6, R = CH_2SiMe_3. The chlorophosphine **6** was prepared and purified as described earlier.[4] A solution of **6** (0.025 mol) in Et_2O (50 mL) was treated with *i*-PrMgCl (0.025 mol) with stirring at 0 °C. Fractional distillation of the product mixture gave both the isopropylphosphine **9** and the P-H phosphine **13** (Table II).

7, R = $N(SiMe_3)_2$. A solution of the bis(silylamino)chlorophosphine **7**[20] (ca. 0.10 mol) was prepared by the reaction of 2 equiv of $(Me_3Si)_2NLi$ with PCl_3. Addition of *i*-PrMgCl (0.10 mol) at 0 °C, followed by the usual workup procedure, gave the P-H phosphine **14** and the isopropylphosphine **10** as the major and minor products, respectively (Table II).

8, R = Ph. A solution of the chlorophosphine **8** was prepared on a 0.50-mol scale from $(Me_3Si)_2NLi$ and $PhPCl_2$, with use of the procedure described above for the preparation of $(Me_3Si)_2NPCl_2$. Reaction with *i*-PrMgCl (0.50 mol) in the usual manner gave only the isopropylphosphine **11** (Table II).

Reactions of Chlorophosphines $(Me_3Si)_2NP(R)Cl$ with $LiAlH_4$. Generally, the chlorophosphine **3** and **5-8** were prepared as described above and, in the same reaction flask, were treated with an ether solution of $LiAlH_4$ at 0 °C. For example, a solution of unpurified **3** (prepared on a 0.10-mol scale from $(Me_3Si)_2NPCl_2$ and *i*-PrMgCl) was stirred at 0 °C and $LiAlH_4$ (25 mL, 1.0 M in ether, 0.025 mol) was added dropwise. The mixture was then warmed to room temperature and stirred overnight. After filtration and solvent removal, distillation afforded the P-H phosphine **2** in good yield (Table II).

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Registry No. **1**, 73270-07-2; **2**, 81072-83-5; **3**, 81072-82-4; **4**, 78614-55-8; **5**, 70009-04-0; **6**, 76946-89-9; **7**, 53327-45-0; **8**, 84174-75-4; **9**, 81072-87-9; **10**, 81072-88-0; **11**, 84174-76-5; **12**, 81072-84-6; **13**, 81072-85-7; **14**, 81072-86-8; **15**, 84174-77-6; *i*-PrCl, 75-29-6; $(Me_3Si)_2NPCl_2$, 54036-90-7; *t*-BuLi, 594-19-4.

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$Ti_2W_{10}PO_{40}^{7-}$ and $[CpFe(CO)_2Sn]_2W_{10}PO_{38}^{5-}$. Preparation, Properties, and Structure Determination by Tungsten-183 NMR

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Single isomers of $Ti_2W_{10}PO_{40}^{7-}$ and $[CpFe(CO)_2Sn]_2W_{10}PO_{38}^{5-}$ have been prepared and their structures determined by ^{183}W NMR. $Ti_2W_{10}PO_{40}^{7-}$ forms isolable complexes with divalent manganese, iron, cobalt, nickel, copper, and zinc.

Introduction

Keggin-structure heteropolyanions containing more than one peripheral heteroatom have generally been restricted to those containing molybdenum and tungsten, vanadium and tungsten, or vanadium and molybdenum as the peripheral atoms. Although such heteropolyanions can exist as more than one isomer, depending on the positioning of the peripheral heteroatoms,[1] few determinations of isomer composition have been made. Among the Keggin anions containing two peripheral heteroatoms, $V_2Mo_{10}PO_{40}^{5-}$ and $V_2W_{10}PO_{40}^{5-}$ have been shown to contain all five possible isomers,[2] and we recently described preparations of $(CH_3Sn)_2W_{10}PO_{38}^{5-}$ and $(C_6H_5Sn)_2W_{10}PO_{38}^{5-}$, which lead to mixtures containing at least four of the possible five isomers.[3] No structural characterization or isolation of a single isomer of a disubstituted Keggin anion has been reported.

We are interested in di- or polysubstituted Keggin anions, particularly those containing peripheral heteroatoms with an oxidation state less than 6, because such anions should have more surface negative charge than normal Keggin anions and exhibit enhanced basicity.

Increasing negative charge on a Keggin anion results in increased resistance to nucleophilic degradation. We therefore explored the preparation of tungstophosphates from tungstate, phosphate, and potential substituent precursors in basic solution, rather than the acid media normally used to prepare heteropolyanions. Only those with substantial negative charge, i.e. di- or polysubstituted, should be stable and therefore able to form under such conditions.

Results and Discussion

Preparations. Reactions of $TiCl_4$ and $CpFe(CO)_2SnCl_3$ with aqueous solutions of sodium tungstate and sodium dihydrogen phosphate at pH 8-8.6 form $Ti_2W_{10}PO_{40}^{7-}$ and $[CpFe(CO)_2Sn]_2W_{10}PO_{38}^{5-}$, respectively. The reactions are pH dependent; in acidic solution $CpFe(CO)_2SnCl_3$ reacts with sodium tungstate and sodium dihydrogen phosphate to form $CpFe(CO)_2SnW_{11}PO_{39}^{4-}$, prepared earlier from $W_{11}PO_{39}^{7-}$ and $CpFe(CO)_2SnCl_3$.[4]

The ready availability of titanium tetrachloride and the simplicity of the reaction makes $Ti_2W_{10}PO_{40}^{7-}$ particularly easy to prepare. Over 100 g can be made at a time in a simple apparatus.

