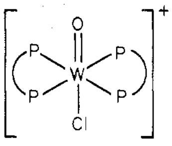
a single ν(WCl) at ~280 cm^{-1}, both fairly insensitive to changes in L-L suggesting a trans structure. This was confirmed by the ^{31}P NMR spectra which showed only a single strong absorption, flanked by weak satellites due to $^{183}W-^{31}P$ coupling (^{183}W = 14% abundance). The magnitude of J_{W-P} ~ 315 Hz is comparable with other complexes containing trans phosphines[12] (V).


T

Comparison between the oxomolybdenum(V) and oxotungsten(V) complexes shows considerable similarities in properties, as would be expected, but also surprising differences. The latter complexes are considerably more difficult to obtain and less stable to moisture and generally less stable in solution. The different behavior of the weaker donor phenyl-substituted diarsines toward W(V) is also unexpected.

Acknowledgment. We are grateful to Ciba-Geigy Ltd. for obtaining the ^{31}P NMR spectra and wish to thank Dr. M. J. Parrott for assistance in obtaining the EPR spectra.

Registry No. [$WOCl_3$(VPP)], 63848-28-2; [$WOCl_3$(dpe)], 63848-27-1; [$WOCl_3$(pp)], 63848-26-0; [$WOCl_3$(VAA)], 63848-25-9; [$WOCl_3$(dmp)], 63848-24-8; [$WOCl_3$(dma)], 63848-23-7; [$WOCl_3$(dmpa)], 63848-22-6; [$WOCl_3$(das)], 63848-21-5; [$WOCl_3$(stars)], 63848-20-4; [$WOCl_3$(mpp)], 63848-19-1; [$WO(dpm)_2Cl_2$][$WOCl_4$], 63848-18-0; [$MoO(dpm)_2Cl_2$][$MoOCl_4$], 63848-16-8; [$WOCl(dpe)_2$]BPh_4, 63848-14-6; [$WOCl(VPP)_2$]BPh_4, 63833-70-5; [$WOCl(pp)_2$]BPh_4, 63865-76-9; [$WOCl_3(PPh_3)_2$], 63833-68-1; [$WOCl_3(MePh_2P)_2$], 63833-67-0; [$WOCl_3(PCy_3)(THF)$], 63833-66-9; [$WOCl_3(THF)_2$], 18131-65-2; [$MoOCl_3(THF)_2$], 20529-42-4; WCl_6, 13283-01-7.

References and Notes

(1) Part 9: C. A. McAuliffe, B. J. Sayle, and W. Levason, *J. Chem. Soc., Dalton Trans.*, in press.

(2) (a) The University, Southampton. (b) The University of Manchester Institute of Science and Technology. (c) Auburn University.

(3) D. A. Edwards, *J. Inorg. Nucl. Chem.*, **27**, 303 (1965).

(4) W. Levason, C. A. McAuliffe, and B. J. Sayle, *J. Chem. Soc., Dalton Trans.*, 1177 (1976).

(5) A. V. Butcher and J. Chatt, *J. Chem. Soc., A*, 2556 (1971).

(6) D. G. Blight, D. L. Kepert, R. Mandyczewsky, and K. R. Trigwell, *J. Chem. Soc., Dalton Trans.*, 313 (1972).

(7) V. C. Adam, U. A. Gregory, and B. T. Kilbourn, *Chem. Commun.*, 1400 (1970).

(8) G. W. A. Fowles and J. L. Frost, *J. Chem. Soc., A*, 671 (1967).

(9) B. J. Brisdon, *Inorg. Chem.*, **6**, 1791 (1967).

(10) P. C. Crouch, G. W. A. Fowles, P. R. Marshall, and R. A. Walton, *J. Chem. Soc., A*, 1634 (1968).

(11) W. Levason, C. A. McAuliffe, and F. P. McCullough, *Inorg. Nucl. Chem. Lett.*, **12**, 843 (1976).

(12) A. V. Butcher, J. Chatt, G. J. Leigh, and P. L. Richards, *J. Chem. Soc., Dalton Trans.*, 1064 (1972).

(13) K. Feenan and G. W. A. Fowles, *Inorg. Chem.*, **4**, 310 (1965).

(14) G. W. A. Fowles and J. L. Frost, *J. Chem. Soc., A*, 1631 (1966).

(15) B. N. Figgis and J. Lewis, *Prog. Inorg. Chem.*, **6**, 37 (1964).

(16) G. W. A. Fowles, D. A. Rice, and R. A. Walton, *J. Inorg. Nucl. Chem.*, **31**, 3119 (1969).

(17) C. A. Tolman, *J. Am. Chem. Soc.*, **92**, 2956 (1970).

(18) D. L. Kepert and R. Mandyczewsky, *J. Chem. Soc., A*, 530 (1968).

(19) I. N. Marov, Y. N. Dubrov, V. K. Belyaeva, and A. N. Ermalov, *Dokl. Akad. Nauk SSSR*, **171**, 385 (1966).

(20) C. D. Garner, M. R. Hyde, F. E. Mabbs, and V. I. Routledge, *J. Chem. Soc., Dalton Trans.*, 1175 (1975).

(21) E. M. Shustorovich, M. A. Porai-Koshits, and V. A. Buslaev, *Coord. Chem. Rev.*, **17**, 1 (1975).

(22) W. W. Foglemann and H. B. Jonassen, *J. Inorg. Nucl. Chem.*, **31**, 1536 (1969).

(23) K. K. Chow and C. A. McAuliffe, *Inorg. Chim. Acta*, **10**, 197 (1974).

(24) E. A. Allen, B. J. Brisdon, D. A. Edwards, G. W. A. Fowles, and R. G. Williams, *J. Chem. Soc.*, 4649 (1963).

(25) B. A. Goodman and J. B. Raynor, *Adv. Inorg. Chem. Radiochem.*, **13**, 135 (1970).

Contribution from the Laboratoire de Chimie des Mêtaux de Transition, E.R.A. 608,
Universitê Pierre et Marie Curie, 75230 Paris Cedex 05, France

^{31}P NMR Studies on Molybdic and Tungstic Heteropolyanions. Correlation between Structure and Chemical Shift

RENÉ MASSART,* ROLAND CONTANT, JEAN-MARC FRUCHART, JEAN-PIERRE CIABRINI, and MICHEL FOURNIER

Received March 3, 1977 AIC701712

^{31}P NMR has been carried out on 24 tungstic and molybdic heteropolyanions, the structures of which are derived from $(PM_{12}O_{40})^{3-}$ and $(P_2M_{18}O_{62})^{6-}$ by the removal or the partial substitution of metallic atoms. The chemical shift value is correlated with the PO_A bond strength, O_A being the oxygen atom of the central PO_4 tetrahedron. For those compounds containing several P atoms, the existence of one or several peaks allows one to suggest a structure. From considerations of δ values, the positions of holes or substituting elements are determined.

