5900 (29)	1931 (25)	75 (15)
O(15)	2833 (35)	5902 (32)	989 (27)	83 (16)
O(16)	2535 (25)	6673 (23)	1929 (19)	51 (11)
O(17)	1424 (33)	5949 (29)	2712 (25)	75 (15)
O(18)	1492 (55)	7500	2408 (42)	94 (25)
O(19)	1488 (33)	5900 (29)	1387 (26)	80 (15)
O(20)	531 (18)	6614 (16)	1706 (15)	26 (7)
O(21)	1366 (28)	7500	1377 (22)	27 (11)
O(22)	-808 (40)	7500	1487 (32)	60 (17)
O(23)	245 (24)	6788 (22)	722 (20)	49 (10)
O(24)	-316 (29)	6232 (25)	-319 (22)	59 (12)
O(25)	562 (27)	7500	-228 (21)	24 (11)
O(26)	933 (29)	5534 (26)	293 (22)	65 (13)
O(27)	1122 (31)	6276 (29)	-757 (24)	72 (14)
O(28)	1577 (28)	7500	-1377 (23)	31 (11)
O(29)	1098 (33)	6138 (29)	-2048 (26)	76 (15)
O(30)	2255 (30)	5568 (26)	-1378 (24)	72 (14)
O(31)	3322 (33)	4591 (30)	-871 (27)	80 (16)
O(32)	2313 (30)	5407 (29)	-97 (25)	72 (15)
O(33)	1898 (26)	4606 (23)	869 (21)	56 (11)
O(34)	3934 (41)	4771 (41)	785 (33)	110 (21)
O(35)	6700 (40)	6047 (36)	-1763 (30)	101 (20)
O(36)	6368 (63)	7500	-985 (49)	112 (31)
O(37)	4907 (49)	7500	-3383 (39)	83 (23)
O(38)	-1206 (53)	5597 (50)	805 (41)	147 (31)
N(1)	4630 (36)	4418 (33)	-1458 (30)	68 (16)
N(2)	2106 (41)	4574 (35)	2225 (32)	80 (19)
N(3)	3436 (71)	7500	-4215 (54)	98 (34)

<sup>a</sup> Equivalent isotropic  $U$  defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

typical Co(II) ion in an octahedral environment. There is an unsymmetrical intense band with a maximum at 543 nm ( $18400 \text{ cm}^{-1}$ ), followed by two shoulders toward the UV region. The crystal field portion of the absorption spectrum of the complex is closely related to the spectrum of the  $[Co(H_2O)_6]^{2+}$  ion and to various other Co(II) species in which the cobalt atom is known to be in an octahedral or approximately octahedral ligand environment; it differs only in intensity. The energy levels calculated for a spin-free  $d^7$  ion [ $^4T_{1g}(F)$ ] ground state by Tanabe and Sugano<sup>12</sup> are such that there are three quartet terms above the ground state. The  $^4T_{1g}(F) \rightarrow ^4T_{2g}(F)$  transition normally occurs in the near-IR region between  $7000$  and  $10000 \text{ cm}^{-1}$  well separated from

