Oxygen-Transfer Reaction of the A-Type Molybdenum-Trisubstituted Tungstophosphate Anion Salt and Spectroscopic Properties of the Isolated Oxygen-Deficient Reduced Species

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The A-type trisubsituted, β-isomer of tetrabutylammonium 3-molybdo-9-tungstophosphate(3-), A-β-$[NBu^n_4]_3[PMo^{VI}_3W_9O_{40}]$, reacted with triphenylphosphine in acetonitrile to afford triphenylphosphine oxide and an oxygen-deficient two-electron reduced species, A-β-$[NBu^n_4]_3[PMo^{VI}Mo^V_2W_9O_{39}]$. The reduced species was isolated and characterized by IR, ^{31}P NMR, and X-ray photoelectron spectroscopies. The corner-sharing bridging oxygen atom in a Mo(VI)–O–Mo(VI) skeleton was eliminated upon the reduction, affording two Mo(V) ions in the polyanion moiety retaining the Keggin-type structure.

Redox mechanisms of 12-molybodophosphates have been systematically studied in relation to their catalytic functions.[1] Behavior of the lattice oxygen atoms of the polyanion has attracted much attention. Among oxygen atoms in the Keggin-type polyanion, the bridging oxygen is exclusively reactive, which was shown not only by the heterogeneous (vapor/solid phase) reduction processes[1—5] but also by the electronic structure calculation for the polyanion.[6] Our previous work[7] on an oxygen-transfer reaction of tetrabutylammonium 12-molybdophosphate(3-), $[NBu^n_4]_3[PMo_{12}O_{40}]$ (abbreviated $PMo_{12}O_{40}$), in a non-aqueous solution has demonstrated that the polyanion is homogeneously reduced, accompanied by elimination of the bridging oxygen atom in the Mo–O–Mo bond. The bridging oxygen atoms in the Keggin-type polyanion are classified into two species, the corner-sharing one (O_{bc}) and the edge-sharing one (O_{be}) between two MoO_6 octahedra.[8] However, no investigations have been done to clarify the difference in the reactivity between these two bridging oxgyen atoms so far. On the other hand, we have found that neither $[PW_{12}O_{40}]^{3-}$ nor $[PMoW_{11}O_{40}]^{3-}$ anion underwent an oxygen-transfer reaction under the same conditions. Therefore, to evaluate the individual reactivity of each bridging oxygen atom, we have used a structurally designed mixed addenda polyanion of A-$[PMo_3W_9O_{40}]^{3-}$, in which three Mo atoms are linked to each other through only the O_{bc} atoms, and three MoO_6 octahedra are coordinated to the "unreactive" PW_9O_{34} unit. This is the first report on the reactivity of the O_{bc} atom in the Mo–O–Mo bond of the Keggin-type polyanion in the absence of the corresponding O_{be} atom.

In this work, we investigated an oxygen-transfer reaction of the A-type trisubstituted, β-isomer of tetrabutylammonium 3-molybdo-9-tungstophosphate(3-), A-β-$[NBu^n_4]_3[PMo_3W_9O_{40}]$ (abbreviated A-$PMo_3W_9O_{40}$), with triphenylphosphine (PPh_3) in a non-aqueous solution. The reduction process was directly followed by IR and ^{31}P NMR spectra. The reduced species, A-β-$[NBu^n_4]_3[PMo_3W_9O_{39}]$ (abbreviated A-$PMo_3W_9O_{39}$), was ioslated and characterized by IR, ^{31}P NMR, and X-ray photoelectron spectra. Behavior of the lattice oxygen atoms of the mixed addenda polyanion upon the reduction is also discussed.