Introduction

The accurate determination of the structures of heteropolyanions by x-ray diffraction is generally difficult and has been undertaken for compounds containing one kind of heavy atom. Thus some physical techniques, namely IR and Raman spectroscopy, UV and visible spectroscopy, EPR, NMR, etc., have been lately used to explain the properties related to the Keggin structure.[1] For compounds with phosphorus as the central atom, ^{31}P NMR studies have been recently carried out.[2–6] However, only a few compounds were concerned, and no satisfactory correlation between chemical shift and structure had been proposed until now. In the present work, which deals with 24 compounds, we intend to correlate more exactly chemical shift and structure and to shed more light on the properties of the different series of heteropolyanions. The complexes are related to the $(PM_{12}O_{40})^{3-}$ series (noted as PM_{12}) and the $(P_2M_{18}O_{62})^{6-}$ series (noted as P_2M_{18}), M = W or Mo.

The structure of PM_{12} consists of a central PO_4 tetrahedron sharing its oxygen atoms (called O_A) with four M_3O_{13} groups (noted as (M_3)). These M_3O_{13} groups, made of three edge-sharing octahedra, are linked together by corners. The α isomer has the well-known Keggin structure (T_d symmetry)[1,7–9] shown in Figures 1a and 2a. The β isomer[10] is derived from the α by rotating one (M_3) group by $\pi/3$ about a threefold axis (C_{3v} symmetry). "Unsaturated" compounds, i.e., compounds with a "defect-Keggin structure", are derived from α-PM_{12} by removing one MO_6 octahedron (α-PM_{11},

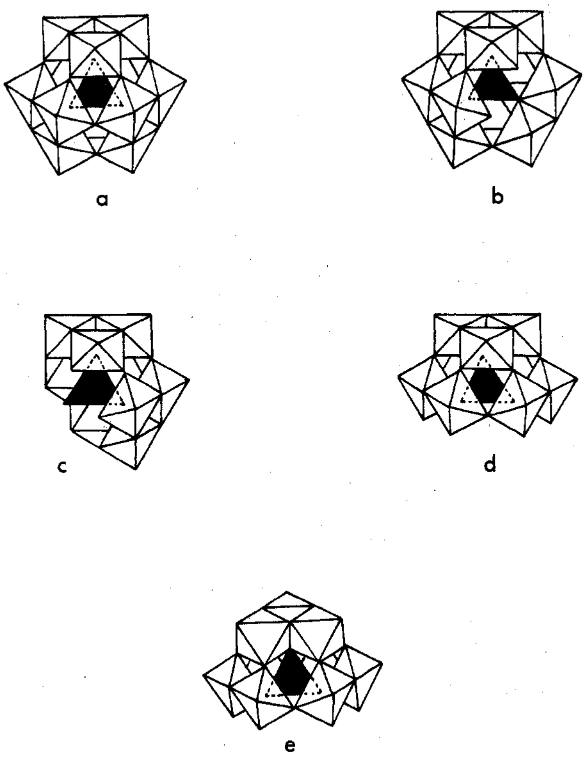


Figure 1. (a) α-PM_{12}, (b) α-PM_{11}, (c) B-type α-PM_9, (d) A-type α-PM_9, (e) A-type β-PM_9.

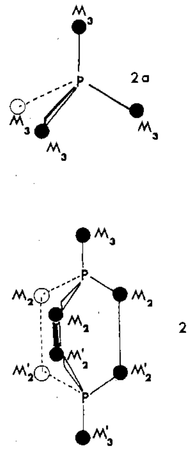


Figure 2. Schematic drawings of (a) PM_{12} and (b) P_2M_{18}.

Figure 1b) or three MO_6 octahedra of a same (M_3) set (B-type α-PM_9, Figure 1c).[11-14] Metal atoms, different from M, can partly or wholly fill these holes, giving rise to compounds such as PW_9Mo_2 (PW_9 + 2 Mo), PW_9Mo_3 (PW_9 + 3 Mo), or $PW_{11}Mo$ (PW_{11} + Mo). As opposed to saturated compounds, the structures of the "unsaturated" heteropolyanions have not been established by direct means. However, structures have been proposed from considerations on chemical and spectrophotometrical properties.[13,14]

An 18-metallo-2-phosphate anion, P_2M_{18}, consists of two PM_9 half-anions. These PM_9 half-anions differ from the former defined above (B-type α-PM_9) and are called A-type PM_9.[15] The A-type PM_9 is obtained by removing one M atom from three different (M_3) sets (Figure 1d). Thus, the A-type PM_9 structure is built with an (M_3) group and three (M_2) groups. Two forms of P_2M_{18} have been described. The α isomer,[16] also called B isomer,[17] has a D_{3h} symmetry with one equatorial mirror plane, perpendicular to the axis linking the two phosphorus atoms (Figure 2b).[18-20] Sasaki[21] postulates that the β isomer is derived from the former by rotating a PM_9 half-anion by $\pi/3$ about the P–P axis. Contant et al.[22] have recently isolated and characterized in solution several compounds related to α-P_2W_{18} according to the following experimental path

$$\begin{tikzcd}
\alpha\text{-}P_2W_{18} \arrow[r, "OH^-"] & \alpha_2\text{-}P_2W_{17} \arrow[r, "OH^-"] & \alpha\text{-}P_2W_{16} \arrow[d, "OH^-"] \\
 & \alpha_1\text{-}P_2W_{17} \arrow[ul, "H_3O^+"] \arrow[u] & \alpha\text{-}P_2W_{12} \arrow[l, "H_3O^+"']
\end{tikzcd}$$

The 1 and 2 indices are chosen according to the irreversible isomerization α_1-P_2W_{17} → α_2-P_2W_{17}, the latter compound being obtained by alkaline degradation of α-P_2W_{18}.

The holes in the structures of "unsaturated" compounds P_2W_{17}, P_2W_{16}, and P_2W_{12} can be filled by other metals than tungsten, e.g., molybdenum and zinc.