Characterization. ^{31}P NMR shows that, barring coincident chemical shifts, both $[CpFe(CO)_2Sn]_2W_{10}PO_{38}^{5-}$ and $Ti_2W_{10}PO_{40}^{7-}$ consist of essentially one isomer. ^{183}W NMR studies, detailed below, confirm this and further reveal that the isomers are isostructural with 1,4-substitution of the Keggin structure[1b] (Figure 1).

The ^{31}P NMR spectrum of $[(CH_3)_3NH]_5[CpFe(CO)_2Sn]_2W_{10}PO_{38}$ in aqueous dimethyl sulfoxide exhibits a single sharp resonance, at -9.58 ppm. The corresponding spectrum of one sample of $Li_5[CpFe(CO)_2Sn]_2W_{10}PO_{38}$ in water had, in addition to a major resonance at -9.67 ppm, several quite minor lines between -9.0 and -11.7 ppm, which may have represented other isomers. Similarly, the ^{31}P NMR spectrum of $Li_7Ti_2W_{10}PO_{40}$ (Figure 2) reveals that one isomer (δ -11.43) predominates but that small amounts of other isomers may be present, evidenced by the three smaller resonances at -10.96, -12.02, and -12.42 ppm. Attempted sep-

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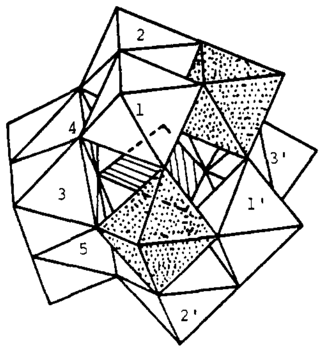

Figure 1. Structures of $Ti_2W_{10}PO_{40}^{7-}$ and $[CpFe(CO)_2Sn]_2W_{10}PO_{38}^{5-}$. The shaded octahedra show the positions of the peripheral heteroatoms.

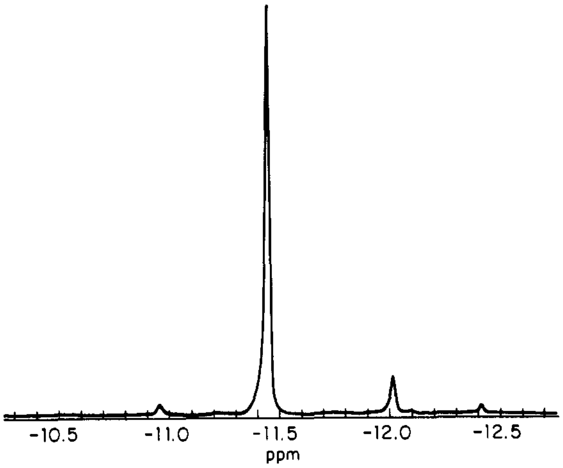

Figure 2. ^{31}P NMR spectrum (146.1 MHz) of $Li_7Ti_2W_{10}PO_{40}$ in water at 25 °C, referenced to external phosphoric acid.

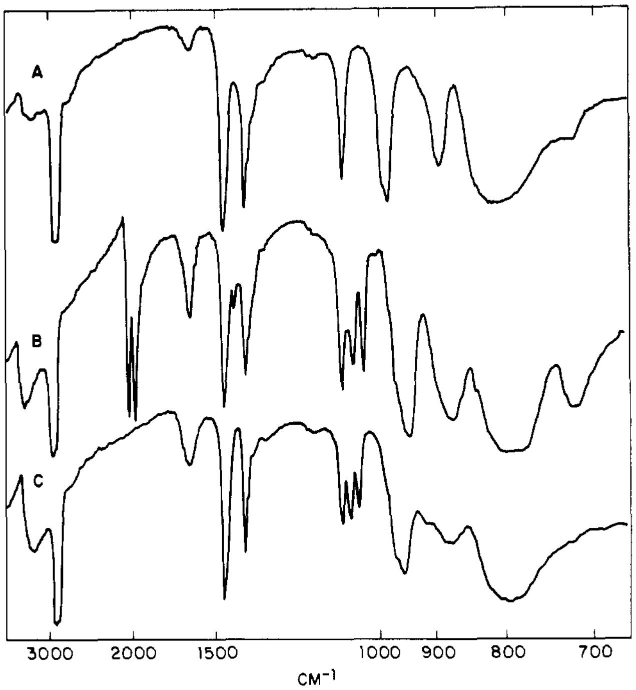

Figure 3. Infrared spectra (mineral oil mulls) of hydrated $K_3W_{12}PO_{40}$ (A), $K_5[CpFe(CO)_2Sn]_2W_{10}PO_{38}$ (B), and $K_7Ti_2W_{10}PO_{40}$ (C).

aration of these by fractional crystallization has given samples with spectra in which the −12.02-ppm resonance is about one-third the intensity of the major resonance, but this isomer has not been identified.