Experimental

Preparations of Tetrabutylammonium Salts of Heteropoly Anions. The potassium salt of the mixed addenda polyanion, $K_3[PMo_3W_9O_{40}]$, was prepared by the reaction of A-$Na_9PW_9O_{34}\cdot 7H_2O$[9] and $Na_2MoO_4\cdot 2H_2O$ in an HCl and 1,4-dioxane mixed solution, as previously reported.[10] The potassium salt (12.0 g, 4.39 mmol) was dissolved in methanol (300 cm^3) and to the solution was added $[NBu^n_4]Br$ (5.00 g, 15.5 mmol) dissolved in methanol (50 cm^3). The resulting yellow precipitate was collected by filtration, washed with methanol and dried in vacuo to afford A-$PMo_3W_9O_{40}$ (11.0 g, 75% yield). It was recrystallized from acetonitrile to give yellow columns. Found: C, 17.24; H, 3.20; N, 1.24; Mo, 8.3; P, 0.90; W, 49%. Calcd for $C_{48}H_{108}N_3Mo_3O_{40}PW_9$: C, 17.26; H, 3.26; N, 1.26; Mo, 8.26; P, 0.93; W, 49.53%.

Tetrabutylammonium 12-tungstophosphate(3-), $[NBu^n_4]_3[PW_{12}O_{40}]$ (abbreviated $PW_{12}O_{40}$), was prepared by the cation-exchange reaction of commercically available 12-tungstophosphoric acid with an excess of $[NBu^n_4]Br$ in methanol, according to a method similar to that described for $PMo_{12}O_{40}$.[7]

Tetrabutylammonium 1-molybdo-11-tungstophosphate(3-), $[NBu^n_4]_3[PMoW_{11}O_{40}]$ (abbreviated $PMoW_{11}O_{40}$), was prepared by the reaction of $[PW_{11}O_{39}]^{7-}$ and $[NBu^n_4][MoOCl_4]$ in acetonitrile, as previously reported.[11]

Reactions of Tetrabutylammonium Salts of Heteropoly Anions with PPh_3 in Acetonitrile. A reaction of A-$PMo_3W_9O_{40}$ (1.77 g, 0.530 mmol) with an equimolar amount of PPh_3 (0.139 g, 0.530 mmol) was done in acetonitrile (100 cm^3) at 60 °C 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 measured from the intensity of the IR band of $OPPh_3$, by the method previously reported.[7] The same reaction was done in acetonitrile-d_3 degassed by the freeze-thaw cycle method. The ^{31}P NMR spectrum of the solution contained in a sealed NMR tube was measured at different times.

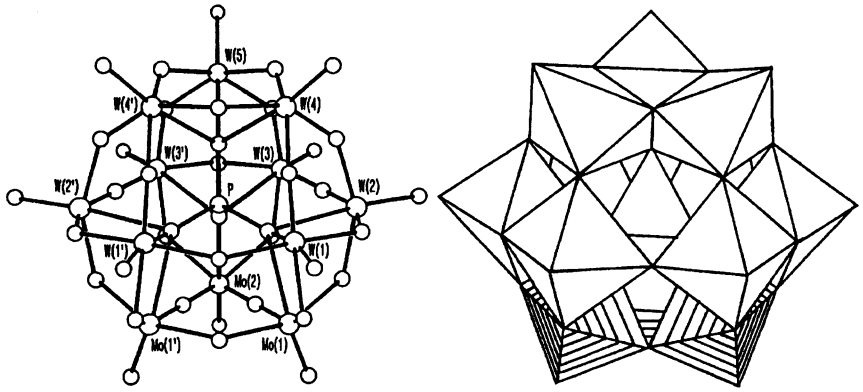

Fig. 1. Molecular geometry of the anion of A-β-$[NMe_4]_3[PMo_3W_9O_{40}]$; ball and stick (left) and polyhedral (right) representations. Hatched parts indicate MoO_6 octahedra.[10]