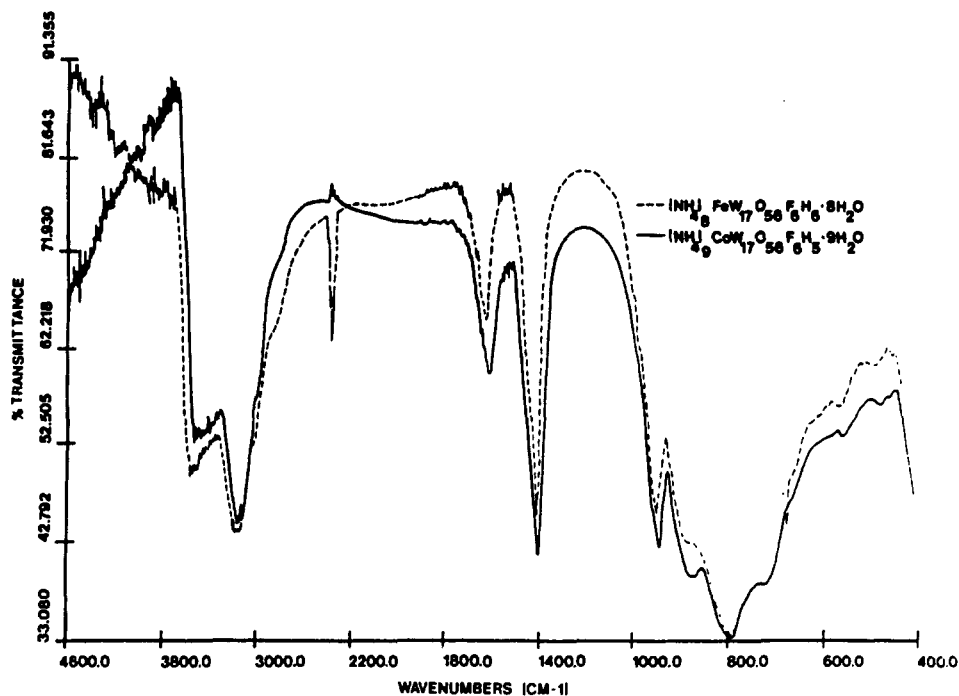


Figure 3. Comparison of the infrared spectra of  $(\text{NH}_4)_9(\text{CoW}_{17}\text{O}_{56}\text{F}_6\text{NaH}_4)\cdot 9\text{H}_2\text{O}$  and  $(\text{NH}_4)_8(\text{FeW}_{17}\text{O}_{56}\text{F}_6\text{NaH}_4)\cdot 8\text{H}_2\text{O}$ .

the other spin-allowed transitions. The band at  $7050\text{ cm}^{-1}$  in 11-tungsto(aquacobalto(II))ferrate(III),  $(\text{H}_2\text{OCoO}_5\text{FeO}_4\text{W}_{11}\text{O}_{30})^{7-}$ , was assigned to the  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$  transition. The band in the visible region at  $17\,540\text{ cm}^{-1}$  was assigned to the  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$  transition.<sup>13</sup> The visible portions of the spectra of octahedral cobaltous complexes consist of a band at around  $20\,000\text{ cm}^{-1}$ . The energies of both the  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$  transition and the  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$  transition are expected in this frequency range. Weakley<sup>14</sup> has made the following assignment for Co(II) in octahedral symmetry in  $[\text{P}_2\text{CoW}_{17}\text{O}_{62}]^{10-}$ . The band at  $7600\text{ cm}^{-1}$  with molar absorptivity 0.812 is due to  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ , and the following two bands at  $18\,300$  and  $19\,800$  with  $\epsilon = 113$  and  $104$ , respectively, are due to the transition  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ . Similarly, we assign the bands at  $18\,085\text{ cm}^{-1}$  ( $\epsilon = 100$ ) and  $20\,200\text{ cm}^{-1}$  to the same transition, i.e.,  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ , although the spectral assignments were made on basis of  $O_h$  symmetry and the true site symmetry of Co(II) is likely to be lower and lack a center of symmetry.

The IR spectrum of the hydrated compound  $(\text{NH}_4)_8(\text{FeW}_{17}\text{O}_{56}\text{F}_6\text{NaH}_4)\cdot 8\text{H}_2\text{O}$  was very similar to that of the compound  $(\text{NH}_4)_9(\text{CoW}_{17}\text{O}_{56}\text{F}_6\text{NaH}_4)\cdot 9\text{H}_2\text{O}$ . The similarity of the IR spectra of the two compounds extends over the whole range ( $4600\text{--}400\text{ cm}^{-1}$ ), as shown in Figure 3.