Experimental Section

Spectroscopy. NMR spectra were recorded on a Perkin-Elmer spectrograph, Model R 10, operating at 24.29 MHz for ^{31}P and at room temperature. Chemical shifts are expressed in parts per million with respect to 85% H_3PO_4 as an external standard and are counted positively toward strong fields. All samples have been studied in solution. The slightly soluble potassium salts are dissolved in aqueous lithium perchlorate; the insoluble potassium perchlorate is filtered off.

Preparations and Characterizations. The preparations of the following compounds are well-known: α-$H_3PW_{12}O_{40}$,[23a] $Na_7PV_{12}O_{36}$,[23b] α-$K_7PW_{11}O_{39}$,[23c] α- and β-$H_6P_2W_{18}O_{62}$,[23d] α-$H_3PMo_{12}O_{40}$.[24] With the exception of PV_{12}, a review of their polarographic properties has been published.[25]

α-$K_{12}H_6P_2W_{12}O_{50}$, α_1-$LiK_9P_2W_{17}O_{61}$, α_2-$K_6P_2W_{17}MoO_{62}$, α_1-$K_6P_2W_{17}MoO_{62}$, α-$K_6P_2W_{16}Mo_2O_{62}$, α-$K_6P_2W_{12}Mo_6O_{62}$, α_2-$K_8H_2P_2W_{17}ZnO_{62}$, α_1-$K_8H_2P_2W_{17}ZnO_{62}$, α-$Na_{10}H_4P_2W_{16}Zn_2O_{62}$. The preparations and polarographic properties of these new compounds are described in another paper by two of us.[22]

α_2-$K_{10}P_2W_{17}O_{61}$,[23e] $K_8HP_3W_{18}O_{66}$,[29] and $K_6P_2W_{21}O_{71}$.[23f] These compounds have been prepared according to methods described elsewhere.

Potassium Salts of α-9-Tungsto-2-molybdophosphate and α-9-Tungsto-3-molybdophosphate. These two compounds are prepared from β-PW_9 which is easier to isolate than α-PW_9. The addition of two molybdenum atoms to β-PW_9 leads firstly to β-PW_9Mo_2, which is quickly isomerized into α-PW_9MO_2.[11]

β-$Na_8HPW_9O_{34}$. Sodium tungstate $Na_2WO_4 \cdot 2H_2O$ (120 g) is dissolved in water (150 mL). Orthophosphoric acid, H_3PO_4 (3 mL, 14.7 F), and concentrated acetic acid (22 mL, 17.4 F) are successively added to the solution. The white salt $Na_8HPW_9O_{34} \cdot 24H_2O$ precipitates out.

α-$K_7PW_9Mo_2O_{39}$. β-$Na_8HPW_9O_{34} \cdot 24H_2O$ (11 g) is dissolved in an aqueous mixture of sodium molybdate (20 mL, 1 F) and hydrochloric acid (16 mL, 1 F). Then hydrochloric acid (about 12 mL, 1 F) is added dropwise until the pH lies between 6 and 6.5. The potassium salt $K_7PW_9Mo_2O_{39} \cdot 19H_2O$ is precipitated out by addition of solid potassium chloride.

α-$K_3PW_9Mo_3O_{40}$. Quantities of dioxane (20 mL), aqueous hydrochloric acid (30 mL, 5.45 F), and aqueous sodium molybdate (10 mL, 1 F) are mixed. Upon addition of $K_7PW_9Mo_2O_{39} \cdot 19H_2O$ (10 g) to this solution, the yellow salt $K_3PW_9Mo_3O_{40} \cdot 25H_2O$ precipitates out. This compound, unstable in aqueous solution, is stable in hydroorganic mixtures, as water–dioxane, 1/1 in volume.

$(NH_4)_6HPMo_{11}ZnO_{40} \cdot 25H_2O$. The previously described preparation[28] has been modified. An aqueous mixture of orthophosphoric acid (10 mL, 1 F) and monochloracetic acid (10 mL, 4 F) is poured onto solid ammonium heptamolybdate, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (19.5 g). After the solid is dissolved, and aqueous zinc chloride solution (10 mL, 1 F) is quickly added. The resulting solution is kept at 0 °C. After about 10 h, pale yellow hygroscopic crystals are obtained.

A-Type α-$Na_3H_6PMo_9O_{34} \cdot 13H_2O$. Sodium monohydrogen phosphate $Na_2HPO_4 \cdot 12H_2O$ (18 g) is dissolved in a mixture of perchloric acid (73 mL, 11.7 F) and water (20 mL). The solution is cooled to -10 °C. Then a solution of sodium molybdate $Na_2MoO_4 \cdot 2H_2O$ (108 g) in water (200 mL) is added dropwise to the above solution kept at -10 °C. The resulting solution is pale yellow

Table I

Compd	Medium	Electrode	$E_{1/2}$ (V vs. SCE)
α-PW_3Mo_9	Dioxane/0.5 F aq perchloric acid = 1/1	Pt	+0.33 ($2e^-$), +0.12 ($2e^-$), −0.10 ($2e^-$), −0.26 ($2e^-$)
α-PW_9Mo_2	1 F acetic acid/1 F sodium acetate = 1/1	Hg	−0.23 ($2e^-$), −0.85 ($4e^-$), −0.97 ($8e^-$)
α-PW_9Mo_3	Dioxane/0.5 F aq sodium acetate/1 F aq HCH_2ClCOO = 2/1/1	Pt	+0.32 ($1e^-$), +0.06 ($1e^-$), −0.34 ($1e^-$)
α-$PW_{11}Mo$	Dioxane/0.5 F aq sodium acetate/1 F aq HCH_2ClCOO = 2/1/1	Pt	+0.28 ($1e^-$), −0.42 ($1e^-$)
B-type β-PW_9	1 F acetic acid/1 F sodium acetate = 1/1	Hg	−0.80 ($2e^-$), −0.89 ($2e^-$)
$α_2$-P_2W_{17}	1 F acetic acid/1 F sodium acetate = 1/1	Hg	−0.44 ($2e^-$), −0.60 ($2e^-$), −0.86 ($2e^-$)
P_2W_{21}	Dioxane/0.5 F aq hydrochloric acid = 1/1	Hg	−0.39 ($2e^-$), −0.66 ($2e^-$)
P_3W_{18}	1 F acetic acid/1 F sodium acetate = 1/1	Hg	−0.58 ($5e^-$?), −0.84 ($1e^-$) −0.96 ($1e^-$), −1.08 ($1e^-$)

