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Fluorotungstates of the Metatungstate Family: Identification and Properties of One Compound of the 2–18 Series

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A new fluorotungstate of the metatungstate family is identified by ^{19}F NMR and ^{1}H NMR under the same conditions as shown previously for $[H_2W_{12}FO_{39}]H_5$, $[H_2W_{12}F_2O_{38}]H_4$, $[HW_{12}F_2O_{38}]H_5$, and $[HW_{12}F_3O_{37}]H_4$. The new fluorotungstate shows similar NMR characteristics: a ^{1}H resonance signal and a ^{19}F resonance multiplet. Its NMR properties are consistent with a structure in which one or more nonexchangeable protons are bound to three identical fluorines. This heteropolyacid was synthesized by using ^{19}F NMR as a control method. Its properties are distinct from those of other fluorotungstates: preparation, composition, molecular weight, polarogram, and stability with respect to OH^-. Unlike other fluorotungstates, it does not belong to the 1–12 series; its X-ray powder pattern and properties enable its classification in the 2–18 series, whose structure is ordered around two centers: the two nonexchangeable protons. The established formula is $[H_2W_{18}F_6O_{56}]H_8$. This structure has never been identified in the unfluorinated series.

Introduction

The basic structural model of molybdic and tungstic heteropolyanions is the Keggin[1] structure: assembly of 12 WO_6 (MoO_6) octahedra around a central cavity, whose center is occupied by an element such as P, As, B, etc. This very symmetrical structure may be used to obtain less condensed structures such as those deficient in one or three W (Mo) (the 11 or 9 W (Mo) structures)[2–5] or more condensed structures including two tetrahedral cages such as the $P_2W_{18}O_{62}K_6\cdot 14H_2O$, whose structure was established by Dawson in 1953.[6]

However, when the central cavity is occupied by protons (metatungstate $H_2W_{12}O_{40}{}^{6-}$),[7] it is impossible to induce a different condensation in the Keggin structure.

By introducing fluorine into this metatungstate molecule, we have already notably modified its properties; for instance, some of our earlier products[8] contained only one central proton instead of two. In this report, we shall show that by fluorination we can diminish the rigidity of the metatungstic structure to a condensation similar to that of the $P_2W_{18}O_{62}K_6\cdot 14H_2O$ structure.

Experimental Section

(A) Preparations. 1. Acid. Two solutions are prepared: solution A, 40% hydrofluoric acid (12 mL) and hydrochloric acid (30 mL, 5 M) mixed with water (110 mL); solution B, 104 g of $Na_2WO_4\cdot 2H_2O$ dissolved in hot water (140 mL).

Place solution A in a poly(tetrafluoroethylene) beaker and add solution B while heating to boiling and stirring constantly. After the solution is cooled, a white residue in suspension in the solution is filtered, 40% hydrofluoric acid (36 mL) is added, and, after a few minutes, 37% hydrochloric acid (220 mL) is added while the mixture is stirred. After being cooled in ice, the synthesized heteropolyacid is collected by extraction with 200 mL of ether according to Drechsel's method.[9] The heteropolyacid is separated from ether by evaporation. It crystallizes in water with a tungstic acid deposit and is then recrystallized three or four times at room temperature until tungstic acid no longer precipitates out. The yield is 20%.

2. Potassium Salt. This is obtained from the parent acid by precipitation with potassium chloride.

Table I. Correlation of Percent Heteropolyacid with the W Concentration (C_W) in the Reaction Medium

C_W, M	0.5	0.75	1
% heteropolyacid	43	55	95

Dissolve 3.4 g of the parent acid and 11 g of potassium chloride in water (60 mL). The potassium salt which precipitates is rapidly washed with water and then ethyl alcohol and dried with ether.

3. Tetramethylammonium Salt. This is obtained from the parent acid by precipitation with tetramethylammonium chloride.

Use the same working method as for the potassium salt, but, instead of 11 g of potassium chloride, add 3 g of tetramethylammonium chloride.

(B) Analysis. W is determined gravimetrically by the cinchonine method.[10] F is checked by specific Orion fluoride electrode with the use of lanthanum fluoride.[11]

After decomposition, the fluorinated compound is placed in an acetic buffer (0.5 M and pH 5.5). Electrode calibration is carried out at this pH and with different concentrations in sodium fluoride (10^{-4}–5×10^{-3} M), with a constant F/W quotient. The relative potentials measured are a linear function of pF ($-\log(F^-)$), and the slope of the line is 58 mV at 20 °C.