**X-ray Determinations.** The powder X-ray patterns taken from  $2$  to  $60^\circ$  for the two hydrated compounds were also identical. The crystal structure of  $(\text{NH}_4)_8(\text{FeW}_{17}\text{O}_{56}\text{F}_6\text{NaH}_4)\cdot 8\text{H}_2\text{O}$  was determined for a yellow green crystal mounted on a glass fiber. X-ray crystallographic results for  $(\text{NH}_4)_8(\text{FeW}_{17}\text{O}_{56}\text{F}_6\text{NaH}_4)\cdot \text{H}_2\text{O}$  (Table I, Figure 4, and supplementary material) showed that it belongs to the orthorhombic space group  $Pnma$ ; this assignment was confirmed by the structural results for the tungstate anion, which showed a chemically reasonable framework. Correction for absorption used an empirical method that obtains an absorption tensor from an expression relating  $F_0$  and  $F_c$  written by H. Hope.

The structure was solved by direct methods. The crystallographic data are summarized in Tables I and II. All non-hydrogen atoms of the  $\text{W}_{17}$  anion were located, along with five of the eight ammonium ions and some of the lattice water molecules. The crystallographic asymmetric unit consists of half of the  $\text{W}_{17}$  anion situated on a mirror plane defined by W(1), Na, and W(6). The

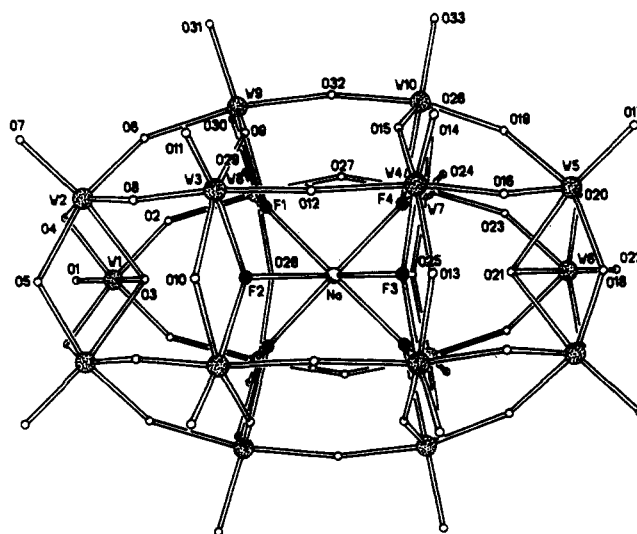


Figure 4. Crystallographically determined structure of the anion for  $(\text{NH}_4)_8(\text{FeW}_{17}\text{O}_{56}\text{F}_6\text{NaH}_4)\cdot 8\text{H}_2\text{O}$ . A crystallographic mirror plane passes vertically through W(1), Na, and W(6).

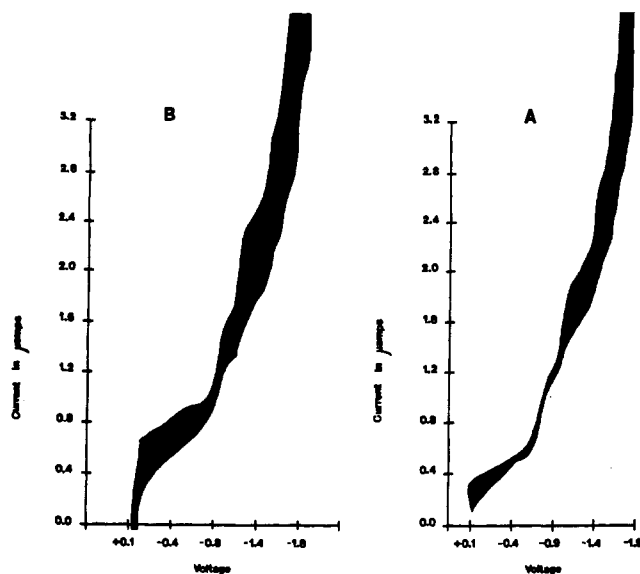
W atoms were refined anisotropically; the remaining non-hydrogen atoms, isotropically. Fe was not included as a contributor in the refinement of the W positions. No attempt to include the contributions of hydrogen atoms was made. It was not possible to resolve any information about the location of Fe in the anion. (It could be distributed more or less equally over 12 sites, as noted out by one reviewer.) The placement of Fe in the belt was done in analogy to the structure of  $[\text{ZnW}_{17}\text{O}_{56}\text{F}_6\text{NaH}_4]^{9-}$  reported by Baker et al.<sup>11</sup>