Except for the carbonyl region, the infrared spectra of $K_5[CpFe(CO)_2Sn]_2W_{10}PO_{38}$ and $K_7Ti_2W_{10}PO_{40}$ are similar.

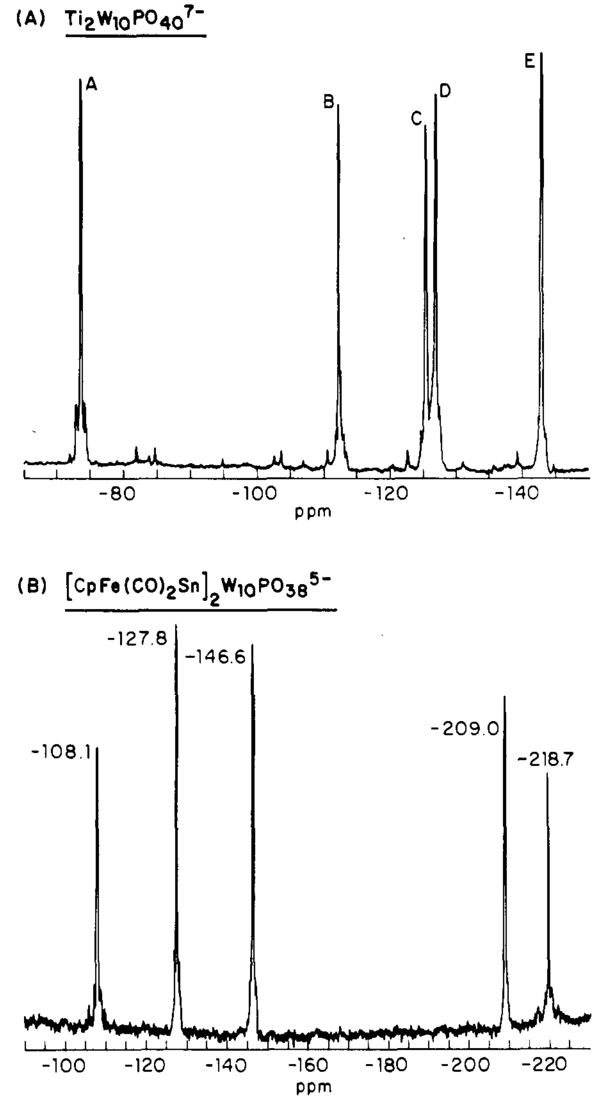

Figure 4. ^{183}W NMR spectra (15.0 MHz) of (A) $Li_7Ti_2W_{10}PO_{40}$ in H_2O/D_2O at 35 °C and (B) $Li_5[CpFe(CO)_2Sn]_2W_{10}PO_{38}$ in H_2O/D_2O at 60 °C. Chemical shifts are with respect to 2 M Na_2WO_4 in D_2O at 25 °C with negative values to lower frequency. In (A) peaks are labeled alphabetically in sequence for later identification.

These spectra are compared with that of $K_3W_{12}PO_{40}$ in Figure 3. The most notable difference below 1300 cm^{-1}, other than band shifts, is in the asymmetric phosphate stretch, which is triply degenerate in the $W_{12}PO_{40}^{3-}$ spectrum but is nondegenerate in the two disubstituted derivatives.

^{183}W NMR Spectra. Of the five isomers possible from bis-substitution of the Keggin structure, two are of C_s, one is of C_2, one is of C_{2v}, and one is of C_1 symmetry. In principle then it is possible to distinguish between all except the pair of C_s structures on the basis on *number* and *intensity* of distinct tungsten sites. A C_s structure produces 6 sites (2:2:2:2:1:1), and C_2 gives 5 sites (2:2:2:2:2), C_{2v} gives 3 sites (4:4:2), while C_1 has 10 distinguishable positions.

The ^{183}W NMR spectra of both $Ti_2W_{10}PO_{40}^{7-}$ and $[CpFe(CO)_2Sn]_2W_{10}PO_{38}^{5-}$ (Figure 4) show *five* equally intense peaks, which must be ascribed to the C_2 isomer formed by 1,4-substitution.[1b] The spectra shown include some saturation effects as a result of small-pulse recycle time, and intensity rolloff because of long pulses, but increasing recycle times and shorter pulse lengths confirm the peaks are of equal intensity.

All ^{183}W resonances appear as doublets because of coupling with the ^{31}P heteroatom. Satellite peaks are observed at the base of all lines, indicative of ^{183}W–^{183}W coupling in all the

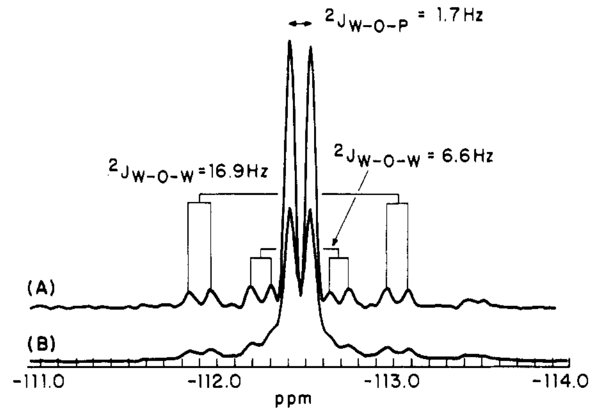

Figure 5. Expanded region around ^{183}W resonance B (Figure 4) at −112.4 ppm showing the two couplings of the isotopomers: (A) resolution-enhanced spectrum; (B) normal spectrum.

