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Isolation and characterization of oxygen-deficient reduced forms of the dodecamolybdophosphate anion salt

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Abstract

By a reaction of $[NBu^n_4]_3[PMo(VI)_{12}O_{40}]$ with PPh_3 in acetonitrile, two- and four-electron reduced compounds, $[NBu^n_4]_3[PMo(VI)_{12-2n}Mo(V)_{2n}O_{40-n}]$ ($n = 1$ and 2), were isolated and characterized by means of X-ray diffractometry, FT-IR, electronic absorption, ^{31}P NMR and X-ray photoelectron spectroscopies. The bridging oxygen atom in a Mo(VI)–O–Mo(VI) skeleton is eliminated upon the reduction, affording two Mo(V) ions in the polyanion moiety, where the anion structure of the Keggin type is essentially retained during the reduction. An exchange reaction between $[PMo(VI)_{10}Mo(V)_2O_{39}]^{3-}$ and $[PMo(VI)_8Mo(V)_4O_{38}]^{3-}$ via a bridging oxygen atom occurs in solution within the NMR time scale.

Introduction

Dodecamolybdophosphates are known as practical oxidation catalysts and their redox mechanisms have systematically been studied in relation to their catalytic functions [1–14]. In heterogeneous (vapor/solid phase) redox processes, behaviour of the lattice oxygen atoms of the polyanion has attracted much attention and it has been well clarified that the dodecamolybdophosphate anion is reduced by hydrogen or organic substrates (methacrolein, cyclohexane and isobutyric acid) accompanied by elimination of the bridging oxygen atom in the Mo–O–Mo bond [1, 6, 8, 9, 11, 13]. In addition, the electronic structure calculation for the polyanion has revealed that the bridging oxygen atom is exclusively reactive among the oxygen species [14]. However, only a few studies have been reported on the characterization of the oxygen-deficient reduced forms, which were isolated by the heterogeneous reduction of the polyanion with hydrogen or organic substrates at elevated temperature [4, 5, 11–13]. Under these conditions, the polyanion reduced in the solid state is liable to decompose [7] and to be reduced with some heterogeneity [11, 13]. Although the polyanion can be characterized as a structurally well-defined oxomolybdenum complex [7, 8], an oxygen-transfer reaction of the polyanion in a homogeneous system has not been reported so far. It is therefore of interest to investigate a stoichiometric reduction of the polyanion under rather mild conditions and properties and geometries of the oxygen-deficient reduced polyanion species.

In this work, triphenylphosphine (PPh_3) has been chosen as a reducing agent, which is known to abstract an oxygen atom from oxomolybdenum complexes [15], and the reaction of tetrabutylammonium dodecamolybdophosphate(3−), $[NBu^n_4]_3[PMo(VI)_{12}O_{40}]$ (abbreviated as $PMo_{12}O_{40}$), with PPh_3 has been investigated in a non-aqueous solution. In this system, the polyanion is homogeneously reduced without hydrolytic decomposition. The progress of the reduction can be followed directly by Fourier transform infrared (FT-IR) and ^{31}P NMR spectra. The oxygen-deficient reduced compounds are isolated and characterized by X-ray diffractometry, FT-IR, ^{31}P NMR and X-ray photoelectron spectroscopies. A part of this study has been reported in preliminary communications [16, 17].

Experimental

Reaction of $PMo_{12}O_{40}$ with PPh_3

The sample $PMo_{12}O_{40}$ was prepared by the cation-exchange reaction of commercially available dode-

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camolybdophosphoric acid (Kanto Chemical Co., Inc.) with an excess of tetrabutylammonium bromide in methanol. The precipitate was filtered and recrystallized from acetonitrile to give yellow crystals. The reaction of $PMo_{12}O_{40}$ with one or two equimolar amounts of PPh_3 was homogeneously carried out in acetonitrile at 23 °C and at the reflux temperature under a nitrogen atmosphere. The progress of the reaction was followed by the amount of triphenylphosphine oxide ($OPPh_3$) formed in the solution, which was determined from the intensity of the FT-IR band of $OPPh_3$ measured at different time intervals.