**Polarographic Studies.** The studies showed that the reduction of the heteropoly cobalt anion is reversible and diffusion controlled. The electrolytic reduction of the complex anion substantiates the Keggin-like structure, since only heteropoly complexes with structures closely related to the Keggin structure are known to form heteropoly blues.

The heteropoly blue of the complex anion was prepared by electrolysis at constant potential,  $0.8\text{ V}$  for  $20\text{ min}$ . Figure 5A shows the polarogram of this reduced species. When exposed to air, the solution reverted to the original red color and gave a typical polarogram of the anion at  $25^\circ\text{C}$ , as represented in Figure 5B.

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(14) Malik, S. A.; Weakley, T. J. R. *J. Chem. Soc. A* **1968**, 2647.



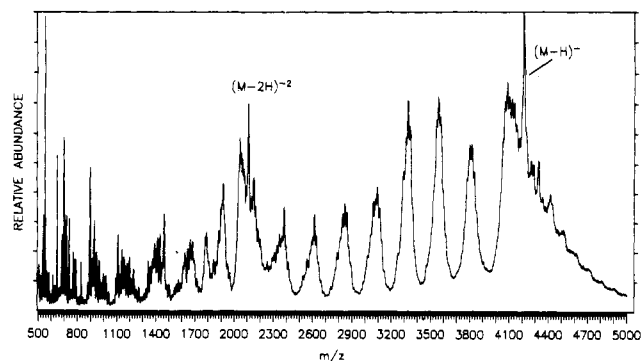
**Figure 5.** (A) Polarogram of the heteropoly blue solution prepared by electrolysis at 0.8 V (for 20 min) of a  $4 \times 10^{-4}$  M solution of  $(\text{NH}_4)_9(\text{CoW}_{17}\text{O}_{56}\text{F}_6\text{NaH}_4) \cdot 9\text{H}_2\text{O}$  in 0.9 M  $\text{Na}_2\text{SO}_4$  at 25 °C. (B) Polarogram of the same solution after reoxidation by air. The solution had regained its original red color.

The first wave is well-defined, has a plateau, and is followed by three other well-defined waves. This set of three waves was followed by another undefined wave, possibly representing decomposition of the heteropoly structure.

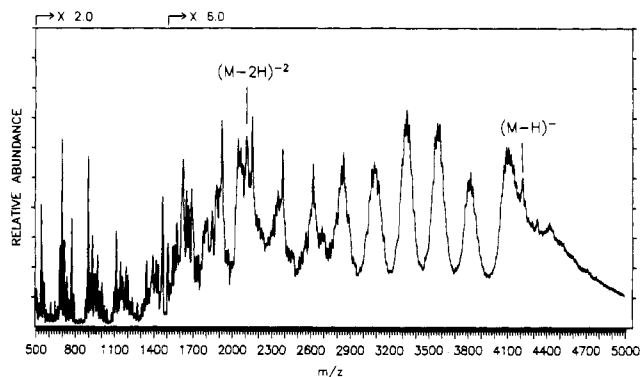
The overall half-wave potential of the first set of waves moves to a more positive potential as the pH decrease with a general change in the polarogram, which is an indication of decomposition of the heteropoly anion. No polarographic study was performed for the iron complex because of its insolubility.

