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SIMULTANEOUS DETERMINATION OF GROUP 5A ELEMENTS IN AQUEOUS SOLUTION BY PHOSPHORUS-31 NUCLEAR MAGNETIC RESONANCE SPECTROMETRY

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Group 5A elements, such as V(V), Nb(V), and Ta(V), react with a molybdophosphate to form ternary heteropoly molybdates quantitatively in the acidic solution. ^{31}P NMR spectra of the compound for each ion exhibit its specific chemical shift and relative peak area in proportion to the concentration of the corresponding complexes. This reaction endues the simultaneous determination of group 5A elements without any separation procedure.

During the course of determination of phosphorus in aqueous solution by means of formation of 12-molybdophosphate, a severe interference from group 4A and 5A elements was experienced. We found that the interference was caused by the formation of new compounds of group 4A elements and molybdophosphate, which are called ternary heteropoly molybdates. UV spectrophotometry,[1)] Raman scattering spectrometry,[2)] and nuclear magnetic resonance spectrometry[3)] have been used to investigate the structures of the complexes. The Raman spectra show that the wave number for the terminal Mo=O stretching vibration of the molybdophosphate shifts in the presence of group 4A elements. The values of the shift for the above elements, however, are similar. It was found that the peaks originated from the complexes containing Zr(IV) or Hf(IV), having nearly identical ionic radius, have the same wave number. However, ^{31}P NMR study on the ternary heteropoly molybdates indicated that each complex containing the group 4A element gives a peak at different position.

The present work reports the reaction of the molybdophosphate and group 5A elements studied by NMR spectrometry. The relation between the chemical shift and the character of the element will be discussed and the possibility of the simultaneous determination of group 4A and 5A elements will be presented.

All chemicals used were of analytical reagent grade. The stock solution of vanadium was prepared by dissolving ammonium metavanadate in dil. sodium hydroxide (C_V = 0.1 mol dm^{-3}). The stock solutions of tantalum and niobium were prepared by dissolving an aliquot amount of the respective metal(purity 99.9%) with the mixed acid of 47% hydrofluoric acid and nitric acid(1+1). Sulfuric acid(1+1) was added to the solution and excess hydrofluoric acid was removed by heating to fume. It was finally diluted to the definite volume by sulfuric acid(1+1)(C_{Ta}=C_{Nb}= 0.1 mol dm^{-3}).

Other stock solutions and preparation of ternary heteropoly molybdates used were described previously.[3)] The ^{31}P NMR instrument was operated under the conditions specified in Table 1. These operating conditions were selected to obtain the maximum signal-to-noise ratio for the spectrum of 12-molybdophosphate solution. A typical running time for each NMR measurement was approximately two hours. Negative values of δ represent a resonance at higher field than that of external standard.

Table 1. Instrument and Operating Conditions

Instrument	JEOL JNM-FX200
^{31}P resonance frequency	80.74 MHz
External standard	1-aminoethylidene bis(phosphonic acid)
Lock	D_2O
Temperature	23 - 25 °C
Scans	1000 - 3000 times
Interval	3.05 s
Pulse sequence	progressive saturation (45° pulse)

Figure 1 shows the ^{31}P NMR spectra of ternary heteropoly molybdate solutions. Addition of vanadium ion decreases the peak pertaining to 12-molybdophosphate and develops a new peak, at -17.66 ppm, higher field than that for 12-molybdophosphate. Addition of niobium or tantalum ion gives a new peak at -17.11 or -17.90 ppm, respectively. The ^{31}P NMR spectra show that the peak for each ternary heteropoly molybdate appears at a different chemical shift and that the peak area for niobium and vanadium is proportional to the concentration. Molybdotantalophosphate is, however, unstable and a hydrolysis product precipitates gradually in the solution. This reaction is not, therefore, adequate to determine tantalum in an aqueous solution. We can determine metal ion concentration over the range of 5.0×10^{-4} to 1.0×10^{-2} mol dm^{-3} with the standard deviation of 7% except of tantalum. The solution having equimolar amounts of phosphate and metal ion gives a single peak in the NMR spectrum and the peak is assigned to the ternary heteropoly molybdate from the chemical shift. Consequently, although the equivalent amount of molybdenum has not been estimated yet, it seems that the composition of these complexes is P:X:Mo = 1:1:11 taking into account the previous work on group 4A elements.[2)]