Isolation of the reduced compounds

An acetonitrile (200 cm^3) solution containing $PMo_{12}O_{40}$ (4.00 g, 1.57 mmol) and an equimolar amount of PPh_3 was refluxed for 50 h under a nitrogen atmosphere. The solvent was evaporated to dryness under reduced pressure. A dark blue residue was washed with methanol to remove $OPPh_3$ and dried *in vacuo* to afford the dark blue, two-electron reduced compound, $[NBu^n_4]_3[PMo(VI)_{10}Mo(V)_2O_{39}]$ (abbreviated as $PMo_{12}O_{39}$) (3.31 g, 83% yield). *Anal.* Found: C, 22.86; H, 4.28; N, 1.59; Mo, 45.1; P, 1.26. Calc. for $C_{48}H_{108}N_3Mo_{12}O_{39}P$: C, 22.76; H, 4.30; N, 1.66; Mo, 45.4; P, 1.22%. A similar reaction of $PMo_{12}O_{40}$ (4.00 g, 1.57 mmol) with two equimolar amounts of PPh_3 afforded the dark blue, four-electron reduced compound, $[NBu^n_4]_3[PMo(VI)_8Mo(V)_4O_{38}]$ (abbreviated as $PMo_{12}O_{38}$) (3.24 g, 82% yield). *Anal.* Found: C, 22.71; H, 4.20; N, 1.62; Mo, 45.5; P, 1.26. Calc. for $C_{48}H_{108}N_3Mo_{12}O_{38}P$: C, 22.90; H, 4.32; N, 1.67; Mo, 45.7; P, 1.23%. Molybdenum was determined by atomic absorption spectrophotometry and phosphorus by the photometric phosphomolybdenum blue method [18].

Reoxidation of the reduced compounds

These reduced compounds were heated at 200 °C in the air for half an hour to change from dark blue to bluish-green. The bluish-green powder was dissolved in acetonitrile and oxygen gas was bubbled through the solution. After the solution turned pale greenish-yellow, it was evaporated to dryness under reduced pressure to afford the reoxidized compound, $PMo_{12}O_{40}$.

Physical measurements

FT-IR spectra were measured with a Nicolet 5DX spectrophotometer using a KRS-6 cell with a 0.1 mm light path and in KBr pellets. Electronic absorption spectra were measured with a Hitachi 340 spectrophotometer using a quartz cell with a 1 mm light path. Both the measurements were carried out under a nitrogen atmosphere.

X-ray photoelectron spectra were measured for compressed pellet samples with a Shimadzu ESCA-750 spectrometer employing Mg Kα radiation at 5 kV and 30 mA. All the spectra were referenced to the C $1s_{1/2}$ signal of the tetrabutylammonium cation at 285.0 eV for correction of the charge effect. Deconvolution of the spectra of Mo 3d electrons was carried out with a Shimadzu ESCAPAC-760 data system employing a Gaussian-Lorentzian shape fit.

X-ray diffraction patterns were measured with a Rigaku Denki roterflex X-ray diffractometer RAD-rA employing Cu Kα radiation at 40 kV and 100 mA.

^{31}P NMR spectra were measured with a JEOL JNM-FX90Q spectrometer operating at 36.23 MHz and at 23 °C. The sample (*c.* 0.01 mol dm^{-3}) was dissolved in acetonitrile-d_3 degassed by the freeze–thaw cycle method and sealed. Chemical shifts were determined by using the sample replacement method [19] externally referenced to 30% phosphoric acid and reported in ppm with negative value upfield from the standard. NMR parameters: 30° pulse width, 6 μs; sweep width, 400, 1000 and 2500 Hz; relaxation delay, 20 s; number of acquisition, 100–300.

Results and discussion

Reaction of $PMo_{12}O_{40}$ with PPh_3 in acetonitrile

The FT-IR spectral changes of an acetonitrile solution containing $PMo_{12}O_{40}$ and an equimolar amount of PPh_3 at 23 °C are shown in Fig. 1. The absorption band ascribed to PPh_3 at 505 cm^{-1} decreases in intensity with time. Concomitantly, the bands ascribed to $OPPh_3$ arise at 1194 (ν(P=O)) [20] and 544 cm^{-1}. These findings indicate that PPh_3 reduces $PMo_{12}O_{40}$ accompanying the oxygen atom transfer from the polyanion to PPh_3. In accordance with this, the yellow solution gradually turned green and finally dark blue. The progress of the reduction was followed by the amount of $OPPh_3$ formed in the solution. The concentration of $OPPh_3$ can be determined by the intensities of the bands at 1194 and 544 cm^{-1}, since a linear relationship between them is obtained independent of the coexistence of the other species in the solution [21]. As shown in Fig. 2, all amounts of PPh_3 are finally oxidized to $OPPh_3$ in the reaction.