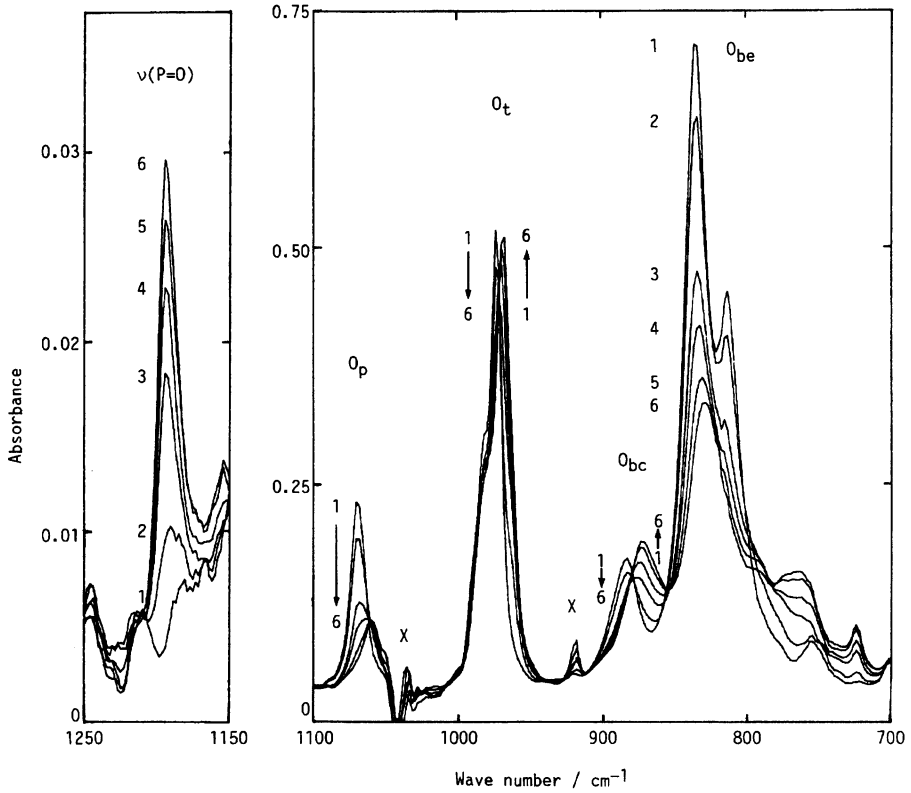

Fig. 2. IR spectral changes of an acetonitrile solution containing A-$PMo_3W_9O_{40}$ (5.30×10^{-3} mol dm^{-3}) and an equimolar amount of PPh_3. (reaction time at 60 °C; 0(1), 24(2), 97(3), 151(4), 241(5), and 465 h(6), ×; peaks of the solvent)

On the other hand, neither $PW_{12}O_{40}$ nor $PMoW_{11}O_{40}$ reacted with PPh_3 under similar conditions, which was confirmed by IR spectra of the reaction solution. This behavior is in contrast with that of $PMo_{12}O_{40}$, which is readily reduced by PPh_3 in acetonitrile.[7]

Isolation of the Reduced Species of A-$PMo_3W_9O_{40}$. After all of the PPh_3 were oxidized to $OPPh_3$, the solution 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 dark blue solids of A-$PMo_3W_9O_{39}$ (1.46 g, 83% yield). Found: C, 17.37; H, 3.15; N, 1.26; Mo, 8.6; P, 0.97; W, 48%. Calcd for $C_{48}H_{108}N_3Mo_3O_{39}PW_9$: C, 17.34; H, 3.27; N, 1.26; Mo, 8.66; P, 0.93; W, 49.77%.

Physical Measurements. Fourier transform-IR and X-ray photoelectron spectra were measured as previously reported.[7] ^{31}P and ^{183}W NMR spectra were measured with JEOL JNM-EX270 and GSX-400 spectrometers operating at 109.36 and 16.625 MHz, respectively. Chemical shifts were measured for a sample dissolved in acetonitrile-d_3 (0.005—0.01 mol dm^{-3}) using the sample replacement method[12] externally referenced to 85% H_3PO_4 or Na_2WO_4 in D_2O (2 mol dm^{-3}). ^{31}P and ^{183}W NMR parameters: pulse width, 4.7 and 80 μs; sweep width, 5400 and 8000 Hz; number of