Table I. Chemical Shift[a] (ppm) and Spin-Spin Coupling Parameters (Hz) for 0.6 M $Li_7Ti_2W_{10}PO_{40}$ at 30 °C

	A	B	C	D	E	J_{W-P}
A	−73.74	6.71	20.92	17.97		1.73
B	6.70	−112.48			16.79	1.75
C	20.84		−125.47	17.5[b]	7.84	1.43
D	17.91		17.5[b]	−126.98	6.39	1.19
E		16.70	(7.84)[c]	(6.39)[c]	−143.00	1.34

[a] Chemical shifts with respect to 2 M Na_2WO_4 at 30 °C with negative values to lower frequency. [b] Strong second-order pattern. The coupling is derived from computer simulation of the inner two lines of the AB quartet relative to the zero-order position of the parent peak. [c] Not measured directly because of strong overlap. However, two overlapped lines with $5 < J < 9$ are apparent.

pairwise isotopomers.[5,11] These splittings are easily measured in $Ti_2W_{10}PO_{40}^{7-}$ but not in $[CpFe(CO)_2Sn]_2W_{10}PO_{38}^{5-}$ because of poorer S/N and broader lines. The data for $Ti_2W_{10}PO_{40}^{7-}$ are sufficiently good that resolution enhancement can be used to more clearly reveal the innermost satellites (Figure 5). The spin–spin couplings and chemical shifts for $Ti_2W_{10}PO_{40}^{7-}$ are collected in Table I.

The spin couplings can be used to assign the chemical shifts of each site in $Ti_2W_{10}PO_{40}^{7-}$ in a manner similar to that reported earlier[5] for $TiW_{11}PO_{40}^{5-}$. Atom positions are labeled in Figure 1. The significant difference is that there is no unique position to begin this assignment. However, W_1 with both edge bonding and corner bonding to Ti octahedra has only *two* couplings to other W atoms, so we expect only *two* sets of couplings. Resonance B at −112.4 ppm is the only peak that fulfills this criterion. With this starting point, and the established rule[5,11] that edge couplings are typically 5–10 Hz and corner couplings approximately 20 Hz, an almost complete assignment is possible. W_1 is W_B, W_2 is W_A, W_3 is W_E, W_4 is W_C or W_D, and W_5 is W_D or W_C. The last ambiguity, distinguishing between resonances W_C and W_D, results from the heavily overlapped small edge couplings. The only coupling not clearly resolved is J_{45}. Second-order AB patterns again[5] proved a useful aid in assignment.

The assignment appears consistent with that of $TiW_{11}PO_{40}^{5-}$ insofar as location of tungsten resonances relative to the Ti substitution site.[5] In both cases the *highest* frequency resonance is due to tungsten, which shares only an octahedral *edge* with titanium. In $Ti_2W_{10}PO_{40}^{7-}$ the *lowest* frequency line is due to tungsten, which shares only an octahedral *corner* with titanium, while in $TiW_{11}PO_{40}^{5-}$ this resonance is the next to lowest frequency.[5] Perhaps fortuitously, W_1 in $Ti_2W_{10}PO_{40}^{7-}$, which shares *both* corner- and edge-bonded titanium octahedra, is approximately at the center of the chemical shift range.

Charge Effects. As the negative charge is increased on the surface of the Keggin structure by successive replacement of WO^{4+} groups by groups of lesser charge, the basicity should increase. One earlier example of this is the reversible protonation of $ClTiW_{11}PO_{39}^{4-}$ under conditions where $W_{12}PO_{40}^{3-}$ does not protonate.[5] As would be expected, the increase in basicity for $Ti_2W_{10}PO_{40}^{7-}$ is more striking. The anion not only protonates reversibly to form $H_2Ti_2H_{10}PO_{40}^{5-}$ but also forms complexes of the type $MTi_2W_{10}PO_{40}^{5-}$, where M is divalent manganese, iron, cobalt, nickel, or zinc. These complexes are obtained as the potassium salts simply by recrystallizing $K_7Ti_2W_{10}PO_{40}$ from water containing the appropriate metal cation. The copper complex has also been characterized as the tetramethylammonium salt. To determine whether these $MTi_2W_{10}PO_{40}^{5-}$ anions are actually inner-sphere complexes, we explored the visible spectra of the copper, nickel, and cobalt complexes, which have maxima at 810, 725, and 525 nm, respectively, using the method of continuous variations.[6] In each case the corrected optical density was greatest at 50 mol %, consistent with the formation of a 1:1 complex.