In the region between 1100 and 700 cm^{-1} (Fig. 1), there are four major bands characteristic of the Keggin anion structure; they are assigned to P–O

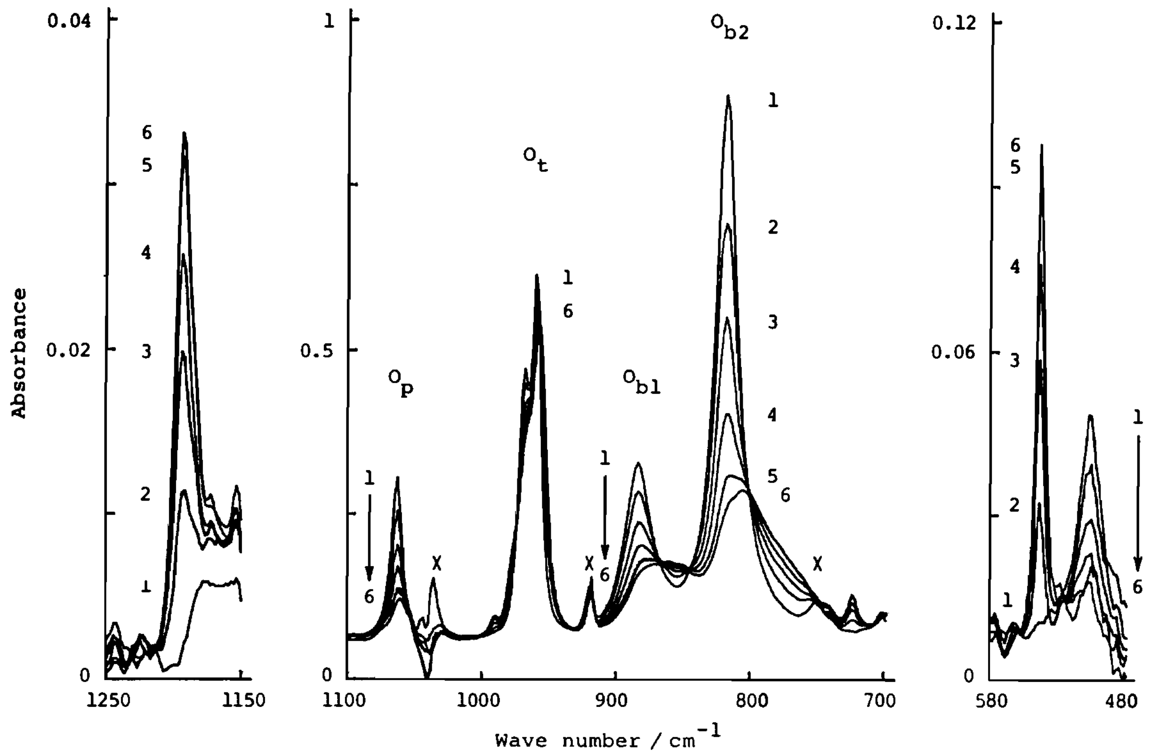


Fig. 1. FT-IR spectral changes of an acetonitrile solution containing $PMo_{12}O_{40}$ (6.00×10^{-3} mol dm^{-3}) and an equimolar amount of PPh_3; reaction time at 23 °C: 0.1 (1), 24 (2), 73 (3), 174 (4), 506 (5), 1039 (6) h; X: peaks of the solvent.

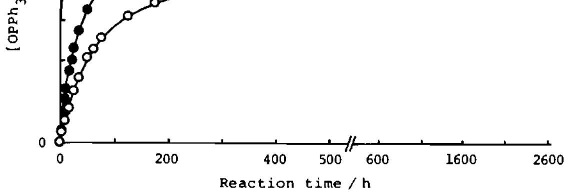


Fig. 2. Amounts of $OPPh_3$ formed in a reaction of $PMo_{12}O_{40}$ with an equimolar amount of PPh_3 at 23 °C (a) and two equimolar amounts of PPh_3 at 23 °C (b) and at the reflux temperature (c) in acetonitrile: $[PMo_{12}O_{40}]_{init}$ = the initial concentration of $PMo_{12}O_{40}$.