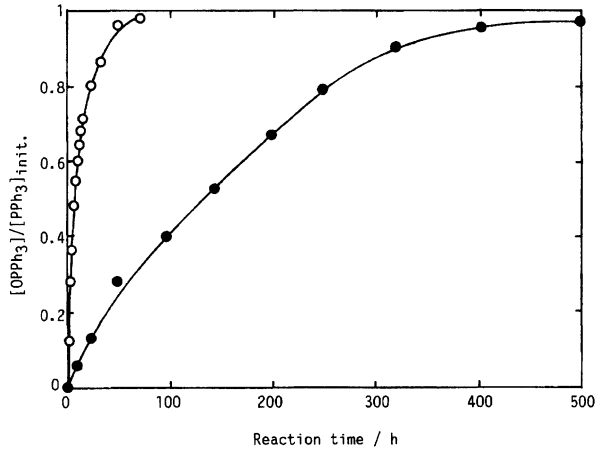

Fig. 3. Amounts of $OPPh_3$ formed in a reaction of A-$PMo_3W_9O_{40}$ (●) or $PMo_{12}O_{40}$ (○)[7] with an equimolar amount of PPh_3 in acetonitrile at 60 °C. ($[PPh_3]_{init.}$; the initial concentration of PPh_3)

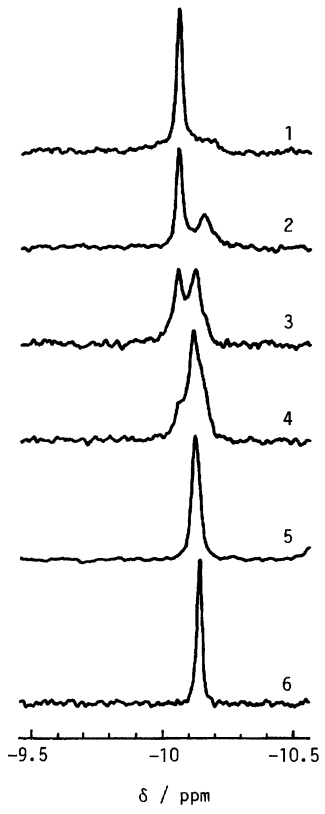

Fig. 4. ^{31}P NMR spectral changes of an acetonitrile-d_3 solution containing A-$PMo_3W_9O_{40}$ and an equimolar amount of PPh_3. (reaction time at 60 °C; 0(1), 18(2), 44(3), 64(4), 204(5), and 424 h(6))

acquisitions, 500 and 30000, respectively.

Results and Discussion

Structure of the Polyanion of A-$PMo_3W_9O_{40}$. In our previous work,[10] the structure of the polyanion of A-β-$[NMe_4]_3[PMo_3W_9O_{40}]$ was analyzed by a single crystal X-ray analysis, as depicted in Fig. 1. This tetra-

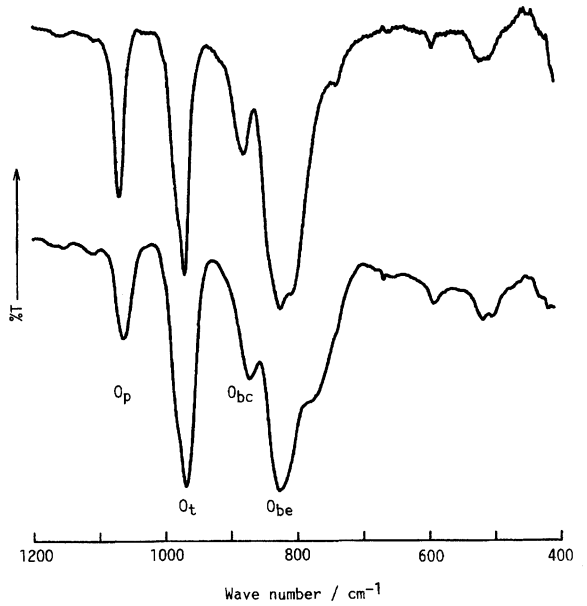

Fig. 5. IR spectra of A-$PMo_3W_9O_{40}$ (upper) and A-$PMo_3W_9O_{39}$ (lower) in KBr disks.