The infrared spectrum of $Cs_4KH_2Ti_2W_{10}PO_{40}$ displays a triply degenerate asymmetric phosphate stretch at 1060 cm^{-1}, in contrast to the nondegenerate absorption described above for unprotonated $Ti_2W_{10}PO_{40}^{7-}$. Ho[7] has observed a similar conversion of a doublet P–O stretching absorption in the spectrum of $TiW_{11}PO_{40}^{5-}$ to a singlet upon protonation to $HTiW_{11}PO_{40}^{4-}$. He has ascribed this to significant restoration of the tetrahedral symmetry about the phosphorus upon protonation of the anion and concluded that the terminal oxygen on titanium is the most likely protonation site; i.e., $HTiW_{11}PO_{40}^{4-}$ is best formulated as $HOTiW_{11}PO_{39}^{4-}$. We agree with this and assume for similar reasons that $H_2TiW_{10}PO_{40}^{5-}$ is better represented as $(HOTi)_2W_{10}PO_{38}^{5-}$. ^{17}O NMR studies support this contention; exchange studies with $H_2{}^{17}O$ show that the Ti–O is labile while the W–O sites are substitutionally inert.

The asymmetric phosphate stretch in the infrared spectra of hydrated $K_5MTi_2W_{10}PO_{40}$ salts dried under vacuum at ambient temperatures is not degenerate; the spectra resemble that of $K_7Ti_2W_{10}PO_{40}$ except that the three P–O stretching absorptions are more closely spaced by about 10 cm^{-1}. However, if the salts are heated at 125 °C under vacuum, resolution of the three P–O stretching bands is largely lost; it is restored upon subsequent exposure to water. This loss of resolution is not observed when hydrated $K_7Ti_2W_{10}PO_{40}$ is dried at elevated temperature. The change in infrared spectra when the complex salts are dried may reflect stronger bonding between the divalent metal M and $Ti_2W_{10}PO_{40}^{7-}$ as water is removed but does not aid in assigning bonding sites. The present complexes are most likely similar to $MnNb_{12}O_{38}^{12-}$ and $(OC)_3ReNb_2W_4O_{19}^{3-}$ in their metal to polyoxoanion bonding mode. The manganese and rhenium in the two latter anions have been shown to bond to a triangle of bridging oxygen atoms in the polyoxoanions.[8,9] We are pursuing this point further.

Experimental Section

$Ti_2W_{10}PO_{40}^{7-}$. Sodium dihydrogen phosphate (6 g, 43 mmol) was added to a solution of sodium tungstate dihydrate (30 g, 91 mmol) in water (100 mL). Titanium tetrachloride (1.8 mL, 16 mmol) was added dropwise with stirring. The mixture was then refluxed for 20 min followed by filtration through analytical filter aid. The clear, colorless filtrate, pH 8.2, was divided into three equal portions. The first was stirred 5 min with cesium chloride (10 g) to precipitate a

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Table II. Analyses of $K_5MTi_2W_{10}PO_{40}\cdot xH_2O^a$

M	x	% K	% M	% Ti	% W	% H_2O
Mn	9	6.48 (6.22)	1.82 (2.20)	3.17 (3.77)	60.92 (60.19)	5.01 (5.33)
Fe	8	6.51 (5.68)	1.86 (2.53)	3.19 (3.85)	61.26 (61.59)	4.80 (4.64)
Co	7	6.55 (5.96)	1.97 (2.53)	3.21 (3.58)	61.58 (61.07)	4.22 (3.89)
Ni	4	6.67 (6.44)	2.00 (2.26)	3.27 (3.82)	62.72 (60.74)	2.46 (2.34)
Cu	6	6.58 (6.08)	2.14 (2.87)	3.22 (3.66)	61.85 (61.32)	3.63 (3.35)
Zn	6	6.57 (5.87)	2.20 (2.78)	3.22 (3.60)	61.79 (61.32)	3.60 (3.49)

[a] Calculated values are given with the corresponding values found given in parentheses.

white solid, which was recrystallized from water (10 mL) to obtain 5.3 g of $Cs_7Ti_2W_{10}PO_{40}$. The second portion was stirred for 10 min with potassium chloride (10 g) to precipitate a white solid, which was recrystallized twice from water to obtain 3.3 g of $K_7Ti_2W_{10}PO_{40}$. The third portion was stirred for 10 min with excess tetramethylammonium chloride. This precipitated a white solid, which was recrystallized from water (30 mL) to obtain 3.3 g of $[(CH_3)_4N]_7Ti_2W_{10}PO_{40}$. Anal. Calcd for $K_7Ti_2W_{10}PO_{40}\cdot 6H_2O$: K, 9.16; Ti, 3.21; W, 61.54; H_2O, 3.62. Found: K, 9.04; Ti, 3.63; W, 60.82; H_2O, 3.49. Calcd for $[(CH_3)_4N]_7Ti_2W_{10}PO_{40}\cdot 4H_2O$: C, 10.50; H, 2.90; N, 3.06; Ti, 2.99; W, 57.41; H_2O, 2.25. Found: C, 10.14; H, 2.68; N, 2.94; Ti, 2.88; W, 57.68; H_2O, 2.38. Calcd for $Cs_7Ti_2W_{10}PO_{40}\cdot 3H_2O$: Ti, 2.67; W, 51.22; H_2O, 1.50. Found: Ti, 2.99; W, 50.91; H_2O, 1.53.

A number of subsequent preparations were run on 8 times the above scale, and the entire preparation was worked up by the addition of 240 g of potassium chloride to the filtrate. The product that separated after overnight chilling was recrystallized from water (200 mL) to obtain, typically, 106 g (56%) of $K_7Ti_2W_{10}PO_{40}\cdot 6H_2O$.