**Mass Spectrometry.** The molecular weights of the two compounds were determined by FABMS. For the first time, collision-induced decomposition (CID) has been employed as an aid in the structural determination of a large inorganic complex. The CID spectrum of  $(M - H)^-$  shows clearly that the abundant fragments arise via sequential losses of small neutrals from the molecular species. The spectra were recorded at low (1:500) resolution. (Because of the number of elements present that have multiple isotopes, recording the mass spectra at unit resolution reduces sensitivity and produces an extremely complex isotopic pattern that does not add structural information.) The peak centers represent the average mass of the cluster, and were used to determine the values reported. The broad, rather unsymmetrical shape of some peaks made assignment of these peak centers somewhat arbitrary. The negative-ion signal was 2–3 times that obtained in the positive-ion mode. This observation is consistent with the anionic compounds' strong preference for carrying a negative charge.

The major compound observed in the positive-ion FAB mass spectra was the anhydrous ammonium salt of each of the two anions. The calculated anhydrous molecular weights are 4362.6 Da for the iron analogue and 4383.6 Da for the cobalt. At low mass, only clusters of  $(\text{glycerol})_n + \text{H}^+$  and  $(\text{glycerol})_n + \text{NH}_4^+$  were observed in the positive-ion spectra. In the molecular ion region of the positive-ion spectrum obtained for the iron complex, the small but fairly well-defined signal was centered about  $m/z$  4360. The calculated  $(M + H)^+$  for this ammonium salt is  $m/z$  4363.6. Water losses from the molecular ion lead to a series of clusters having similar abundances that terminated at  $m/z$  4270  $(M + H - 5\text{H}_2\text{O})^+$ . A less abundant series at 232-u  $(\text{WO}_3)$  intervals began with the cluster at about  $m/z$  3880  $[M + H - 2\text{WO}_3 - \text{O}]^+$ . The positive-ion spectrum of the cobalt complex [calculated  $(M + H)^+$   $m/z$  4384.6] had a broad, weak peak extending from about  $m/z$  4200 to  $m/z$  4600 and even lower abundance fragment clusters at  $(\text{WO}_3)_n$  intervals below the molecular ion region.



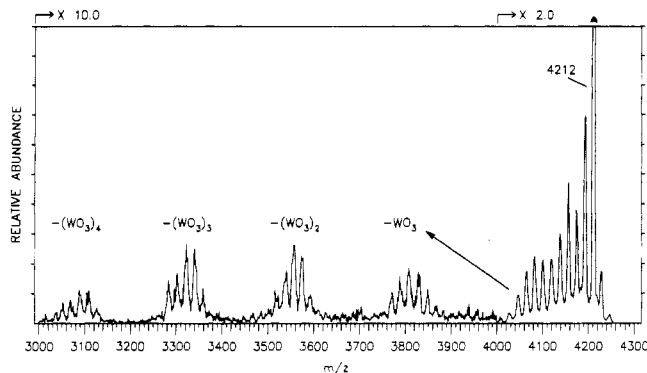
**Figure 6.** Negative-ion FAB mass spectrum of  $(\text{NH}_4)_9(\text{FeW}_{17}\text{O}_{56}\text{F}_6\text{NaH}_4) \cdot 8\text{H}_2\text{O}$  in 1:1 water/glycerol.  $(M - H)^-$  refers to the molecular species in which all of the cations are protons.



**Figure 7.** Negative-ion FAB mass spectrum of  $(\text{NH}_4)_9(\text{CoW}_{17}\text{O}_{56}\text{F}_6\text{Na}) \cdot 9\text{H}_2\text{O}$  in 1:1 water/glycerol.  $(M - H)^-$  refers to the molecular species in which all the cations are protons.