butylammonium salt has been prepared by the same procedure described for the tetramethylammonium salt using $[NBu^n_4]Br$ instead of $[NMe_4]Br$. The ^{31}P NMR spectrum of A-$PMo_3W_9O_{40}$ had only a single sharp signal at −10.03 ppm and the ^{183}W NMR spectrum two sharp signals at −91.1 and −101.3 ppm with integrated intensities in the ratio 1:2, where both the ^{183}W signals split into doublets ($^2J_{W-O-P}=1.5$ Hz). These findings are almost identical to those for A-β-$[NMe_4]_3[PMo_3W_9O_{40}]$.[10] The X-ray structural analysis of A-$PMo_3W_9O_{40}$[13] showed the geometry of the polyanion as an A-type molybdenum-trisubstituted, β-isomer of a PW_9 unit, which is the same as that of A-β-$[NMe_4]_3[PMo_3W_9O_{40}]$.

Reaction of A-$PMo_3W_9O_{40}$ with PPh_3 in Acetonitrile. A yellow acetonitrile solution containing A-β-$PMo_3W_9O_{40}$ and PPh_3 gradually turned green and finally dark blue. The IR spectral changes of the solution are shown in Fig. 2. New bands ascribed to $OPPh_3$ occurred with time, which is demonstrated by the representative band at 1194 cm^{-1} (ν (P=O)).[14] These spectral changes indicate that PPh_3 reduces A-$PMo_3W_9O_{40}$, with an oxygen atom transfer from the polyanion to PPh_3, as observed for the reduction of $PMo_{12}O_{40}$ with PPh_3.[7] The progress of the reduction has been estimated by the IR band of $OPPh_3$ (see the Experimental Section).

In the region of 1100—700 cm^{-1}, there occurred four major bands characteristic of the Keggin-type structure (Fig. 2). They are assigned to P–O (O_p band), M=O (terminal oxygen, O_t band, M=Mo or W), M–O_{bc}–M (O_{bc} band), and M–O_{be}–M (O_{be} band) stretching modes on the basis of the analogy to the assignments of the β-isomer of the $[PMo_{12}O_{40}]^{3-}$ anion salt.[8]

Table 1. Binding Energies (eV) of the Mo 3d, P 2p, and W 4f Electrons of the Mixed Addenda Heteropolyanion Salts[a)]

Compound	Mo(VI) $3d_{3/2}$	Mo(V) $3d_{3/2}$	Mo(VI) $3d_{5/2}$	Mo(V) $3d_{5/2}$	P(V) 2p	W(VI) $4f_{5/2}$	W(VI) $4f_{7/2}$
A-$PMo_3W_9O_{40}$	236.6	—	233.4	—	134.3	38.2	36.0
	(1.4)		(1.4)		(2.0)	(1.4)	(1.4)
A-$PMo_3W_9O_{39}$	236.6	234.8	233.3	231.7	134.2	37.8	35.7
	(1.8)	(2.1)	(1.9)	(1.9)	(2.3)	(1.6)	(1.6)

a) Peak width (eV) for deconvoluted bands in parentheses.