Acidities are determined by potentiometric titrations of sodium hydroxide, and the high-speed titration is recorded on Beckman Electroscan 30. The acidities determined by this method are all strong.[12]

The central protons are determined quantitatively by NMR spectroscopy in D_2O with pivalic acid as the internal standard.[7] This method is not applicable to the salts.

Potassium is determined by gravimetry of potassium tetraphenylborate.[13] The tetramethylammonium in the fluorotungstate is determined by elemental analysis of carbon and nitrogen.

(C) UV Spectroscopy. The measurements are recorded on a Beckman 25.

(D) Polarography. The polarograms are recorded on a Tacussel instrument. All potentials are referred to the saturated calomel electrode.

(E) Ultracentrifuging. The ultracentrifuge is a Beckman Spinco E equipped with a Schlieren optic. The speed of rotation adopted to determine the molecular weight is 40 000 rpm. The solutions are centrifuged with 0.2 M sodium chloride. The Archibald method[14] is employed.

(F) X-ray Diffraction. The powder patterns are recorded with a Siemens diffractometer using Cu radiation.

(G) Nuclear Magnetic Resonance Spectroscopy. 1. ^{1}H NMR. Spectra are recorded on a Varian EM X L 100 at 100 MHz at 20 °C.

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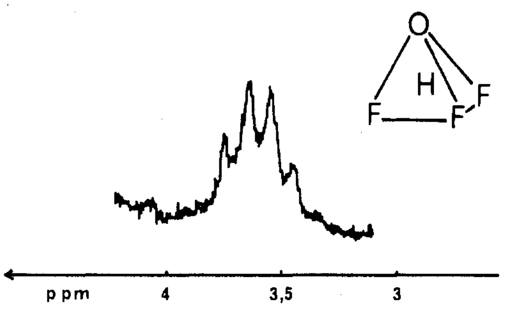

Figure 1. ^{1}H NMR spectrum at 100 MHz. The shift is given relative to pivalic acid.

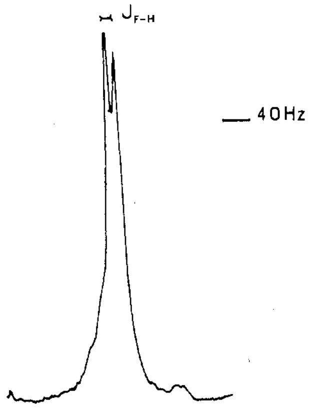

Figure 2. ^{19}F NMR spectrum at 87.6 MHz.

2. **^{19}F NMR.** The instrument is a Bruker WH 90 used in Fourier transform at 84.6 MHz. Proton decoupling is obtained by noise band decoupling.

Results and Discussion

(A) Identification and Synthesis. The new heteropolyacid is formed in the same medium as the species already studied.[8,15] These species are extracted in 3 M hydrochloric acid by the use of the method given in the previous sections. The new heteropolyacid is extracted by increasing the acidity of the medium: the maximum yield occurs at 5 M hydrochloric acid; there is competition between the formation reactions of the different heteropolyacids. The systematic variation of the W concentration in the reaction medium caused a variation in heteropolyacid yield with W concentration. The values obtained for different concentrations are given in Table I. They were calculated by using ^{19}F NMR integrated peaks.

Table I shows that the heteropolyacid is prepared in the pure state for $C_W = 1$ M. This concentration is consistent with the synthesis procedure given in the previous section.

(B) ^{19}F and ^{1}H NMR Spectra. Like the compounds previously studied, the new heteropolyacid also shows a ^{1}H NMR signal and a ^{19}F NMR multiplet, due to coupling of ^{19}F with protons on the one hand and with ^{183}W on the other (^{183}W natural abundance 14.3%, $I = {}^1/_2$; ^{184}W natural abundance 85%, $I = 0$).

The ^{1}H NMR signal is a quadruplet due to protons surrounded by three fluorine atoms. It has a chemical shift of 3.62 ppm relative to pivalic acid (Figure 1).

The ^{19}F NMR multiplet is a doublet (Figure 2). The coupling measured agrees with J_{F-H} measured in ^{1}H NMR. The doublet results from the coupling of fluorines with one proton. After spin decoupling of the proton by double irradiation, the spectrum consists of a broad singlet (Figure 3) without a hyperfine structure. In contrast to other fluorotungstates,[8] no F–^{183}W coupling can be measured. The chemical shift is 82.5 ppm relative to trifluoroacetic acid as the external standard.