Table II

Heteropolyanion (simplified formula)	Solvent	Cation	[P], M	Chemical shift, ppm from 85% H_3PO_4
α-PW_{12}	Water	H	0.42	14.9
α-PW_{12}	Water–dioxane	H	0.32	14.9
α-PMo_{12}	Water	H	0.48	3.9
PV_{12}	Water	Na	0.32	−1
α-PW_{11}	Water	Li	0.70	10.4
α-PW_9Mo_2	Water	Na	0.63	9.4
α-$PW_{11}Mo$	Water–dioxane	H	0.30	14.2
α-PW_9Mo_3	Water–dioxane	H	0.18	12.9
α-PW_3Mo_9	Water	H	0.40	6.2
α-$PMo_{11}Zn$	Water	NH_4	0.30	1.2
β-P_2W_{18}	Water	H	0.68	11, 11.6
α-P_2W_{18}	Water	Na	0.50	12.7
$α_1$-$P_2W_{17}Mo$	Water	H	0.84	12.2, 13
$α_2$-$P_2W_{17}Mo$	Water	H	0.60	11.9, 12.6
$α_1$-$P_2W_{17}Zn$	Water	Li	0.44	8.6, 13.3
$α_2$-$P_2W_{17}Zn$	Water	Li	0.38	8.6, 13.8
$α_1$-P_2W_{17}	Water	Li	0.34	9, 13.1
$α_2$-P_2W_{17}	Water	Li	0.70	7.1, 13.6
α-$P_2W_{16}Zn_2$	Water	Li	0.14	4.4, 14.05
α-$P_2W_{16}Mo_2$	Water	Li	0.35	10.2, 12.7
α-$P_2W_{12}Mo_6$	Water	Li	0.36	9.75
α-P_2W_{12}	Water (buffer pH 4.8)	Li	0.30	7.8
α-P_2Mo_{18}	Water	Na	0.96	3.4
P_2W_{21}	Water (buffer pH 2)	Na	0.64	13.3
P_3W_{18}	Water	Li	0.79	9.9

Table III[a]

Compd	This paper	Pope[6]	Kazanskii[5]	Lebedeva[3]
α-PW_{12}	14.9	14.96 ± 0.5	15.1	17.7 ± 0.5
α-PMo_{12}	3.9		4.8	4.3 ± 0.5
α-PW_{11}	10.4		11.3	
$α_2$-P_2W_{17}	7.1, 13.6		10	

[a] Chemical shifts in ppm from 85% H_3PO_4. The results are in good agreement, except those for $α_2$-P_2W_{17}. This discrepancy will be discussed below.

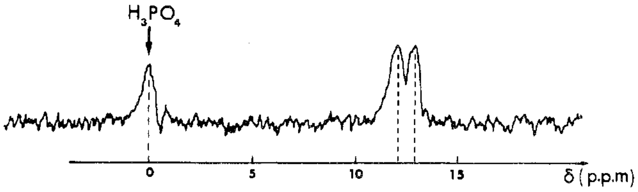


Figure 3. NMR ^{31}P spectrum of $α_1$-$H_6P_2W_{17}MoO_{62}$.

because of the occurrence of some dodecamolybdophosphate anion $(PMo_{12}O_{40})^{3-}$. Sodium salt is collected after standing overnight at 0 °C.

$Na_6P_2Mo_{18}O_{62}·11H_2O$. The preparation is the same as the preceding one, except that it is performed at 20 °C. The solution is allowed to evaporate in the air. After several days, orange crystals are obtained.

$K_3PMo_9W_3O_{40}·5H_2O$. A-Type α-$Na_3H_6PMo_9O_{34}$ (10 g) is dissolved in an aqueous mixture of sodium tungstate (18 mL, 1 F) and hydrochloric acid (20 mL, 1 F). After 2 h, solid potassium chloride is added in order to precipitate out the yellow potassium salt. The precipitate is dissolved in the minimum of water (20 °C). Recrystallization is carried out at 0 °C.

α-$H_3PW_{11}MoO_{40}$. The reduced $(PW_{11}Mo^VO_{40})^{4-}$ is prepared by the procedure described by Pope et al.[26] The potassium salt is isolated from the solution and then dissolved in hydrochloric acid (3 F). The molybdoundecatungstophosphoric acid is then extracted by diethyl oxide. Water is added, and crystals of the reduced complex are obtained by allowing the solution to evaporate at room temperature. The unreduced anion $(PW_{11}MoO_{40})^{3-}$, unstable in aqueous solution, is prepared by anodic oxidation on a platinum electrode (+0.7 V vs. SCE) of the reduced anion in hydroorganic medium (dioxane/0.5 F HCl = 1/1).

Analyses. Tungsten was precipitated out by cinchonin. The precipitate was ignited and weighted as tungsten oxide.

Molybdenum was determined by the polarographic method (dropping mercury electrode DME) in 5 F hydrochloric acid, after alkaline degradation.

Tungsten–Molybdenum Mixture. When tungsten and molybdenum were both present, the complex was destroyed in alkaline medium and the W/Mo ratio was determined by the polarographic method (DME) in pyrocatechol (0.2 F), acetic acid (0.5 F), and sodium acetate (0.5 F) aqueous solution.

Phosphorus. The complex was destroyed by an excess of lithium hydroxide and separated off as lithium phosphate. Phosphorus was then determined by spectrophotometry in acidic medium as dodecamolybdophosphate anion (in the 400–440-nm range).

Zinc was determined by the polarographic method (DME) in 1 F sodium hydroxide. Potassium was determined by gravimetry with tetraphenylborate. Sodium and lithium were determined by atomic absorption spectrophotometry. Ammonium was determined by direct and back-protometric titration of the complex. The amount of water was estimated by difference.

Polarographic Characteristics. The half-wave potentials ($E_{1/2}$) of polyanions described in this paper are shown in Table I, with the exception of $(PMo_{11}ZnO_{40}H)^{6-}$ which is unstable at polarographic concentration.

Results

Experimental results are shown in Table II. No solvent effect on chemical shifts was observed, probably because the central atom is efficiently screened by the surrounding metal–oxygen framework. As an example, the spectrum of $α_1$-$P_2W_{17}Mo$ is shown in Figure 3.