(O_p band), Mo=O (terminal oxygen, O_t band), Mo–O–Mo (corner-sharing oxygen, O_{b1} band) and Mo–O–Mo (edge-sharing oxygen, O_{b2} band) stretching modes [22]. During the reaction, the O_p and two O_b bands drastically decrease in their intensities and gradually shift to lower frequencies, whereas the O_t band is appreciably broadened. The absorbances of the O_p and two O_b bands decrease quite linearly with the degree of the reduction progress. Although the O_t band apparently decreases in absorbance, its band area is almost unchanged during the reaction, as illustrated in Fig. 3.

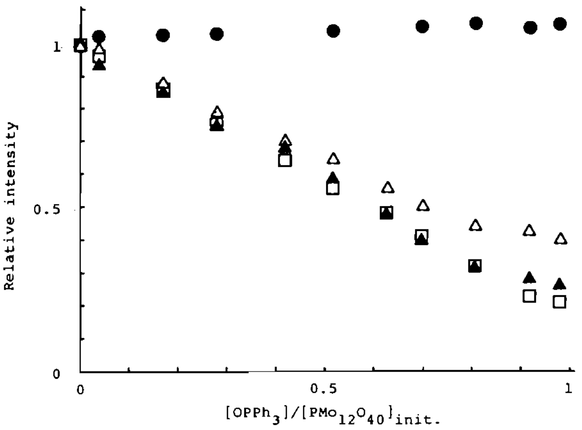


Fig. 3. The variation in intensity of the FT-IR bands of the polyanion for the reaction of $PMo_{12}O_{40}$ with an equimolar amount of PPh_3 in acetonitrile at 23 °C. Relative intensity is based on the absorbance for the O_p (□), O_{b1} (△) and O_{b2} (▲) bands and on the band area for the O_t band (●).

These findings suggest that the bridging oxygen atom in the Mo–O–Mo bond is eliminated in the reduction of the polyanion, which results in depression of the symmetry of the polyanion and weakened O_p and two O_b bands. A similar spectral behaviour was also observed for the reduction of the dodecamolybdophosphate anion in a heterogeneous (vapor/solid phase) system [1, 6, 8, 11, 13]. Furthermore, the electronic structure calculation for the dodecamolybdophosphate anion has revealed that the bridging oxygen atom in the Mo–O–Mo bond is exclusively reactive among the oxygen species [14]. Consequently, in the present reaction, two-electron reduction of $PMo_{12}O_{40}$ by PPh_3 homogeneously proceeds according to reaction (1), accompanied by the transfer of one bridging oxygen atom in the Mo–O–Mo bond to PPh_3.

$$[NBu^n_4]_3[PMo_{12}O_{40}] + PPh_3 \longrightarrow [NBu^n_4]_3[PMo_{12}O_{39}] + OPPh_3 \quad (1)$$

The reaction of $PMo_{12}O_{40}$ with two equimolar amounts of PPh_3 in acetonitrile at 23 °C proceeds very slowly in the reduction process of the two-electron reduced species, whereas at the reflux temperature all amounts of PPh_3 are finally oxidized to $OPPh_3$ (Fig. 2); that is, $PMo_{12}O_{40}$ undergoes four-electron reduction by two equimolar amounts of PPh_3 according to reaction (2).

$$[NBu^n_4]_3[PMo_{12}O_{40}] + 2PPh_3 \longrightarrow [NBu^n_4]_3[PMo_{12}O_{38}] + 2OPPh_3 \quad (2)$$

The FT-IR spectral changes of reaction (2) in acetonitrile at the reflux temperature have shown considerable decreases in absorbance of the O_p and two O_b bands, while the band area of the O_t band was almost unchanged during the reaction. Figure 4 shows the FT-IR spectra of the isolated two- and four-electron reduced compounds in acetonitrile together with that of $PMo_{12}O_{40}$. Similar features were observed for these spectra when measured as KBr pellets. This spectral behaviour indicates that the second oxygen atom eliminated from $PMo_{12}O_{39}$ is also attributed to the bridging oxygen atom in the Mo–O–Mo bond.