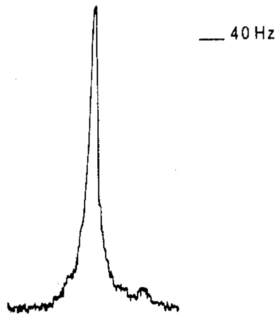

Figure 3. ^{19}F NMR spectrum at 87.6 MHz after proton decoupling.

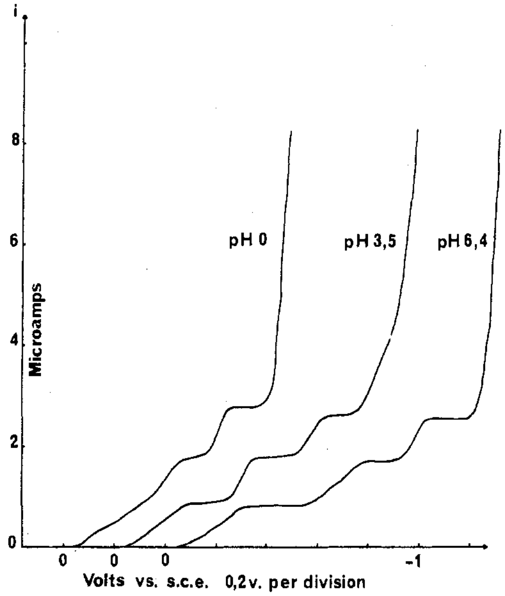

Figure 4. Polarograms at different pH (5×10^{-3} M tungsten): pH 0, 0.1 N HCl, 1 M NaCl; pH 3.5, 0.5 M formic buffer; pH 6.4, 0.5 M succinic buffer.

Table II. Correlation of $t_{1/2}$ Values with pH

pH	7.2	7.45	7.7	7.9	8.2	8.4
$t_{1/2}$, min	160	76	56	47	28	19

The heteropolyacid shows NMR properties similar to those of a fluorotungstate of the 1–12 series which would contain a proton surrounded by three identical fluorines; on the basis of other properties, we shall demonstrate that its structure is actually even more condensed.

(C) Polarography. The polarograms obtained at different pH are given in Figure 4. We observed three two-electron reduction waves, the first weakly split into two one-electron waves at every pH and the second also split at pH 7.

Two remarks can be made: the compound is more reducible than the fluorotungstates of the 1–12 series (half-wave potential 0.100 V instead of 0.240 V for the more reducible fluorotungstate of the 1–12 series);[15,16] the two-electron waves are lower than that of the 1–12 series (this may correspond to a more condensed structure).

(D) Optical Spectrum. The heteropolyanion exhibits intense absorption in the UV region due to charge-transfer bands. We observed two shoulders at 260 and 295 nm (Figure 5). Pope gave a similar description for $P_2W_{18}O_{62}^{6-}$.[17]

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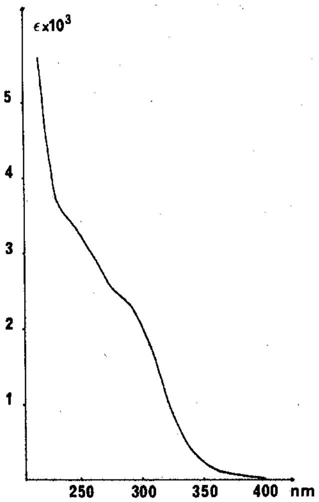

Figure 5. Absorption spectrum (5 × 10⁻³ M tungsten, 0.1 N HCl, and 1 M NaCl). ε is relative to 1 g-atom of W.

Table III

compd (fw[a])		% W	% F	% center H	% M[b]	% H_2O[c]
$[H_2W_{18}O_{56}F_6]H_8\cdot 41H_2O$ (5070)	found	65.3	2.2	0.043	0.15	
	calcd		2.2	0.039	0.16	14.5
$[H_2W_{18}O_{56}F_6]F_8\cdot 42H_2O$ (5400)	found	61.4	2		5.9	
	calcd		2.1		5.8	14
$[H_2W_{18}O_{56}F_6](N(CH_3)_4)_8\cdot 21H_2O$ (5290)	found	62.5	2.1		11.3	7.1
	calcd		2.1		11.2	7.1

[a] Determined from the percentage of W. [b] M = H^+, K^+, or tetramethylammonium. [c] Calculated by difference.

(E) Stability as a Function of pH. Table II gives the $t_{1/2}$ for the hydrolysis reaction at different pH levels and room temperature. The reactions are observed by polarography in tris(hydroxymethyl)aminomethane buffers of 0.25 M concentration, with 1 M sodium chloride as the background electrolyte and pH ranging from 7.2 to 8.4. The solutions are 5 × 10⁻³ M in tungsten.