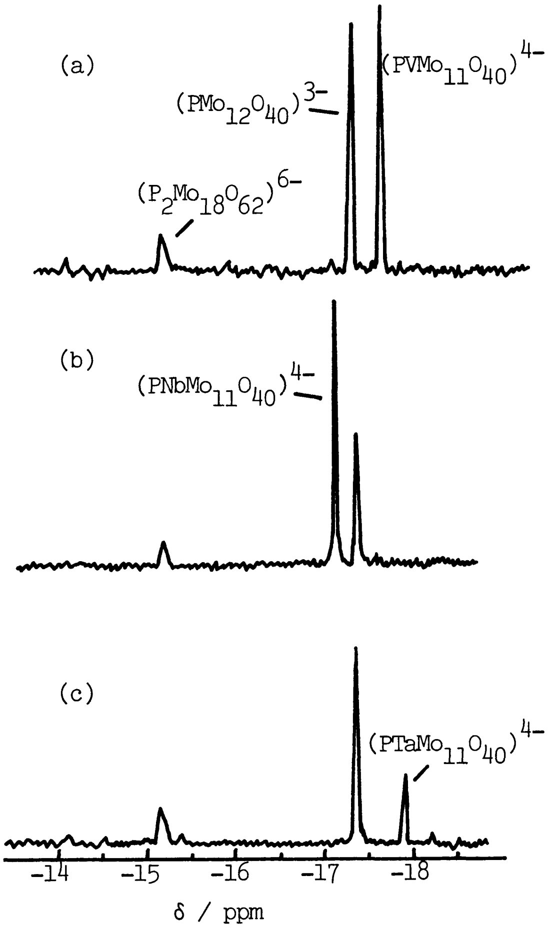

Fig. 1. ^{31}P NMR spectra of ternary heteropoly molybdates.

$C_P = 1.0 \times 10^{-2}$

(a) $C_V = 4.0 \times 10^{-3}$, $C_{Mo} = 1.5 \times 10^{-1}$

(b) $C_{Nb} = 5.6 \times 10^{-3}$, $C_{Mo} = 3.0 \times 10^{-1}$

(c) $C_{Ta} = 2.6 \times 10^{-3}$, $C_{Mo} = 2.0 \times 10^{-1}$

(mol dm^{-3}) pH 0.6 - 0.8

If the excess amount of vanadium is added, two new peaks, as shown in Fig.2, appear at higher field than that for molybdovanadophosphate. These peaks must be pertained to poly-substituted ternary heteropoly molybdates formed in the solution.[4] The species, $PV_2Mo_{10}O_{40}^{5-}$, has two structural isomers. Keggin structure has overall Td symmetry and is based on a central PO_4 tetrahedron surrounded by twelve MoO_6 octahedra arranged in four groups of three edge-shared octahedra, Mo_3O_{13}. These groups ("Mo_3 triplets") are linked by shared corners to each other and to the central PO_4 tetrahedron. We consider that two isomers can be present as follows; type I, substitution of two molybdenum atoms in the same Mo_3 triplet with vanadium atoms; type II, substitution in the different Mo_3 triplets. There is no doubt about the presence of the isomers. The further detailed interpretation of these peaks is under investigation. An excess of niobium gave rise to the gradual decomposition of molybdoniobophosphate and produced a hydrolysis product of niobium which phenomenon is similar to that observed in the case of tantalum.

$$2H_2PO_4^- + 3Mo_6O_{19}^{2-} + 2H^+ \rightleftharpoons P_2Mo_{18}O_{62}^{6-} + 3H_2O \qquad (1)$$

$$P_2Mo_{18}O_{62}^{6-} + Mo_6O_{19}^{2-} + 2H^+ \rightleftharpoons 2PMo_{12}O_{40}^{3-} + H_2O \qquad (2)$$

$$PMo_{12}O_{40}^{3-} + 3H_2O \rightleftharpoons PMo_{11}O_{39}^{7-} + HMoO_4^- + 5H^+ \qquad (3)$$

$$PMo_{11}O_{39}^{7-} + XO_2^+ + 2H^+ \rightleftharpoons PXMo_{11}O_{40}^{4-} + H_2O \qquad (4)$$