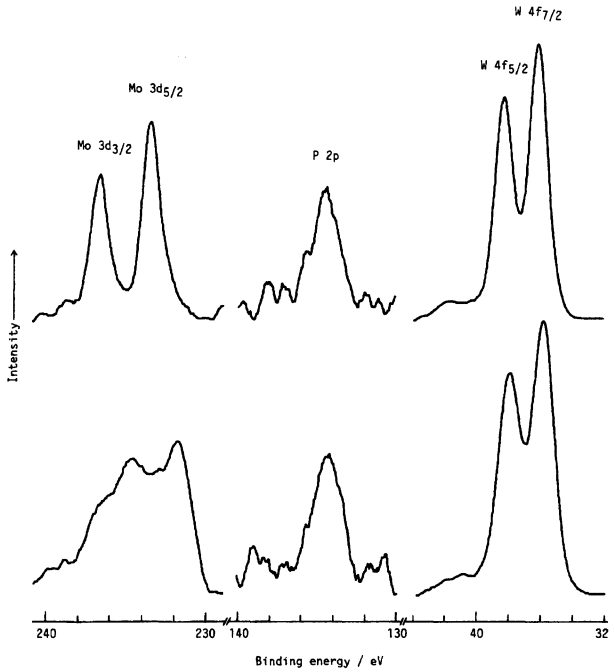

Fig. 6. X-Ray photoelectron spectra of A-$PMo_3W_9O_{40}$ (upper) and A-$PMo_3W_9O_{39}$ (lower).

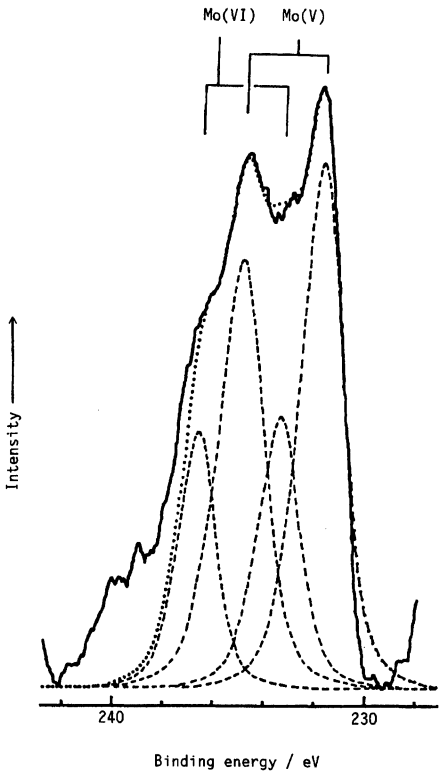

Fig. 7. X-Ray photoelectron spectrum of Mo 3d electrons for A-$PMo_3W_9O_{39}$. Dashed and dotted lines represent deconvoluted and synthesized curves, respectively.

During the reaction, the O_p and O_{be} bands drastically decreased in their intensities and the O_{bc} band gradually shifted to lower frequencies, but the O_t band was slightly broadened and shifted to lower frequencies. These spectral changes were essentially similar to those observed for the reduction of $PMo_{12}O_{40}$ with PPh_3[7] and suggest that the bridging oxygen atom in the M–O–M bond of this mixed addenda polyanion was also eliminated during the reduction. However, the difference in the reactivity between the O_{bc} and O_{be} atoms was equivocal, since even the reduction of the Keggin-type polyanion without any elimination of the lattice oxygen atom resulted in the symmetry depression of the polyanion to weaken the O_p, O_{bc}, and O_{be} bands, as reported for the electrochemical reduction of $H_3[PMo_{12}O_{40}]$.[5,15] As shown in Fig. 3, all of PPh_3 were found to be finally oxidized to $OPPh_3$ in the reaction. The reduction rate of A-$PMo_3W_9O_{40}$ with PPh_3 is much smaller than that of $PMo_{12}O_{40}$,[7] which may be attributed to the number of the bridging oxygen atoms in the Mo–O–Mo bonds; only three O_{bc} atoms exist in A-$PMo_3W_9O_{40}$, but there are twelve O_{bc} and twelve O_{be} atoms in $PMo_{12}O_{40}$.