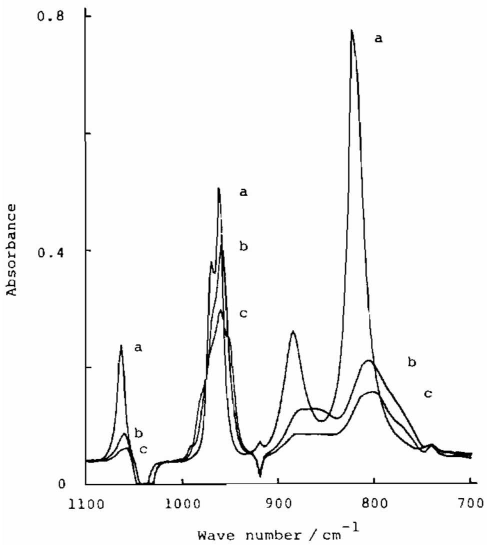


Fig. 4. FT-IR spectra of $PMo_{12}O_{40}$ (a), $PMo_{12}O_{39}$ (b) and $PMo_{12}O_{38}$ (c) (5.00×10^{-3} mol dm^{-3}) in acetonitrile.

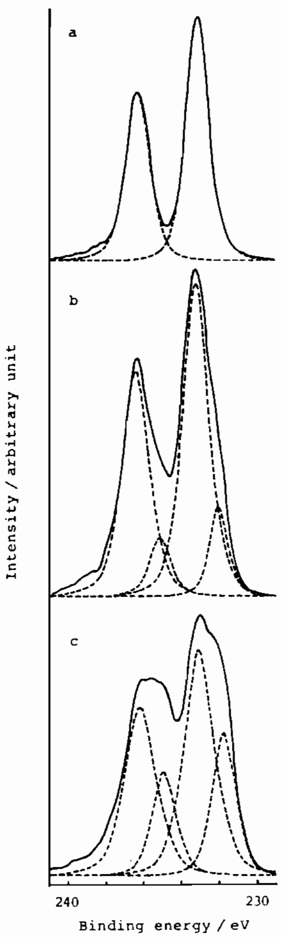


Fig. 5. X-ray photoelectron spectra of $PMo_{12}O_{40}$ (a), $PMo_{12}O_{39}$ (b) and $PMo_{12}O_{38}$ (c). Broken lines represent deconvoluted curves.

Spectroscopic properties of the isolated reduced compounds

The X-ray photoelectron spectra of the Mo 3d electrons of $PMo_{12}O_{40}$ and the reduced compounds are shown in Fig. 5. The spectrum of $PMo_{12}O_{40}$ exhibits the characteristic doublet due to Mo(VI) $3d_{5/2}$ and Mo(VI) $3d_{3/2}$ electrons which is caused by the spin–orbit coupling [23]. The doublet observed for $PMo_{12}O_{39}$ is broadened on the lower binding energy sides and that for $PMo_{12}O_{38}$ further broadened. The parameters for deconvolution of these spectra are summarized in Table 1. The separation between $3d_{5/2}$ and $3d_{3/2}$ bands is found to be 3.2 eV and the intensity ratio of them to be 1.2–1.4 for all the deconvoluted curves; these values are in good agreement with those reported for molybdenum oxides [23, 24]. The new doublet which appears at 1.2–1.3 eV lower than that of the Mo(VI) ion can be assigned to the Mo(V) 3d electrons, based on the binding energies for the Mo(V) 3d electrons in dodecamolybdophosphate anions [4, 11, 13] and molybdenum oxides [23, 24]. No signals due to Mo(IV) and further reduced molybdenum ions were observed in a lower binding energy region. The contents of Mo(VI) and Mo(V) ions in the reduced compounds estimated from peak areas of the deconvoluted curves are also given in Table 1. These results indicate that the two- and four-electron reduced anions are $[PMo(VI)_{10}Mo(V)_2O_{39}]^{3-}$ and $[PMo(VI)_8Mo(V)_4O_{38}]^{3-}$, respectively. On the other hand, the binding energies of the P 2p electrons of the reduced compounds are almost the same as that of $PMo_{12}O_{40}$ (Table 1). This indicates that no internal oxygen atoms ligating the phosphorus atom are eliminated during the reduction, the valence state of P(V) being preserved. Therefore, the elimination of one oxygen atom in the Mo(VI)–O–Mo(VI) bond is reasonably concluded to produce two Mo(V) ions in the polyanion.