To prepare more soluble salt for the ^{183}W NMR studies, we passed an aqueous solution of $K_7Ti_2W_{10}PO_{40}\cdot 6H_2O$ (50 g) through an anion-exchange column containing 100 mL of a sulfonated polystyrene ion-exchange resin (Li salt). Evaporation of the effluent left 45.9 g of hydrated $Li_7Ti_2W_{10}PO_{40}$, which had an infrared spectrum identical with that of the potassium salt.

$H_2Ti_2W_{10}PO_{40}^{5-}$. A warm solution of $K_7Ti_2W_{10}PO_{40}\cdot 6H_2O$ (10 g, 3.4 mmol) in water (100 mL) was brought to pH 3 with aqueous hydrochloric acid. Cesium chloride (4 g) was added to precipitate a white solid, which was recrystallized from water (100 mL) to obtain 4.3 g (40%) of $Cs_4KH_2Ti_2W_{10}PO_{40}$. Anal. Calcd for $Cs_4KH_2Ti_2W_{10}PO_{40}\cdot 3H_2O$: Cs, 16.6; K, 1.22; W, 57.73; Ti, 2.99. Found: Cs, 16.5; K, 0.86; W, 57.16; Ti 3.38.

Metal Complexes of $Ti_2W_{10}PO_{40}^{7-}$. Complexes of the type $K_5MTi_2W_{10}PO_{40}\cdot xH_2O$ (M = divalent Mn, Fe, Co, Ni, Cu, Zn) were prepared as illustrated for the nickel complex, except that manganese sulfate, ferrous sulfate, and zinc acetate rather than the nitrates were used for the preparations of the manganese, iron, and zinc complexes.

A mixture of $K_7Ti_2W_{10}PO_{40}\cdot 6H_2O$ (10.0 g, 3.3 mmol) and water (30 mL) was heated until the solid dissolved. Nickel(II) nitrate hexahydrate (3 g, 10 mmol) was added; the solution was heated briefly to boiling and filtered hot through analytical filter aid. Hydrated $K_5NiTi_2W_{10}PO_{40}$ (7.1 g, 76%) separated as a green crystalline solid as the solution cooled. This was recrystallized from water (15 mL, 1.5-g recovery) for analysis. The infrared spectra of the crude and recrystallized products were identical. Analytical data for this and similar complexes are in Table II. The copper complex was converted to a tetramethylammonium salt by dissolution in warm water, addition of tetramethylammonium chloride, and recrystallization of the resulting precipitate from water. Anal. Calcd for $[(CH_3)_4N]_5CuTi_2W_{10}PO_{40}\cdot 3H_2O$: C, 7.76; H, 2.15; N, 2.26; Cu, 2.05; Ti, 3.10. Found: C, 8.00; H, 2.17; N, 2.22; Cu, 2.05; Ti, 3.42.

$[CpFe(CO)_2Sn]_2W_{10}PO_{38}^{5-}$. A solution of $CpFe(CO)_2SnCl_3$[10] (12 g, 29.8 mmol) in tetrahydrofuran (40 mL) was added to a solution of sodium tungstate (60 g, 182 mmol) and sodium dihydrogen phosphate (12 g, 87 mmol) in water (200 mL). The mixture was stirred at 60–65 °C for 15 min and filtered. The filtrate pH was 8.6. Potassium nitrate (10 g) was added to the filtrate, which was then stirred 15 min and filtered to obtain 17.8 g (31%) of crude $K_5[CpFe(CO)_2Sn]_2W_{10}PO_{38}\cdot 28H_2O$. Anal. Calcd for $K_5[C_5H_5Fe(CO)_2Sn]_2W_{10}PO_{38}\cdot 28H_2O$: C, 4.46; H, 1.76; K, 5.19; Fe, 2.96; P, 0.82; Sn, 6.30; W, 48.78; H_2O, 13.38. Found: C, 4.94; H, 0.89; K, 4.16; Fe, 3.27; P, 1.11; Sn, 6.52; W, 50.52; H_2O, 13.36.