By hydrolysis, the heteropolyanion breaks down without giving the intermediate polarographable compound. The reaction is first order with respect to the polyanion and OH^- ions. It is more stable with respect to OH^- than the most stable fluorotungstate of the metatungstate series, which degrades instantly at pH 7.2, $H_2W_{12}FO_{39}^{5-}$.[15]

(F) Ultracentrifuging. Since the foregoing observations show that the properties of the heteropolyacid are markedly different from those of the previously examined 1–12 series, we had to check the molecular weight by ultracentrifuging. In these experiments, we found a molecular weight of 4930 for the potassium salt (calculated value 4630). This value differs significantly from that obtained for the 1–12 condensed species (3190).[7]

(G) Structure. A more condensed heteropolyanion structure was sought corresponding to the particular properties of the fluorotungstate investigated. A 2–18 structure was assumed.

The fluorotungstate has many properties in common with $P_2W_{18}O_{62}^{6-}$. Like $P_2W_{18}O_{62}^{6-}$, it is prepared in concentrated solutions and is very reducible (Figure 4) and very stable, even at high pH (Table II).[18,19]

According to these properties and by analogy with the general formula $X^{n}{}_2W_{18}O_{62}^{(16-2n)-}$ for the 2–18 series, we suggest the formula $H_2W_{18}O_{56}F_6^{8-}$ matching the results of the analysis given in the Table III.

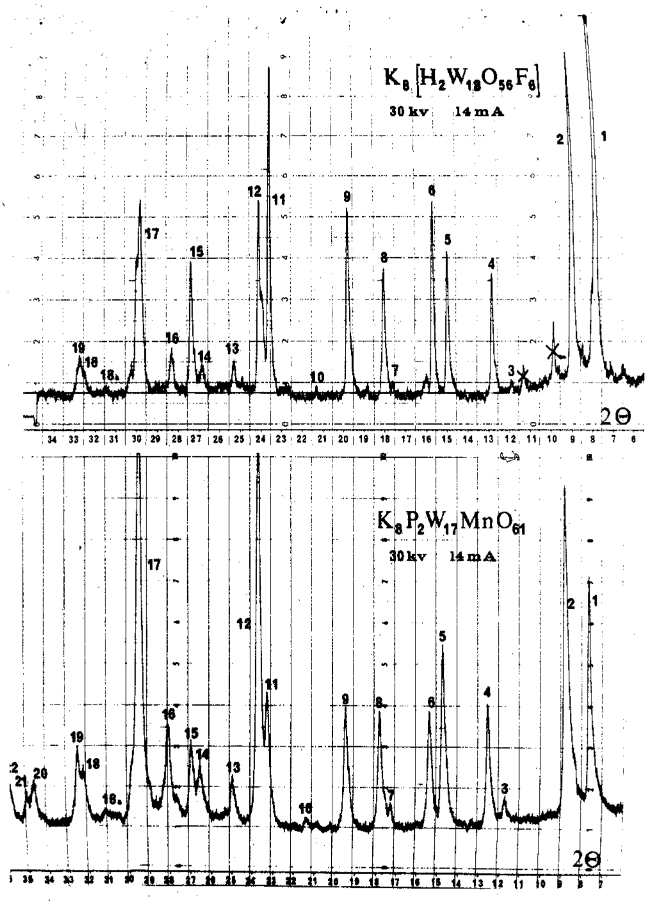

Figure 6. X-ray diffraction powder patterns.

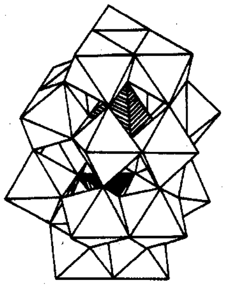

Figure 7. Structure of $P_2W_{18}O_{62}^{6-}$ (Dawson[6]).

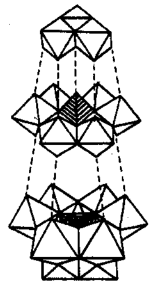

Figure 8. Coupling of the 18 WO_6 octahedra and the 2 XO_4 tetrahedra in the $X_2W_{18}O_{62}$ group.

The fact that it belongs to the 2–18 series is confirmed by X-ray diffraction (Figure 6). Tourné and Tourné[20] have shown that the 1–12 and 2–18 series polyanions are divided into different crystallographic series and the determining factors for each series are the cation species and the number

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of cations per anion respectively; the potassium fluorotungstate crystallizes in a system similar to that of a 2–18 compound such as $P_2W_{17}MnO_{61}(H_2O)K_8$.