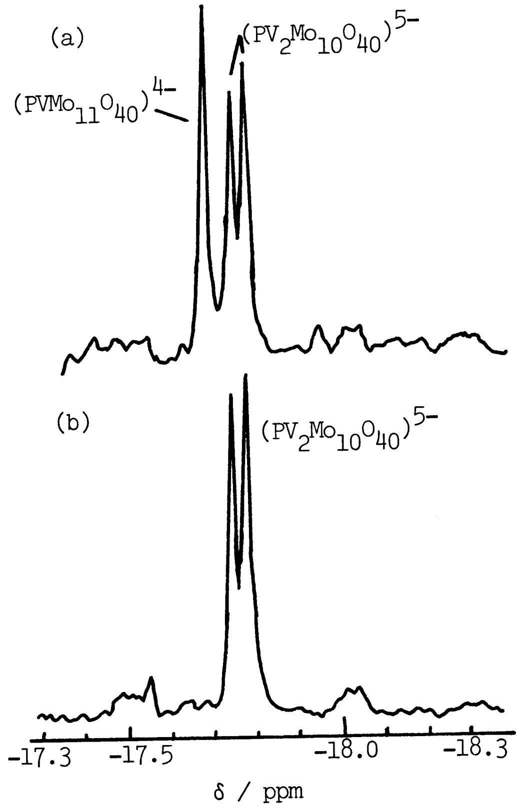

Fig. 2. ^{31}P NMR spectra of poly-substituted molybdovanadophosphate in the solution. $C_P = 1.0 \times 10^{-2}$, $C_{Mo} = 1.5 \times 10^{-1}$ (a) $C_V = 1.6 \times 10^{-2}$ (b) $C_V = 2.4 \times 10^{-2}$ (mol dm^{-3}) (a) pH 2.21 (b) pH 2.14

In an aqueous solution, the above reactions can be considered to participate in the formation of ternary heteropoly molybdates.[3] Hexamolybdate reacts with phosphate to produce a 18-molybdodiphosphate, $P_2Mo_{18}O_{62}^{6-}$, as shown in Eq.1. In the higher acidity, hexamolybdate attacks further 18-molybdodiphosphate and produces 12-molybdophosphate, $PMo_{12}O_{40}^{3-}$,(see Eq.2). In aqueous solution, however, 12-molybdophosphate has a limited stable range as for the acid concentration. It is reversibly converted to the "lacunary type" heteropoly anion,[5] $PMo_{11}O_{39}^{7-}$,(Eq.3). The group 5A metal ions can react with the lacunary type anion to give the ternary heteropoly molybdates, $PXMo_{11}O_{40}^{4-}$, having the Keggin like structure.

We tried to determine "multi-elements" present in a solution by means of the NMR of ternary heteropoly molybdates. Figure 3 shows the ^{31}P NMR spectrum of the solution containing the following metal ions, Th(IV), Zr(IV), Ti(IV), Hf(IV), V(V), Nb(V), Zn(II), Y(III), Cr(III), and Fe(III). Eight peaks are observed in Fig.3 and are identified by their specific chemical shifts. The values of the chemical shift for molybdophosphate and ternary heteropoly molybdates are given in Table 2. For the metal ions which can form ternary heteropoly molybdates a good correlation is found between the relative peak area and concentration in the solution. Inert metal ions, Zn(II), Y(III), Cr(III), and Fe(III), give no peak in the NMR spectrum and they do not interfere with the determination of complexed metal ions. The result of the present NMR experiments indicates that it is possible to determine group 4A and 5A elements without mutual interaction and interference from coexisting other ions.

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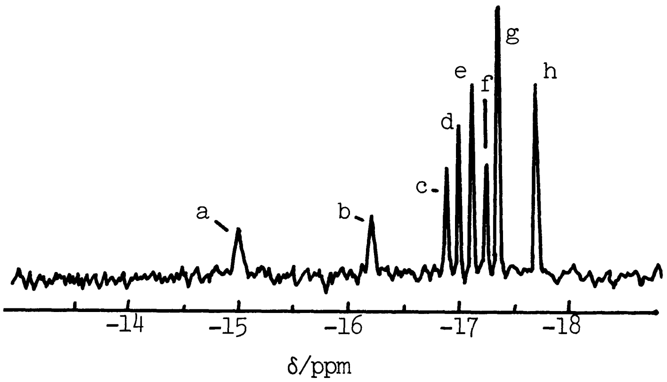

Fig. 3. ^{31}P NMR spectrum.

a - $P_2Mo_{18}O_{62}^{6-}$
b - $PThMo_{11}O_{40}^{5-}$
c - $PZrMo_{11}O_{40}^{5-}$
d - $PTiMo_{11}O_{40}^{5-}$
e - $PNbMo_{11}O_{40}^{4-}$
f - $PHfMo_{11}O_{40}^{5-}$
g - $PMo_{12}O_{40}^{3-}$
h - $PVMo_{11}O_{40}^{4-}$

Table 2. ^{31}P Chemical Shift of Each Heteropoly Molybdate

	δ / ppm[a]
$(P_2Mo_{18}O_{62})^{6-}$	-15.10[c]
$(PThMo_{11}O_{40})^{5-}$	-16.24[b]
$(PZrMo_{11}O_{40})^{5-}$	-16.88[b]
$(PTiMo_{11}O_{40})^{5-}$	-16.98[b]
$(PNbMo_{11}O_{40})^{4-}$	-17.11[c]
$(PHfMo_{11}O_{40})^{5-}$	-17.23[b]
$(PMo_{12}O_{40})^{3-}$	-17.33[b]
$(PVMo_{11}O_{40})^{4-}$	-17.66[c]
$(PTaMo_{11}O_{40})^{4-}$	-17.90[c]

a) Relative to 1-aminoethylidene bis(phosphonic acid).

b) See Ref.3.

c) This work.

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