For the previously studied compounds, our results and those reported by other authors are listed in Table III. The results are in good agreement, except those for $α_2$-P_2W_{17}. This discrepancy will be discussed below.

Discussion

Correlation between Structures and Chemical Shifts. α-P_2W_{18} and Related Compounds. Two essential features have

Table IV

	PV_{12}	PMo_{12}	$PMo_{11}Zn$	PMo_{11}	PW_{12}	PW_{11}
$\nu_{asym}(PO_A)$, cm^{-1}	1058	1070	$\left.\begin{matrix}1065\\1045\end{matrix}\right\}1060^a$	$\left.\begin{matrix}1060\\1010\end{matrix}\right\}1047^a$	1080	$\left.\begin{matrix}1085\\1045\end{matrix}\right\}1075^a$
$\nu_{sym}(MO_A)$, cm^{-1}		248			217	
δ, ppm from 85% H_3PO_4	−1	3.9	1.2		14.9	10.4

[a] The symmetry decrease of the PO_4 tetrahedron leads to a splitting of $\nu(PO_A)$. The reported value is a weighted mean of the two observed frequencies.

to be emphasized. Firstly, the occurrence of either one peak or two equal peaks is consistent with two phosphorus atoms equivalent or not. The number of peaks thus shows whether both half-anions are identical or not. It is worth noticing that the chemical shift of the phosphorus atom of an unperturbed PW_9 half-anion is practically constant; i.e., it does not practically depend upon the change (hole or substitution) which may occur in the other half-anion. The NMR spectra of α_1- and α_2-P_2W_{17}, $P_2W_{17}Zn$, and $P_2W_{17}Mo$ illustrate these facts quite well. In these cases, only one half-anion is affected by the removal or substitution of a tungsten atom. The two half-anions thus become unequivalent and two peaks of equal height are observed. In each pair of chemical shift (δ) values, the higher value remains practically constant (13.2 ± 0.6 ppm) and equal to the value observed for α-P_2W_{18}. This δ value characterizes the A-type PW_9 half-anion. The lower δ value is assigned to the phosphorus atom of the half-anion affected by a removal or a substitution. This will be explained below.

P_2W_{17}, $P_2W_{17}Zn$, $P_2W_{17}Mo$ (α_1 and α_2 Isomers). The occurrence of two equal peaks in the spectra of these six compounds has been explained above. Kazanskii[5] has recently reported that only one peak (δ 10 ppm) is observed in the NMR spectrum of the potassium salt of α_2-P_2W_{17}. As explained above, this chemical shift cannot characterize a P_2W_{17} compound. It seems rather related to another anion, probably P_3W_{18} (δ 9.9 ppm, see Table II). This compound, described by Preyssler,[29] is always formed in the same time as α-P_2W_{18}. It would have been necessary to separate carefully α-P_2W_{18} and P_3W_{18} to get pure α_2-P_2W_{17} by alkaline degradation of α-P_2W_{18}. An incomplete separation leaves some P_3W_{18} in solution, which precipitates out since its potassium salt has a low solubility.

α-$P_2W_{16}Zn_2$ and α-$P_2W_{16}Mo_2$. The occurrence of two equal peaks shows that both half-anions are not identical. Furthermore, in both pairs of δ values, the highest values (14.05 ppm for $P_2W_{16}Zn_2$ and 12.7 ppm for $P_2W_{16}Mo_2$) are nearly equal to the δ value of α-P_2W_{18} (12.7 ppm). These values correspond to unperturbed PW_9 half-anions. These two compounds are formulated (PW_9–PW_7Zn_2) and (PW_9–PW_7Mo_2).

α-P_2W_{12} and α-$P_2W_{12}Mo_6$. The occurrence of a single peak implies two equivalent phosphorus atoms. Electrochemical studies[22] suggest that the six missing tungsten atoms belong to the (M_3) and (M'_3) sets (see Figure 2b). These compounds are formulated ($P(W_2)_3$–$P(W_2)_3$) and ($P(W_2)_3(Mo_3)$–$P(W_2)_3(Mo_3)$).

α-P_2Mo_{18} and α- and β-P_2W_{18}. One peak is observed for α-P_2Mo_{18} and α-P_2W_{18}, in agreement with the solved structures (two equivalent phosphorus atoms). For β-P_2W_{18}, the two phosphorus atoms have slightly different chemical shifts (11 and 11.6 ppm). This is in disagreement with the structure proposed by Sasaki et al.[21] In this proposed structure, both PW_9 half-anions are considered identical. However Sasaki has not determined the positions of oxygen atoms. Therefore it is difficult to make a choice between both possibilities: (i) $\pi/3$ rotation of a PW_9 group (Sasaki's structure), (ii) $\pi/3$ rotation of one of the two (M_3) groups (see Figure 1e). In both cases, there is indeed practically no difference between the projection of tungsten atoms on a plane perpendicular to the P–P′ axis. Because of the slight splitting of the ^{31}P signal, we believe that the second possibility is more likely.[30] The subunit in which there is this $\pi/3$ rotation of a (M_3) group can be also considered as an A-type subunit deriving from β-PM_{12} structure. Thus we propose the following notation: A-type α-PM_9 for the A-type subunit deriving from α-PM_{12} structure (Figure 1d), A-type β-PM_9 for the A-type subunit deriving from β-PM_{12} structure (Figure 1e). The β-P_2W_{18} isomer is formed by the association of an A-type α-PW_9 subunit and of an A-type β-PW_9 subunit. In contrast to the results with substituted or "defect structure" compounds in which substituting or removing of tungsten atoms in a PW_9 group does not influence the δ value of the phosphorus atom of the other group, the rotation of a (M_3) group inside of a PW_9 subunit seems to influence the other subunit, for the two δ values are lower than those corresponding to α-P_2W_{18}.

P_3W_{18} and P_2W_{21}. These two heteropolyanions, formulated as $(P_3W_{18}O_{66}H)$[29] and $(P_2W_{21}O_{71})^{6-}$,[23f] are not directly derived from the 1/12 or the 2/18 series. Their structures are not determined. However, the occurrence of a single ^{31}P signal suggests that the phosphorus atoms are equivalent in each compound.