The fact that the two X-ray powder patterns are very similar leads us to believe that this similarity stems from a structural similarity.

By using $P_2W_{18}O_{62}^{6-}$, Dawson was the first to establish the structure of the 2–18 series:[6] he showed that the molecule consists of two PW_9O_{34} units derived from the Keggin structure and joined together by six oxygen atoms (Figure 7).[21]

A glance at the model representation of the molecule (Figure 8) reveals that every XW_9O_{34} unit consists of a compact group W_3O_{13} of three octahedra joined together by three edges and the remaining six octahedra, ordered at the base of the XO_4 tetrahedron, forming a ring joined alternately by edges and corners.

It is reasonable to assume that in $H_2W_{18}F_6O_{56}^{8-}$ the fluorines are assigned to the corners of the tetrahedron, the center of which is occupied by a proton. NMR spectra show that, in the molecule which contains two tetrahedra, the fluorines are coupled in groups of three with a central proton; the J_{H-F} is very similar to that of the 1–12 series, in which the fluorines are clearly located on the central tetrahedron. Among the oxygens of the tetrahedron, we distinguish the one belonging to the compact group W_3O_{13} from the three others belonging to the ring: the first is bound to three W and the second only to two W. Also, on the basis of the NMR properties, we can assert that the fluorines are identical and that they replace the oxygens of the ring. It is noteworthy that the fluorines all occupy the same type of site, so that the overall symmetry of the molecule X_2W_{18} is preserved.[22]

Conclusion

We characterized by use of NMR data a new metatungstic species belonging to the 2–18 series and having the formula $H_2W_{18}O_{56}F_6^{8-}$.

Its essential properties, which differ from those of the fluorotungstates of the 1–12 series, are very similar to those of the previously examined heteropolyanions of the 2–18 series: stability with respect to OH$^-$, polarogram, molecular weight, and X-ray powder patterns. Hence the compound exhibits a number of remarkable NMR properties which support the hypothesis that it belongs to the 2–18 series.

It can be classified in the heteropolyanion category with the metatungstic structural model, since the two constitutive heteroelements of the 2–18 series molecule are replaced here by a proton. However, no unfluorinated equivalent compound has been observed up to the present. Fluorine probably has a stabilizing effect on such molecules. As in the fluorotungstates of the 1–12 series, the fluorine atoms are located at the center of the molecule and the structure retains a high degree of symmetry.

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Registry No. $[H_2W_{18}O_{56}F_6]H_8$, 74185-24-3; $[H_2W_{18}O_{56}F_6]K_8$, 74185-25-4; $[H_2W_{18}O_{56}F_6](N(CH_3)_4)_8$, 74331-35-4.

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(21) It has been shown that the compounds of the 2–18 series exist in the two isomeric forms α and β. The structure established by Dawson corresponds to the α form. The character of isomerism α–β is now well-known (see for instance: R. Massart, R. Contant, J. M. Fruchart, J. P. Ciabrini, and M. Fournier, *Inorg. Chem.*, **16**, 2916 (1977); R. Acerete, S. Harmalker, C. F. Hammer, M. T. Pope, and L. C. W. Baker, *J. Chem. Soc., Chem. Commun.*, 777 (1979). Only the α form matches the ^{19}F NMR data.

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Selection Rules for Lanthanide Optical Activity

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Selection rules are developed for the electronic factors which govern the *magnitudes* of the chiroptical properties associated with the 4f–4f transitions in optically active lanthanide(III) complexes. These selection rules are based on the *S*, *L*, and *J* angular momentum quantum numbers of lanthanide 4f-electron states perturbed by spin–orbit coupling and 4f-electron/crystal field interactions. The lanthanide term-to-term transitions are classified according to their predicted (relative) electric dipole strengths, rotatory strengths, and dissymmetry factors in a chiral ligand environment. Several types of these transitions are predicted to be particularly favorable for optical activity studies (large rotatory strengths and dissymmetry factors). These transitions are designated as "CD-sensitive" transitions. Comparisons are made between available experimental data and the predictions derived from the selection rules and classification schemes developed in this study.

I. Introduction

The natural optical activity of lanthanide ions in chiral coordination environments has been the subject of a number of experimental studies.[1-17] Generally, the object of these studies has been to relate the spectroscopic observables of optical activity to specific structural features of the lanthanide

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