The reaction has been also followed by ^{31}P NMR spectral changes of an acetonitrile-d_3 solution containing A-$PMo_3W_9O_{40}$ and PPh_3. The solution had two signals at −3.93 and −10.05 ppm ascribed to PPh_3 and A-$PMo_3W_9O_{40}$, respectively. The former signal decreased in intensity with time and, concomitantly, the new broad signal attributable to $OPPh_3$ developed at +28.6 ppm. In accordance with this, a new signal attributed to A-$PMo_3W_9O_{39}$ occurred at a higher magnetic field (−10.11 ppm) than that of A-$PMo_3W_9O_{40}$, as depicted in Fig. 4. However, it is noteworthy that the upfield shift (−0.06 ppm) of the ^{31}P signal of A-$PMo_3W_9O_{40}$ upon the reduction was very slight compared with that (the shift; −2.60 ppm) observed for the reduction of $PMo_{12}O_{40}$.[7]

Spectroscopic Properties of the Isolated Reduced Polyanion Salt. The IR specta of A-$PMo_3W_9O_{40}$ and A-$PMo_3W_9O_{39}$ measured in KBr disks are illustrated in Fig. 5. Although the O_p, O_{bc}, and O_{be} bands decreased in their intensities upon the reduction, the entire spectral pattern of A-$PMo_3W_9O_{39}$ was similar to that of A-$PMo_3W_9O_{40}$. Therefore, the geometry of the β-isomer of the Keggin-type polyanion is essentially retained for both the species. The ^{31}P NMR spectrum of A-$PMo_3W_9O_{39}$ in acetonitrile-d_3 showed only a single sharp signal at -10.12 ppm, confirming a single species of the oxygen-deficient reduced polyanion salt.

Figure 6 shows the X-ray photoelectron spectra of the Mo 3d, P 2p, and W 4f electrons of both A-$PMo_3W_9O_{40}$ and A-$PMo_3W_9O_{39}$. The reduced polyanion salt had bands due to P(V) 2p, W(VI) $4f_{5/2}$ and $4f_{7/2}$ electrons which are very close to those observed for A-$PMo_3W_9O_{40}$. On the other hand, the characteristic doublet band due to Mo(VI) $3d_{3/2}$ and $3d_{5/2}$ electrons, which is appreciably observed for A-$PMo_3W_9O_{40}$, was obscured for A-$PMo_3W_9O_{39}$ by the new bands at the lower energy sides. This indicates the formation of a Mo species in a lower valence in A-$PMo_3W_9O_{39}$. This broad band is deconvoluted into four bands, as depicted in Fig. 7. The bands at the first and the third highest binding energies are ascribed to Mo(VI) $3d_{3/2}$ and $3d_{5/2}$ electrons, respectively, because the binding energies were almost identical to those for A-$PMo_3W_9O_{40}$. The other two bands which occurred at 1.6—1.8 eV lower energies than the bands of the Mo(VI) species could be assigned to the doublet due to the Mo(V) 3d electrons, based on the binding energies for the Mo(V) 3d electrons in the reduced 12-molybdophosphate anions.[4,5,7,16] For both the doublets, the separations between $3d_{3/2}$ and $3d_{5/2}$ bands were found to be 3.1—3.3 eV and the intensity ratio of them to be about 1.1, which agreed with those reported for the reduced species of $PMo_{12}O_{40}$.[7] Binding energies of the Mo 3d, P 2p, and W 4f electons of A-$PMo_3W_9O_{40}$ and A-$PMo_3W_9O_{39}$ are summarized in Table 1. No bands due to Mo(IV) and further reduced molybdenum ions were observed in a lower binding energy region. The ratio of the Mo(VI) and Mo(V) ions in A-$PMo_3W_9O_{39}$ was evaluated to be 1 : 2 from the areas of the deconvoluted bands. These results indicate that the reduction of A-$PMo_3W_9O_{40}$ with PPh_3 does not occur on P(V) or W(VI) atoms but occurs on Mo(VI) atoms, accompanied by elimination of one of the corner-sharing bridging oxygen atoms in the Mo(VI)–O–Mo(VI) bonds and formation of two Mo(V) ions in the polyanion.

Furthermore, these findings are consistent with the facts that neither $PW_{12}O_{40}$ nor $PMoW_{11}O_{40}$ is reduced by PPh_3, that is, the bridging oxygen atoms in the W–O–W and Mo–O–W bonds were not transferred to PPh_3 under the conditions we used.