Interpretation of Chemical Shift Variations. General Features. Chemical shift variations may be explained in terms of changes in electron density surrounding the phosphorus atom. The oxygen atoms O_A of the central PO_4 tetrahedron may be assumed to have the most important influence on this electron density. Besides, from a general discussion of IR and Raman spectra of heteropolyanions,[31,32] some frequencies can be assigned to well-characterized vibrations. Table IV shows the frequencies of tetrahedron $\nu_{asym}(PO_A)$ and $\nu_{sym}(MO_A)$ for heteropolyanions of the 1/12 series. A good correlation appears between these data and the corresponding chemical shift values. Thus the decrease of δ values according to the sequence $PW_{12} \rightarrow PMo_{12} \rightarrow PV_{12}$ is closely paralleled by the frequency decrease of $\nu(PO_A)$ vibration (1080–1070–1058 cm^{-1}) and the frequency increase of $\nu(MO_A)$ vibration, the last one corresponding to a strengthening of the MO_A bond (217 cm^{-1} for PW_{12} and 248 cm^{-1} for PMo_{12}). In the same way, the occurrence of a hole (e.g., PM_{11}) leads to a weakening of the PO_A bond, as shown by the change of mean $\nu(PO_A)$ frequencies, and induces a decrease of the δ value. If the hole is filled by a cation forming with the heteropolyanion a bond with a strong ionic character, the O_A oxygen of the hole is not very affected. Thus, the chemical shift is closely similar to that of the parent "defect structure" compound (compare P_2W_{17} and $P_2W_{17}Zn$). This is the reason why the chemical shift value for a "defect structure" compound unstable in solution may be closely approximated by taking the δ value of its Zn^{2+} derivative. On the other hand, if the hole is filled by a metal rather covalently bonding to the heteropolyanion (e.g., Mo or W), the defect character is greatly attenuated, and the chemical shift value approaches the one of the corresponding saturated compound. Table V illustrates these observations corresponding to the adduct derivatives of α_1-P_2W_{17} and α_2-P_2W_{17}.

The same correlations between vibrational and NMR results are observed when the compounds PM_{12} and P_2M_{18} (M = Mo or W) are compared. The δ value decreases as the $\nu(PO_A)$

Table V[a]

	P_2W_{17}	$P_2W_{17}Zn$	$P_2W_{17}Mo$	α-P_2W_{18}
α_1 isomer	9 (13.1)	8.6 (13.3)	12.2 (13)	12.7
α_2 isomer	7.1 (13.6)	8.6 (13.8)	11.9 (12.6)	

[a] The first number represents the chemical shift value for the phosphorus atom of the PW_9 group in which the removal or the substitution of a tungsten atom has been carried out. The corresponding value for the unperturbed PW_9 group is shown in parentheses. These values are similar to that of α-P_2W_{18}.

Table VI

	α-PMo_{12}	α-P_2Mo_{18}	α-PW_{12}	α-P_2W_{18}
$\nu_{asym}(PO_A)$, cm^{-1}	1070	$\left.\begin{matrix}1082\\1008\end{matrix}\right\}1063$	1080	$\left.\begin{matrix}1090\\1022\end{matrix}\right\}1073$
δ, ppm from 85% H_3PO_4	3.9	3.4	14.9	12.7

Table VII

Compd	Formula of the two half-anions and δ (in ppm) of P atoms
α-P_2W_{18}	2 PW_9 (12.7)
α_1-$P_2W_{17}Mo$	PW_9 (13) + PW_8Mo (12.2)
α_2-$P_2W_{17}Mo$	PW_9 (12.6) + PW_8Mo (11.9)
α-$P_2W_{16}Mo_2$	PW_9 (12.7) + PW_7Mo_2 (10.2)
α-$P_2W_{12}Mo_6$	2 PW_6Mo_3 (9.75)
α-P_2Mo_{18}	2 PMo_9 (3.4)

frequency when going from PM_{12} to P_2M_{18}.

Saturated Molybdotungstophosphates. 1/12 Series. The $PW_{12-x}Mo_x$ compounds studied in this work are formed from "defect structure" B-type PW_9 or B-type PMo_9. Therefore the added metal elements are located in a same (M_3) subunit of the Keggin structure and affect the same O_A oxygen. As pointed out above, the "saturated" character of the heteropolyanion is kept since the MoO_A and WO_A bonds are covalent. The perturbation is relatively weak. In the Keggin structure, the δ values vary roughly linearly with the number of tungsten atoms replaced by molybdenum atoms, as shown on Figure 4.

2/18 Series. In the same way a linear variation is observed (Figure 5). The substitution of W by Mo has, of course, to be considered in each A-type α-PW_9 half-anion, as shown in Table VII.

"Defect Structure" Tungstic Heteropolyanions. For compounds with defect structure, i.e., with one or more holes, the phosphorus is much more perturbed than by the substitution of tungsten atoms by molybdenum atoms. However, a linear dependence of δ against the hole number is no longer observed. In particular, when the successive removals of tungsten atoms affect the same O_A atom of the PO_4 tetrahedron, i.e., when they are carried out in the same (M_3) unit, the formation of the first hole has a larger effect on the chemical shift than the following ones. For instance, the removal of one tungsten atom of a (W_3) unit in the Keggin structure (formation of PW_{11} from PW_{12}) leads to a decrease of the δ value equal to 4.5 ppm. On another hand, when passing from α-P_2W_{18} to α-P_2W_{12}, each phosphorus atom is affected by the removal of three atoms of (W_3) groups analogous to those of the Keggin structure, and the total δ value decrease is only 4.9 ppm. Although the δ value variation vs. the number of holes in the same (W_3) unit is not linear, it is monotonous. Because of this monotonous variation, the α_1- and α_2-P_2W_{17} isomers can be characterized. Let us remember they correspond to the removal of one tungsten atom from α-P_2W_{18}, either in a (W_3) or in a (W_2) group (see Figure 2b). Since the chemical shift of α_2-P_2W_{17} (7.1 ppm) does not lie between those of α-P_2W_{18} (12.7 ppm) and of α-P_2W_{12} (7.8 ppm), the missing tungsten atom does not belong to a (W_3) group; the hole of α_2-P_2W_{17} is then located in a (W_2) group. On the contrary, the δ value of the other isomer α_1-P_2W_{17} (9 ppm) is consistent with a hole located in a (W_3) group. This discussion can be extended to another example, namely, the removal of one molybdenum atom from an (Mo_3) group. When going from PW_9Mo_3 (12.9 ppm) to PW_9Mo_2 (9.4 ppm), the δ value difference is almost the same as the difference between PMo_{12} (3.9 ppm) and $PMo_{11}Zn$ (1.2 ppm). This last compound gives an approximate evaluation (by excess) of the δ value for PMo_{11} which cannot be measured directly owing to the instability of undecamolybdophosphate anion.[12]