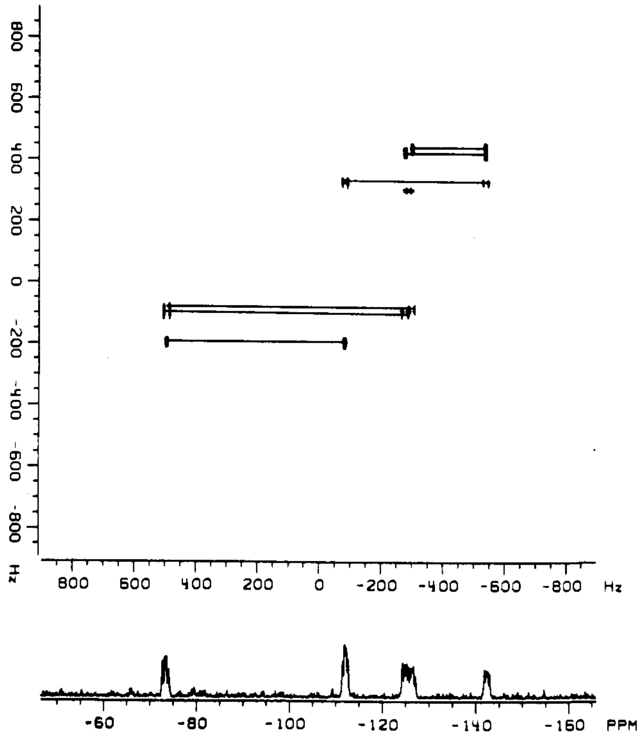

Figure 6. Two-dimensional contour plot of the ^{183}W spectrum of $Li_7[Ti_2W_{10}PO_{40}]$ as a 0.5 M solution in D_2O at 23 °C. The spectrum is 512 accumulations of 4K data points in each of 128 files. Horizontal bars indicate the coupled sites. The lower trace is the projection of the 2-D data onto the normal F_2 axis and is the spectrum of coupled ^{183}W–O–^{183}W isotopomers; singly labeled ^{183}W species are eliminated. The five sets of resonances correspond to the A, B, C, D, E notation of Figure 4A.

Part of this (8.3 g) was dissolved in warm water (100 mL). The solution was filtered, cooled to ambient temperature, and mixed with excess trimethylammonium chloride. The resulting yellow precipitate was separated and recrystallized from water (30 mL) to obtain 5.6 g of $[(CH_3)_3NH]_5[C_5H_5Fe(CO)_2Sn]_2W_{10}PO_{38}\cdot 2H_2O$. Anal. Calcd for $[(CH_3)_3NH]_5[C_5H_5Fe(CO)_2Sn]_2W_{10}PO_{38}\cdot 2H_2O$: C, 10.23; H, 1.89; N, 2.06; Fe, 3.28; Sn, 6.97; W, 53.98; H_2O, 1.05. Found: C, 10.20; H, 1.96; N, 2.03; Fe, 3.51; Sn, 7.41; W, 53.47; H_2O, 0.67.

The ratio of methyl to cyclopentadienyl protons found by ^1H NMR was 4.5:1 (calculated 4.5:1).

After the 15-min reaction period in a similar preparation, hydrochloric acid was added dropwise to lower the pH to 7. Ammonium chloride (20 g) was added, and the precipitated ammonium salt was recrystallized from water. Anal. Calcd for $(NH_4)_5[C_5H_5Fe(CO)_2Sn]_2W_{10}PO_{38}\cdot 6H_2O$: C, 5.15; H, 1.30; N, 2.14; W, 56.27; Sn, 7.27; Fe, 3.42; H_2O, 3.31. Found: C, 5.28; H, 1.20; N, 1.64; W, 56.38; Sn, 7.64; Fe, 4.14; H_2O, 3.37.

To obtain a more soluble salt for NMR studies, an aqueous solution of $(NH_4)_5[C_5H_5Fe(CO)_2Sn]_2W_{10}PO_{38}\cdot 6H_2O$ (12 g) was passed through an ion-exchange column containing 45 mL of a sulfonated polystyrene ion-exchange resin (Li salt). The effluent was evaporated to obtain 12.1 g of hydrated $Li_5[C_5H_5Fe(CO)_2Sn]_2W_{10}PO_{38}$. ^{183}W NMR spectra of the ammonium and lithium salts showed identical features.

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$CpFe(CO)_2SnW_{11}PO_{39}^{4-}$. $CpFe(CO)_2SnCl_3$[10] (3.0 g, 7.5 mmol) in tetrahydrofuran (10 mL) was added to $Na_2WO_4 \cdot 2H_2O$ (15.0 g, 45.4 mmol) and $NaH_2PO_4 \cdot H_2O$ (3.0 g, 21.7 mmol) in water (50 mL). The mixture was heated to 60 °C; hydrochloric acid (12 M, 15 mL) was added dropwise, resulting in a temperature increase to 78 °C. The mixture was stirred 60 min at 60–78 °C and filtered hot. It was refiltered after cooling to room temperature. The addition of excess trimethylammonium chloride to the filtrate precipitated a solid, which was recrystallized from boiling water (100 mL) to obtain 1.5 g (11%) of $[(CH_3)_3NH]_4CpFe(CO)_2SnW_{11}PO_{39} \cdot 3H_2O$, identical by infrared analysis with that prepared earlier from $W_{11}PO_{39}^{7-}$ and $CpFe(CO)_2SnCl_3$.[4] Anal. Calcd for $[(CH_3)_3NH]_4C_5H_5Fe(CO)_2SnW_{11}PO_{39} \cdot 3H_2O$: C, 6.98; H, 1.57; N, 1.71; Fe, 1.71; Sn, 3.63. Found: C, 6.50; H, 1.43; N, 1.62; Fe, 1.42; Sn, 3.75.

NMR Spectra. ^{183}W NMR spectra were obtained on thermostated 20-mm diameter aqueous samples with use of a Nicolet NT360WB spectrometer at 15 MHz. ^{31}P spectra were obtained on the same instrument in 12-mm tubes at 146.1 MHz or on 10-mm samples in a CFT-80A at 32.2 MHz. ^{183}W chemical shifts were referenced to external 2 M Na_2WO_4 while ^{31}P chemical shifts are relative to external 85% H_3PO_4.