The reduced compounds exhibit an intense band in the visible and near IR regions, as depicted in Fig. 6, which is assigned to the intervalence charge transfer (Mo(V)→Mo(VI)) band as was observed for reduced dodecamolybdophosphate anions, 'heteropoly blues' [25]. The intensity of the band has been reported to be proportional to the number of electrons introduced to the polyanion [25, 26]. The intensity of $PMo_{12}O_{38}$ ($\epsilon_{max} = 12\,500$ dm^3 mol^{-1} cm^{-1}) is about twice that of $PMo_{12}O_{39}$ ($\epsilon_{max} = 5800$ dm^3 mol^{-1} cm^{-1}), indicating that the anion structure of the Keggin type is retained in the present two- and four-electron reduced compounds.

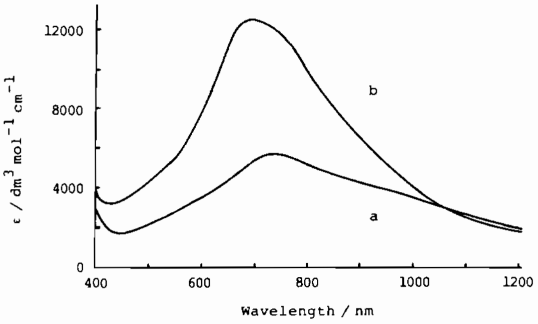


Fig. 6. Electronic absorption spectra of $PMo_{12}O_{39}$ (a) and $PMo_{12}O_{38}$ (b) in acetonitrile.

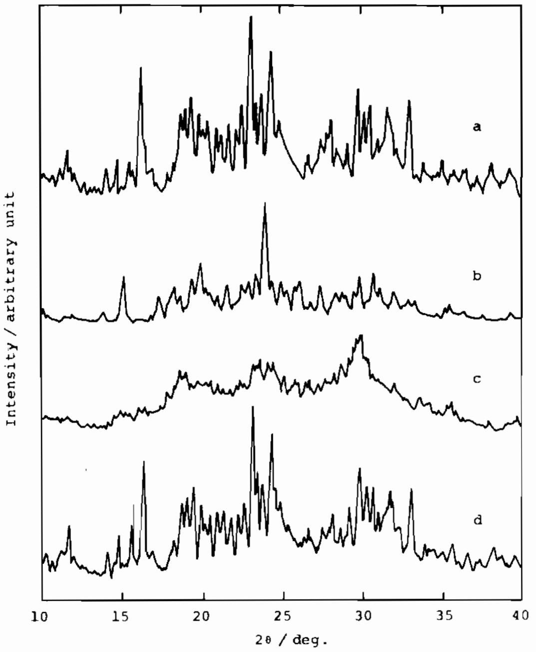


Fig. 7. X-ray diffraction patterns of $PMo_{12}O_{40}$ (a), $PMo_{12}O_{39}$ (b), $PMo_{12}O_{38}$ (c) and the reoxidized compound of $PMo_{12}O_{38}$ (d).

TABLE 1. Binding energies (eV) for deconvoluted curves[a]

Compound	Mo(VI) $3d_{3/2}$	Mo(V) $3d_{3/2}$	Mo(VI) $3d_{5/2}$	Mo(V) $3d_{5/2}$	P[b] 2p
$PMo_{12}O_{40}$	236.1	–	232.9	–	134.4
$PMo_{12}O_{39}$	236.3	235.1 (0.20)	233.1	231.9 (0.20)	135.1
$PMo_{12}O_{38}$	236.2	234.9 (0.47)	233.0	231.7 (0.50)	134.6

[a]Ratio of the peak area of Mo(V) to that of the corresponding Mo(VI) in parentheses. [b]For the original measured peak.