In the negative-ion FAB mass spectra of the two complexes (Figures 6 and 7), a peak was observed that corresponded to the  $(M - H)^-$  ion of the species in which all the ammonium cations and the sodium have been exchanged with protons. This is consistent with the negative-ion FABMS behavior of oligonucleotide tetraethylammonium salts, which exhibit  $(M - H)^-$  for the protonated form.<sup>15</sup> Probably because each of the  $(M - H)^-$  peaks was located on the side of a strong, very broad lower mass cluster, the observed values were slightly higher than the calculated values,  $m/z$  4212.0 for the iron complex [calculated  $(M - H)^-$   $m/z$  4203.3] and  $m/z$  4215.8 for the cobalt complex [calculated  $(M - H)^-$   $m/z$  4207.4]. Doubly charged molecular ions  $(M - 2H)^{2-}$  were observed for each, also accompanied by abundant lower mass clusters. The small peak at about  $m/z$  4325 in Figure 6 may be due to the some residual contribution from the species that contains seven  $\text{NH}_4$  cations (calculated  $m/z$  4322.6). In the negative-ion spectra of both complexes, strong maxima were observed well below the molecular ion regions, at intervals of  $232n$  Da, corresponding to  $\text{WO}_3$  losses, each with some fine structure that suggested minor variance in the total number of oxygen atoms lost. We had observed similar series in the both the positive- and negative-ion FAB mass spectra of  $[\text{Fe}_3\text{Co}_4\text{W}_{17}\text{O}_{70}\text{H}_{11}]^{10-}$ ,<sup>16</sup> but the relative abundance of the fragment ion series was much lower in those spectra than was observed here. Suslick et al.<sup>17</sup> and Finke et al.<sup>18,19</sup> have reported FABMS of heteropoly anions, noting the presence of  $\text{WO}_3$  losses in their negative-ion spectra and their absence in the positive-ion spectra. Their spectra<sup>17-19</sup> showed much more extensive fragmentation and lower abundance molecular ion

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- (16) Wasfi, S. H.; Costello, C. E. *Synth. React. Inorg. Met.-Org. Chem.* **1989**, *19*, 1059.
- (17) Suslick, S.; Cook, J.; Rapko, B.; Droegge, M. W.; Finke, R. G. *Inorg. Chem.* **1986**, *25*, 241.
- (18) Finke, R. G.; Droegge, M. W.; Cook, J. C.; Suslick, K. S. *J. Am. Chem. Soc.* **1984**, *106*, 5750.
- (19) Finke, R. G.; Rapko, B.; Saxton, R. J.; Domaille, P. J. *J. Am. Chem. Soc.* **1986**, *108*, 2947.



**Figure 8.** High-mass region in the negative-ion FAB CID MS/MS spectrum of the  $m/z$  4212 ion from  $(\text{NH}_4)_8(\text{FeW}_{17}\text{O}_{56}\text{F}_6\text{NaH}_4)\cdot 8\text{H}_2\text{O}$ .

regions than are seen in these spectra.

In order to verify the assignments of the molecular species in the negative-ion spectra, CID mass spectra were obtained for these peaks. The high-mass region of the CID mass spectrum of the cluster centered at  $m/z$  4212 in the FAB mass spectrum of the iron complex is shown in Figure 8. The CID mass spectrum for the  $(\text{M} - \text{H})^-$  of the cobalt complex underwent the appropriate mass shifts but was otherwise very similar. The MS/MS spectrum in Figure 8 clarifies the relationships among the major ions in Figure 6. The CID spectrum has a regular series of abundant fragments, at 18–20-u intervals (average 18.2 u), corresponding to very facile multiple water and HF losses from the molecular ion. This spectrum suggests that accumulation of small-molecule losses leads to the broad maximum observed at  $m/z$  4085 (doubly charged,  $m/z$  2042.5 in the normal FAB mass spectrum). There are also sequential losses of  $\text{WO}_3$ . In the CID spectrum, the fine structure due to variations in the total number of oxygens lost is more clear than it is in Figure 6, because the narrow mass window selected by MS-1 limits the width of the isotopic clusters.

These results provide an indication that the MS/MS technique has interesting potential for the elucidation of structural details

in large inorganic complexes. The CID mass spectra of these and other types of heteropolytungstate anions are being investigated, and the fragmentation pathways will be discussed more fully elsewhere.