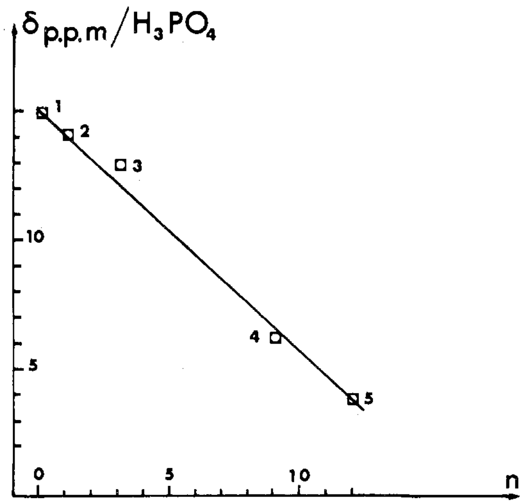


Figure 4. Variation of δ values with respect to the number, n, of Mo atoms replacing W atoms in the α-PW_{12} structure: (1) PW_{12}, (2) $PW_{11}Mo$, (3) PW_9Mo_3, (4) PW_3Mo_9, (5) PMo_{12}.

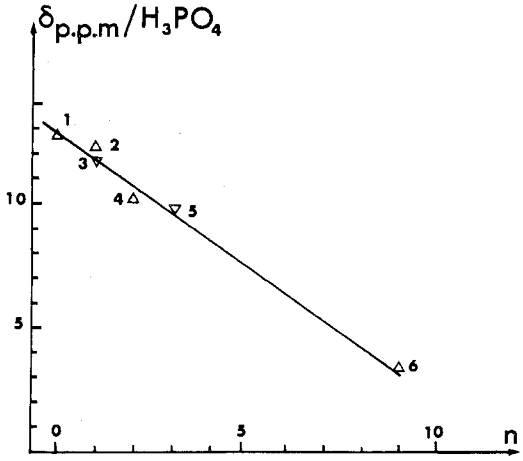


Figure 5. Variation of δ values with respect to the number, n, of Mo atoms replacing W atoms in an A-type α-PW_9 subunit: (1) PW_9 subunit of α-P_2W_{18}, (2) PW_8Mo subunit of α_1-$P_2W_{17}Mo$, (3) PW_8Mo subunit of α_2-$P_2W_{17}Mo$, (4) PW_7Mo_2 subunit of α-$P_2W_{16}Mo_2$, (5) PW_6Mo_3 subunit of α-$P_2W_{12}Mo_6$, (6) PMo_9 subunit of α-P_2Mo_{18}.

Conclusion

NMR and vibrational spectroscopy techniques are revealing very useful information which complements that obtained from electrochemical techniques. ^{31}P NMR was proved more fruitful than ^1H NMR[33-36] for the study of the central atom behavior in heteropolyanions, first because of the number and the diversity of the compounds and above all because the chemical shift variations are more significant; while the δ value range is greater than 10 ppm for ^{31}P, it is lower than 0.5 ppm for ^1H.

Acknowledgment. The authors wish to thank Dr. J. P. Laurent and the Coordination Chemistry Laboratory (Toulouse) for their NMR facilities. They are especially grateful to Mr. Commenges for his technical assistance.

Registry No. $K_{12}H_6P_2W_{12}O_{50}$, 63950-53-8; $LiK_9P_2W_{17}O_{61}$, 63950-56-1; $K_6P_2W_{17}MoO_{62}$, 63950-62-9; $K_6P_2W_{16}Mo_2O_{62}$, 63950-61-8; $K_6P_2W_{12}Mo_6O_{62}$, 63950-60-7; $K_8H_2P_2W_{17}ZnO_{62}$, 63950-55-0; $Na_{10}H_4P_2W_{16}Zn_2O_{62}$, 63950-54-9; $Na_8HPW_9O_{34}$, 63950-57-2; $K_7PW_9Mo_2O_{39}$, 63950-58-3; $K_3PW_9Mo_3O_{40}$, 63956-77-4; $(NH_4)_6HPMo_{11}ZnO_{40}$, 11120-72-2; $Na_3H_6PMo_9O_{34}$, 51913-10-1; $Na_6P_2Mo_{18}O_{62}$, 50811-90-0; $K_3PMo_9W_3O_{40}$, 63950-63-0; $H_3PW_{11}MoO_{40}$, 63950-64-1; PW_{12}, 12534-77-9; PMo_{12}, 12379-13-4; PV_{12}, 12632-06-3; PW_{11}, 12412-84-9; PW_3Mo_9, 56646-36-7; P_2W_{18}, 12269-70-4; P_2W_{21}, 63950-52-7; P_3W_{18}, 63950-51-6; Na_2WO_4, 13472-45-2; H_3PO_4, 7664-38-2; Na_2MoO_4, 7631-95-0; $(NH_4)_6Mo_7O_{24}$, 12027-67-7; Na_2HPO_4, 7558-79-4; $(PW_{11}MoO_{40})^{4-}$, 12776-99-7; $H_6P_2W_{17}MoO_{62}$, 63950-59-4.