The FT-IR spectra of reoxidized compounds of $PMo_{12}O_{39}$ and $PMo_{12}O_{38}$ were essentially identical with that of $PMo_{12}O_{40}$; the O_p, O_t and two O_b bands were regenerated in intensity and in shape. Furthermore, the X-ray diffraction patterns of the reoxidized compounds are very close to that of $PMo_{12}O_{40}$, although the patterns of the reduced compounds are entirely different from that of $PMo_{12}O_{40}$, as depicted in Fig. 7 [17]. These observations indicate that no decomposition occurs on the anion structure of the oxygen-deficient reduced compounds.

^{31}P NMR spectra of the reduced compounds

^{31}P NMR spectra have provided useful information on structures of heteropoly phosphate anions [19, 27–32]. Figure 8 shows ^{31}P NMR spectra of an acetonitrile-d$_3$ solution containing $PMo_{12}O_{40}$ and an equimolar amount of PPh_3 at 23 °C. As the reaction proceeds, the signals observed at +0.24 and −1.76 ppm due to $PMo_{12}O_{40}$ and PPh_3, respectively, decrease in their intensities and two new signals develop at +30.6 and −2.36 ppm which are attributed to $OPPh_3$ and $PMo_{12}O_{39}$, respectively.

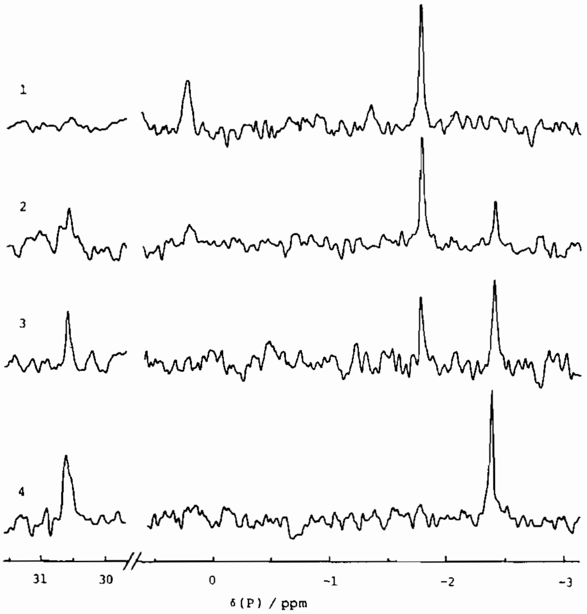


Fig. 8. ^{31}P NMR spectral changes of an acetonitrile-d$_3$ solution containing $PMo_{12}O_{40}$ and an equimolar amount of PPh_3; reaction time at 74 °C: 0 (1), 1.5 (2), 2.3 (3), 23 (4) h.

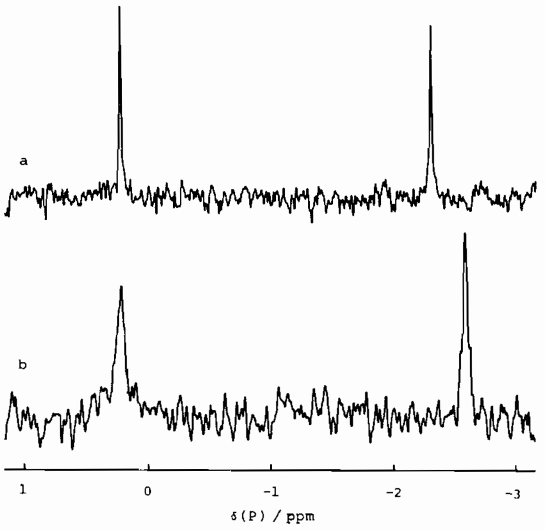


Fig. 9. ^{31}P NMR spectra of equimolar mixtures of $PMo_{12}O_{40}$ and $PMo_{12}O_{39}$ (a) and $PMo_{12}O_{40}$ and $PMo_{12}O_{38}$ (b) in acetonitrile-d$_3$.