The spectrum shown in Figure 4A is the result of 10 000 accumulations of 90° pulses (500 μs) with a recycle delay of 2.05 s. The 12 cm^3 of solution contained 18 g of $Li_7Ti_2W_{10}PO_{40}$. The FID was zero filled to 16K points and apodized with a 0.5-Hz exponential before Fourier transformation. The resolution-enhanced portion shown in Figure 5 was obtained by Gaussian–exponential double multiplication with use of standard Nicolet software.

The spectrum shown in Figure 4B is 26 000 accumulations under the same conditions as above. Approximately 6 g of the salt was contained in 12 cm^3 of D_2O solution. The larger dispersion of resonances results in noticeable reduction of peak intensity toward the extremities because of the long (500-μs) pulses.

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Note Added in Proof. Since submission of this paper, several hardware improvements have allowed more sophisticated ^{183}W NMR experiments to be performed. A two-dimensional $^{183}W\{^{31}P\}$ INADEQUATE spectrum[12] of $Li_7[Ti_2W_{10}PO_{40}]$ has been obtained (Figure 6) and provides an unambiguous measure of the coupled sites without requiring accurate measurement of coupling patterns. Data are presented as a contour plot. Projection of the data onto the F_2 dimension (horizontal) shows a normal spectrum of pairwise ^{183}W–O–^{183}W isotopomers, while the second dimension (F_1, vertical) disperses those coupled peaks on the basis of the sum of the chemical shifts involved. The magnitudes of the couplings are retained so simple inspection of the contour pattern shows A coupled to B (edge), B to E (corner), E to C (edge), E to D (edge), C to A (corner), D to A (corner), and C to D (corner). The C–D edge connection is not observed, but both lines of the second-order C–D corner coupling are obvious.

Brevard and Schimpf[13] have also applied similar sophisticated two-dimensional methods to determining W–W connectivities in heteropolytungstates.

Registry No. $K_5MnTi_2W_{10}PO_{40}$, 84278-83-1; $K_5FeTi_2W_{10}PO_{40}$, 84278-84-2; $K_5CoTi_2W_{10}PO_{40}$, 84278-85-3; $K_5NiTi_2W_{10}PO_{40}$, 84278-86-4; $K_5CuTi_2W_{10}PO_{40}$, 84278-87-5; $K_5ZnTi_2W_{10}PO_{40}$, 84278-88-6; $Li_7Ti_2W_{10}PO_{40}$, 84278-89-7; $Cs_7Ti_2W_{10}PO_{40}$, 84303-03-7; $[(CH_3)_4N]_7Ti_2W_{10}PO_{40}$, 84303-05-9; $K_7Ti_2W_{10}PO_{40}$, 84303-06-0; $Cs_4KH_2Ti_2W_{10}PO_{40}$, 84303-07-1; $[(CH_3)_4N]_5CuTi_2W_{10}PO_{40}$, 84303-08-2; $K_5[CpFe(CO)_2Sn]_2W_{10}PO_{38}$, 84253-84-9; $[(CH_3)_3NH]_5[C_5H_5Fe(CO)_2Sn]_2W_{10}PO_{38}$, 84253-86-1; $(NH_4)_5[C_5H_5Fe(CO)_2Sn]_2W_{10}PO_{38}$, 84253-87-2; $Li_5[C_5H_5Fe(CO)_2Sn]_2W_{10}PO_{38}$, 84253-88-3; $[(CH_3)_3NH]_4CpFe(CO)_2SnW_{11}PO_{39}$, 84303-10-6.

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Electrogenerated Chemiluminescence. 42. Electrochemistry and Electrogenerated Chemiluminescence of the Tris(2,2′-bipyrazine)ruthenium(II) System

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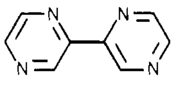
The electrochemical behavior and electrogenerated chemiluminescence (ecl) of $Ru(bpz)_3^{2+}$ (as the PF_6^- salt) in acetonitrile solutions were investigated. Oxidation to the 3+ form and reduction to the 1+, 0, 1−, and 2− forms occur at potentials about 0.5 V more positive than those for the corresponding bipyridine complex. Emission characteristic of $Ru(bpz)_3^{2+*}$ is produced upon the electron-transfer reaction between the 3+ and 1+ species. Weak emission also results from the reaction of the 3+ species with solvent or impurities.

Introduction

Of the numerous compounds that produce chemiluminescence upon the electron-transfer reactions of electrogenerated species (ecl), that observed with the $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) system is among the most intense and best characterized.[2-4] A recent report[5] of a new, related compound,

$Ru(bpz)_3^{2+}$ (bpz = 2,2′-bipyrazine)



bpz

and its spectroscopic and photocatalytic properties suggested a study of the electrochemical and ecl behavior of this compound. Previous studies of $Ru(bpy)_3^{2+}$ showed that ecl is produced by the redox reaction between the 1+ and 3+ species as well as by reaction of the 3+ species with a number of reductants (e.g., especially oxalate).[2d] We were particularly interested in $Ru(bpz)_3^{2+}$ because the redox processes are shifted by ~0.5 V toward more positive potentials, compared with those for $Ru(bpy)_3^{2+}$. This could prove valuable in ecl in aqueous media where proton reduction interferes at negative potentials. A comparison of the ecl efficiency between the bpz

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