Conclusion. The two-electron reduction of A-$PMo_3W_9O_{40}$ with PPh_3 homogeneously proceeded to afford the oxygen-deficient reduced form, A-β-$[NBu^n_4]_3[PMo^{VI}Mo^{V}_2W_9O_{39}]$. Among the bridging oxygen atoms in the Keggin-type polyanion, it was demonstrated that the corner-sharing one in the Mo–O–Mo bond was at least reactive for the oxygen-transfer reaction upon the reduction of the polyanion.

References

1) M. Misono, *Chem. Uses Molybdenum, Proc. Int. Conf.*, **4**, 289 (1982).

2) H. Tsuneki, H. Niiyama, and E. Echigoya, *Chem. Lett.*, **1978**, 645 and 1183.

3) K. Katamura, T. Nakamura, K. Sakata, M. Misono, and Y. Yoneda, *Chem. Lett.*, **1981**, 89; N. Mizuno, K. Katamura, Y. Yoneda, and M. Misono, *J. Catal.*, **83**, 384 (1983).

4) K. Eguchi, Y. Toyozawa, K. Furuta, N. Yamazoe, and T. Seiyama, *Chem. Lett.*, **1981**, 1253.

5) K. Eguchi, Y. Toyozawa, N. Yamazoe, and T. Seiyama, *J. Catal.*, **83**, 32 (1983).

6) H. Taketa, S. Katsuki, K. Eguchi, T. Seiyama, and N. Yamazoe, *J. Phys. Chem.*, **90**, 2959 (1986).

7) I. Kawafune, *Chem. Lett.*, **1986**, 1503; I. Kawafune, *Chem. Lett.*, **1989**, 185; I. Kawafune and G. Matsubayashi, *Inorg. Chim. Acta*, **188**, 33 (1991).

8) C. Rocchiccioli-Deltcheff, R. Thouvenot, and R. Franck, *Spectrochim. Acta, Part A*, **32**, 587 (1976); C. Rocchiccioli-Deltcheff, M. Fournier, R. Franck, and R. Thouvenot, *Inorg. Chem.*, **22**, 207 (1983); R. Thouvenot, M. Fournier, R. Franck, and C. Rocchiccioli-Deltcheff, *Inorg. Chem.*, **23**, 598 (1984).

9) P. J. Domaille and G. Watunya, *Inorg. Chem.*, **25**, 1239 (1986).

10) I. Kawafune and G. Matsubayashi, *Chem. Lett.*, **1992**, 1869.

11) P. T. Meiklejohn, M. T. Pope, and R. A. Prados, *J. Am. Chem. Soc.*, **96**, 6779 (1974).

12) M. A. Leparulo-Loftus and M. T. Pope, *Inorg. Chem.*, **26**, 2112 (1987).

13) Crystal data: $C_{48}H_{108}Mo_3N_3O_{40}PW_9$, FW=3340.82, orthorhombic, space group $Pna2_1$, a=24.135(2), b=14.674(1), c=23.658(4) Å, U=8379(1) Å^3, Z=4, D_x=2.648 g cm^{-3}, D_m(floating)=2.64 g cm^{-3}. Intensity data ($2\theta < 50^\circ$) were collected on a Rigaku four-circle diffractometer by the ω–2θ scan technique using graphite-monochromatized Cu $K\alpha$ radiation (λ=1.5415 Å) and an absorption correction was used. Subsequent Fourier maps showed the positions of all the atoms of the anion. However, the atomic positions of the cation were not identified. The block-diagonal least-squares refinements based on 4209 independent reflections with $|F_o| > 3\sigma(F)$ were done by assuming anisotropic thermal parameters for W, Mo, P, and O atoms and converged to an R factor of 0.154.

14) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen, London (1958), p. 311.

15) M. Akimoto and E. Echigoya, *Chem. Lett.*, **1981**, 1759.

16) M. Akimoto, K. Shima, and E. Echigoya, *J. Chem. Soc., Faraday Trans. 1*, **79**, 2467 (1983).