### Conclusion

We believe that the structure of the  $[\text{XW}_{17}\text{O}_{56}\text{F}_6\text{NaH}_4]^{n-}$  anions is that represented in Figure 1.

The X-ray crystallographic determination of the Fe(III) complex located all non-hydrogen atoms of the  $\text{W}_{17}$  anion. The X-ray powder patterns show that the two compounds are isomorphous. The visible spectrum of the cobalt complex helped us to assign the position of the Co(II) ion as one of the W positions in the two Keggin fragments. Due to the isomorphism of the two compounds, this corresponds to the Fe(III) position in the Fe complex. The electrolytic reduction of the  $[\text{CoW}_{17}\text{O}_{56}\text{F}_6\text{NaH}_4]^{9-}$  anion substantiates the Keggin-like structure, since only heteropoly complexes with structures closely related to the Keggin structure are known to form heteropoly blues.

The characterization of these two compounds,  $(\text{NH}_4)_9(\text{CoW}_{17}\text{O}_{56}\text{F}_6\text{NaH}_4)\cdot 9\text{H}_2\text{O}$  and  $(\text{NH}_4)_8(\text{FeW}_{17}\text{O}_{56}\text{F}_6\text{NaH}_4)\cdot 8\text{H}_2\text{O}$ , is another example of the usefulness of fast-atom-bombardment mass spectrometry in the structural determination of heteropolyoxometalate anions. Although chemical analysis indicates the atomic ratio of different elements in the compounds, molecular weight determination by FABMS helped set this ratio at 1:17. The FABMS/MS spectrum verifies the assignment of the molecular anion and demonstrates that the other abundant high-mass ions observed in the spectrum arise from this species by multiple losses of small neutrals.

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**Supplementary Material Available:** Tables of bond lengths, bond angles, and anisotropic thermal parameters for  $(\text{NH}_4)_8(\text{FeW}_{17}\text{O}_{56}\text{F}_6\text{NaH}_4)\cdot 8\text{H}_2\text{O}$  (4 pages); a listing of structure factors for the same complex (8 pages). Ordering information is given on any current masthead page.

Contribution from the Research School of Chemistry, Australian National University, G.P.O. Box 4, Canberra, ACT 2601, Australia

## Metal Ion Control of Organic Reactivity: Electrophilic and Nucleophilic Reactions of Coordinated 2-Iminopropanoate

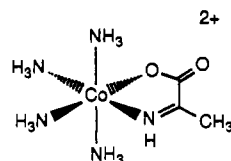
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Chelate complexes derived from 2-imino carboxylate ligands contain both electrophilic and nucleophilic sites for reaction. To explore both the utility and control of these properties, reactions of the simple pyruvate imine complex  $[(\text{NH}_3)_4\text{Co}(\text{NH}=\text{C}(\text{CH}_3)\text{CO}_2)]^{2+}$  with a variety of polyfunctional molecules have been examined. Diethyl oxaloacetate reacts to provide a substituted pyridine, showing that the previously observed reaction of the complex with biacetyl to give a pyrroline can be varied to provide other heterocycles. Reactions with dimethyl acetylenedicarboxylate and methyl vinyl ketone, in contrast, provide branched-chain ligands via cyclization onto the metal center, the pathway for the methyl vinyl ketone reaction being confirmed by a crystal structure determination. Plausible mechanisms for the reactions are discussed in some detail.

### Introduction

The simple chelate complex derived from the imine of pyruvate and tetraamminecobalt(III) ion (I) can behave as both an electrophile and a nucleophile.<sup>2</sup> The elementary reactions used to reveal these capacities, however, did not test their exploitation for the formation of more complex organic species. In order to



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explore them more thoroughly, particularly with regard to heterocycle synthesis, the complex imine has been treated with several bifunctional organic molecules. It is a new way to carry out what is essentially iminium ion chemistry with a remarkably stable

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(2) Harrowfield, J. MacB.; Sargeson, A. M. *J. Am. Chem. Soc.* **1979**, *101*, 1514.