References and Notes

(1) J. F. Keggin, *Proc. R. Soc. London, Ser. A*, **144**, 75 (1934).
(2) L. P. Kazanskii, M. A. Fedotov, M. N. Ptushkina, and V. I. Spitsyn, *Dokl. Akad. Nauk SSSR*, **224**, 866 (1975).
(3) L. I. Lebedeva and E. V. Vanchikova, *Zh. Neorg. Khim.*, **19**, 3285 (1974).
(4) M. T. Pope, S. E. O'Donnel, and R. Prados, *Adv. Chem. Ser.*, **No. 150**, 85 (1976).
(5) L. P. Kazanskii, V. F. Chuvaev, and V. I. Spitsyn, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **2**, 256 (1976).
(6) S. E. O'Donnel and M. T. Pope, *J. Chem. Soc., Dalton Trans.*, 2290 (1976).
(7) M. R. Noe-Spirlet, G. M. Brown, W. R. Busing, and H. A. Levy, *Acta Crystallogr., Sect. A*, **31**, 80 (1975).
(8) R. Strandberg, *Acta Chem. Scand., Ser. A*, **29**, 359 (1975).
(9) R. Allmann and H. D'Amour, *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.*, **141**, 161 (1975).
(10) K. Yamamura and Y. Sasaki, *J. Chem. Soc., Chem. Commun.*, **18**, 648 (1973).
(11) R. Contant, J. M. Fruchart, G. Hervé, and A. Têzé, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **278**, 199 (1974).
(12) M. Fournier and R. Massart, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **279**, 875 (1974).
(13) A. Têzé and G. Hervé, *J. Inorg. Nucl. Chem.*, **39**, 999 (1977).
(14) G. Hervé and A. Têzé, *Inorg. Chem.*, **16**, 2115 (1977).
(15) R. Strandberg, *Acta Chem. Scand., Ser. A*, **28**, 217 (1974).
(16) M. T. Pope, *Inorg. Chem.*, **15**, 2008 (1976).
(17) T. J. R. Weakley, *Struct. Bonding (Berlin)*, **18**, 131 (1974).
(18) B. Dawson, *Acta Crystallogr.*, **6**, 113 (1953).
(19) R. Strandberg, *Acta Chem. Scand., Ser. A*, **29**, 250 (1975).
(20) H. D'Amour, *Acta Crystallogr., Sect. B*, **32**, 729 (1976).
(21) K. Y. Matsumoto and Y. Sasaki, *J. Chem. Soc., Chem. Commun.*, **16**, 691 (1975).
(22) R. Contant and J. P. Ciabrini, *J. Chem. Res.*, in press.
(23) P. Souchay, "Ions Minêraux Condensês", Masson et Cie, Paris, 1969: (a) p 92, (b) p 90, (c) p 93, (d) p 106, (e) p 107, (f) p 98.
(24) H. Copaux, *Bull. Soc. Chim. Fr.*, **31**, 97 (1922).
(25) P. Souchay, R. Massart and G. Hervé, *Rev. Polarogr.*, **14**, 270 (1967).
(26) J. A. Altenau, M. T. Pope, R. A. Prados, and H. So, *Inorg. Chem.*, **14**, 417 (1975).
(27) M. Fournier, Thèse d' êtat, Universitê Paris VI, CNRS AO 12404.
(28) M. Leyrie, M. Fournier, and R. Massart, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **273**, 1569 (1971).
(29) C. Preyssler, *Bull. Soc. Chim. Fr.*, **1**, 30 (1970).
(30) Since his study was not complete, Sasaki thinks that our proposal is not in conflict with his results. The structure is under redetermination in his laboratory.
(31) C. Rocchiccioli-Deltcheff, R. Thouvenot, and R. Franck, *Spectrochim. Acta, Part A*, **32**, 587 (1976).
(32) C. Rocchiccioli-Deltcheff and R. Thouvenot, *J. Chem. Res., Synop.*, 46 (1977).
(33) M. T. Pope and G. M. Varga, *Chem. Commun.*, **653** (1966).
(34) G. M. Varga, E. Papaconstantinou, and M. T. Pope, *Inorg. Chem.*, **9**, 662 (1970).
(35) J. P. Launay, M. Boyer, and F. Chauveau, *J. Inorg. Nucl. Chem.*, **38**, 243 (1976).
(36) P. Courtin and J. Lefebvre, *Bull. Soc. Chim. Fr.*, 1726 (1976).

Contribution from the Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439, and Department of Chemistry, University of Missouri, Columbia, Missouri 65201

Reaction of Fluorine and Hypofluorous Acid with Some Substitution-Inert Complex Ions in Aqueous Perchloric Acid Solutions[1a]

RICHARD C. THOMPSON,[1b] EVAN H. APPELMAN,*[1c] and JAMES C. SULLIVAN[1c]

Received February 14, 1977 AIC701205

This paper examines the reactions of F_2 and HOF with aqueous perchloric acid solutions containing various complexes of trivalent chromium. In no case is the chromium itself oxidized. The complex CrF^{2+} is unreactive toward either oxidant. $CrClO_3^{2+}$, $CrNO^{2+}$, $CrCl^{2+}$, and $CrBr^{2+}$ show increasing reactivity, with the formation of Cr^{3+} as the principal product. In the case of $CrBr^{2+}$ and $CrCl^{2+}$ there is evidence that F_2 can react with the substrate directly, as well as via the intermediate formation of HOF. This direct reaction produces some CrF^{2+} in addition to Cr^{3+}. Azidochromium(III), CrN_3^{2+}, is the most reactive of the complexes studied. It reacts directly with F_2 to form a mixture of Cr^{3+} and CrF^{2+}; it reacts with HOF to form $CrNO^{2+}$. Reaction mechanisms that can account for these observations are discussed.

Introduction

Although it has long been known that F_2 displays strong oxidizing power when passed into aqueous solutions,[2] the mechanism of its interaction with such solutions has never been elucidated. The recent isolation of hypofluorous acid, HOF,[3] has led to the suggestion that this molecule is the reactive intermediate that is responsible for the oxidizing properties of fluorine in aqueous media.[4] Support for this idea comes from the fact that the equilibrium

$$F_2 + H_2O \rightarrow HOF + HF \qquad (1)$$

lies very far to the right and from the observation that HOF and F_2 have generally similar oxidizing properties in aqueous solution.[4] Thus both reagents oxidize Ag^+ to Ag^{2+}, both oxidize water primarily to H_2O_2 in acid and primarily to O_2 in base, and both oxidize BrO_3^- to BrO_4^- in base only.[2d,4] It is therefore tempting to conclude that reaction 1 proceeds very rapidly and that all of the observed chemistry stems from subsequent reaction of HOF. There is, however, some evidence that this concept is an oversimplification. It is known, for example, that F_2 reacts with water to produce OF_2—small amounts in neutral or acid media and quite substantial amounts in base.[2d] The interaction of HOF with water, on the other hand, has never been observed to produce OF_2.[4]

If fluorine can react with aqueous substrates directly as well as through the intermediate formation of HOF, it is conceivable that under some circumstances different and distinguishable products will result from the two modes of reaction. The use of substitution-inert complex ions, such as those of trivalent chromium, would seem to constitute a promising way to search for such distinguishable products. In this article we wish to describe an aqueous reaction system in which oxidation of the complex CrN_3^{2+} by F_2 proceeds partly via HOF and partly by direct attack and in which the