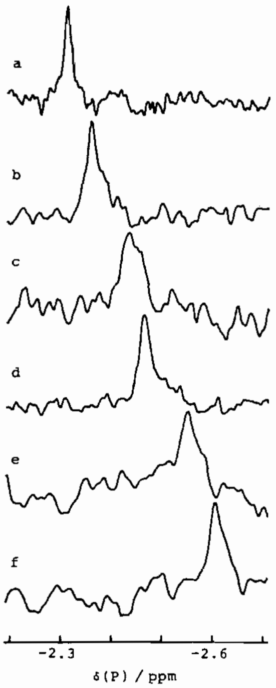
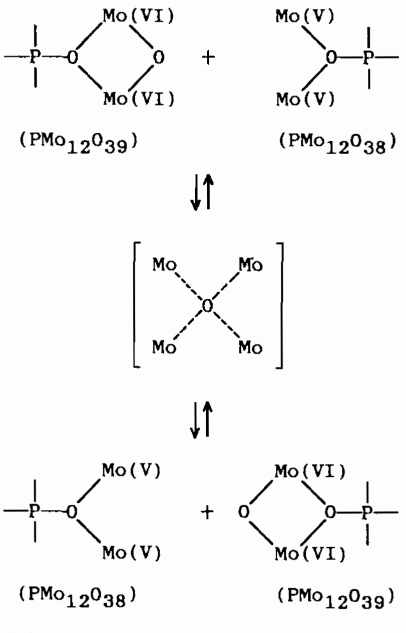


Fig. 10. ^{31}P NMR spectra of mixtures of $PMo_{12}O_{39}$ and $PMo_{12}O_{38}$ in acetonitrile-d$_3$; mole fraction of $PMo_{12}O_{38}$: 0 (a), 0.34 (b), 0.50 (c), 0.66 (d), 0.89 (e), 1 (f).



Scheme 1.

Both the ^{31}P NMR spectra of the isolated reduced compounds, $PMo_{12}O_{39}$ and $PMo_{12}O_{38}$, showed a single peak at -2.31 and -2.60 ppm, respectively. Upfield shifts of the signals of these reduced compounds compared with that of $PMo_{12}O_{40}$ were also the same as those of the electrochemically reduced dodecamolybdophosphate anion species [29, 30]. No other signals were observed besides those of these reduced compounds, indicating that essentially no other oxidation states of the polyanion are present. In addition, the narrow line widths ($\Delta\nu_{1/2} < 1$ Hz) of the observed signals suggest a single anion structure of the Keggin type for each reduced compound.

Figure 9(a) shows the ^{31}P NMR spectrum of an equimolar mixture of $PMo_{12}O_{40}$ and $PMo_{12}O_{39}$ in acetonitrile-d_3. Signals occur at $+0.23$ ppm ($PMo_{12}O_{40}$, $\Delta\nu_{1/2} < 1$ Hz) and at -2.31 ppm ($PMo_{12}O_{39}$, $\Delta\nu_{1/2} < 1$ Hz) with integrated intensities in the ratio 1:1. An equimolar mixture of $PMo_{12}O_{40}$ and $PMo_{12}O_{38}$ in the same solvent also gives the signals at $+0.22$ ppm ($PMo_{12}O_{40}$, $\Delta\nu_{1/2} = 2.9$ Hz) and -2.58 ppm ($PMo_{12}O_{38}$, $\Delta\nu_{1/2} = 1.4$ Hz) with integrated intensities in the ratio 1:0.9, although they are somewhat broad (Fig. 9(b)). These findings indicate that the anion structures of $PMo_{12}O_{39}$ and $PMo_{12}O_{38}$ are not affected by $PMo_{12}O_{40}$ in solution.

On the other hand, a mixture of the two reduced compounds, $PMo_{12}O_{39}$ and $PMo_{12}O_{38}$, in acetonitrile-d_3 exhibits a new single resonance at the averaged position between those of $PMo_{12}O_{39}$ and $PMo_{12}O_{38}$ according to their relative amounts as shown in Fig. 10. In the reduction process of $PMo_{12}O_{39}$ with an equimolar amount of PPh_3 in acetonitrile-d_3, the signal of $PMo_{12}O_{39}$ has continuously been shifted to a higher field and finally to the position of $PMo_{12}O_{38}$, the intensity and the linewidth of the peak being almost unchanged. These findings support some interaction between $PMo_{12}O_{39}$ and $PMo_{12}O_{38}$ in the solution. Thus, a pair of Mo(V) ions in $PMo_{12}O_{38}$ is suggested to interact with a bridging oxygen atom of the Mo(VI)–O–Mo(VI) bond in $PMo_{12}O_{39}$ in solution, accompanied by the transfer of an oxygen atom between them within the NMR time scale, as depicted in Scheme 1.

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