Formation of p-Phenylenediamine–Crown Ether–[PMo$_{12}$O$_{40}$]$^{4-}$ Salts

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Electron transfer from the electron donor of p-phenylenediamine (PPD) to the electron acceptor of (H$^+$)$_3$[PMo$_{12}$O$_{40}$]$^{3-}$ forms a one-electron-reduced Keggin cluster of [PMo$_{12}$O$_{40}$]$^{3+}$, bearing a $S = 1/2$ spin, while proton transfer from the proton donor of (H$^+$)$_3$[PMo$_{12}$O$_{40}$]$^{3-}$ to the proton acceptor of PPD yielded mono- and diprotonated cations of 4-aminoanilinium (HPPD$^+$) and p-phenylenediammonium (H$_2$PPD$^+$). By introduction of crown ether receptors during the crystallization process, supramolecular cations of (HPPD$^+$)(crown ethers) and/or (H$_2$PPD$^+$)(crown ethers) were successfully introduced into three new $\alpha$-[PMo$_{12}$O$_{40}$]$^{4+}$ salts of (H$_3$PPD$^{3-}$)$_2$[(12-crown-4)]$_4$[PMo$_{12}$O$_{40}$]$^{3+}$ (1), (HPPD$^+$)$_3$[(15-crown-5)]$_4$[PMo$_{12}$O$_{40}$]$^{3-}$ (2), and (HPPD$^+$)$_2$(H$_2$PPD$^+$)$_2$[(18-crown-6)]$_4$[PMo$_{12}$O$_{40}$]$^{3-}$ (3) as the countercation. The protonated states of PPD and molecular-assembly structures of the supramolecular cations depended on the size of the crown ethers. In salt 3, a novel mixed-protonated state of HPPD$^+$ and H$_2$PPD$^+$ was confirmed to be complexed in the cation structure. According to the changes in the cation structures, the anion arrangements were modulated from those of the two-dimensional layer for salt 1 to the isolated cluster for salts 2 and 3. The temperature-dependent magnetic susceptibilities of salts 1–3 were consistent with the isolated spin arrangements of [PMo$_{12}$O$_{40}$]$^{4-}$. The electronic spectra of salts 1–3 indicated the interlayer optical transition from pentavalent Mo$^{V}$ to hexavalent Mo$^{VI}$ ions within the [PMo$_{12}$O$_{40}$]$^{4-}$ cluster. Temperature-dependent electron spin resonance spectra of salt 2 revealed the delocalization–localization transition of the $S = 1/2$ spin at 60 K. The spin on the [PMo$_{12}$O$_{40}$]$^{3+}$ cluster was localized on a specific Mo$^{V}$ site below 60 K, which was thermally activated with an activation energy of 0.015 eV.

Introduction

Polyoxometalates (POMs) such as [Mo$_6$O$_{19}$], [Mo$_6$O$_{24}$], [Mo$_{10}$O$_{40}$], and [PMo$_{12}$O$_{40}$] are synthesized by condensation reactions of molybdic acid derivatives under acidic conditions.1,2 The combination of corner-, edge-, and face-sharing [MoO$_x$] units (where $x = 4, 6, 7$) can yield a vast structural diversity of the POMs. Among them, the compound $\alpha$-[PMo$_{12}$O$_{40}$], which displays the archetypal Keggin structure, was the first POM reported by Berzelius in 1826 and has been extensively examined from the viewpoints of catalysis,3 antiviral activity,4 gas adsorption,5 and electronic6,7 and magnetic8 materials. The molecular structure of $\alpha$-[PMo$_{12}$O$_{40}$] is constructed from the corner-sharing of 12


[MoO₄] octahedra, and the central PO₄³⁻ anion is included at the center of the cluster.¹ Three types of O atoms are present in the α-Keggin structure, and these can be identified as terminal Mo–O, bridging Mo–O–Mo, and anionic P–O species. Because each Mo ion is coordinated by six O atoms in an octahedral fashion, the energy levels of the 4d orbitals on the Mo ions are split into t₂g and eg orbitals. Therefore, it is not a surprise that multistep redox properties are one of the most notable properties of the Mo-based α-Keggin. The α-[PMo₁₂O₄₀]³⁻, one-electron-reduced α-[PMo₁₂O₄₀]²⁻, and two-electron-reduced α-[PMo₁₂O₄₀]¹⁻ species, with the α-Keggin structure, have been characterized in the solid state, while the rearrangement of the three-electron-reduced α-[PMo₁₂O₄₀]⁰ to the lacunary [PMo₁₂O₄₀]³⁺ compound is facile.¹² Although the α-[PMo₁₂O₄₀]²⁻ cluster is electrically and magnetically inert because of the (4d)⁰ electronic structure of all 12 Mo⁶⁺ ions, the one-electron-reduced [PMo₁₂O₄₀]¹⁻ species with one pentavalent Mo⁵⁺ ion of the (4d)¹ electronic structure is electrically and magnetically active.⁵–⁸ Indeed, it has been shown that the mixed-valence electronic structure of [PMo₆Mo⁵⁺₁O₄₀]¹⁻ gives rise to the inter-valence optical transition from pentavalent Mo⁵⁺ to hexavalent Mo⁶⁺ within the cluster, and temperature-dependent electron spin resonance (ESR) spectra reveal a localization–delocalization spin transition.⁹ As such, it can be seen that the dynamic properties of electron and spin in the mixed-valence POM system are interesting from the point of view of constructing novel electronic and magnetic materials.¹⁰

In this context, we have been introducing supramolecular cation structures between inorganic or organic cations and crown ethers as the counterions of [Ni(dmit)₂]²⁻ (dmit²⁻ = 2-thioxo-1,3-dithiole-4,5-dithiolate).¹¹–¹³ This approach allows us to modify and modulate the assembled structures of the [Ni(dmit)₂]²⁻ anions in the crystal and thus to modify the magnetic properties of the [Ni(dmit)₂]²⁻ salts.¹² By using this approach, relatively large and complex cations, which consist of an organic ammonium cation such as anilinium and p-phenylenediammonium (H₂PPD⁺), with crown ethers were also introduced into the crystal, which gave rise to a spin ladder of interactions of S = ½ spin on [Ni(dmit)₂]²⁻ anions.¹³ However, the [Ni(dmit)₂]²⁻ anions are relatively small for embedding large and structurally diverse supramolecular cations in the crystal lattice. Therefore, in the present study, we used the Keggin cluster as a counterion of the supramolecular cations [these supramolecular cations are comprised of the 4-aminoanilinium (H₂PPD⁺) or H₂PDP⁺ complex via H-bonded interactions to the cavity of the crown ether]. In the course of crystallization, both the electron- and proton-transfer processes between the electron donor (proton acceptor) of p-phenylenediamine (PPD) and electron acceptor (proton donor) of (H⁺)[PMo₁₂O₄₀]³⁻ yield the H-bonded supramolecular cations and the one-electron-reduced [PMo₁₂O₄₀]¹⁻ in the crystal. The two –NH₂ sites of the PPD molecule have the potential to form two kinds of cations of H₂PDP⁺ and H₂PDP⁺ via a proton-accepting process according to the reaction between PPD and (H⁺)[PMo₁₂O₄₀]³⁻ in solution. When the acid-dissociation constant of (H⁺)₃[PMo₁₂O₄₀]³⁻ is lower than that of PPD, complete proton transfer from (H⁺)[PMo₁₂O₄₀]³⁻ to PPD occurs, giving rise to the dication, H₃PDP⁺, during the crystallization process.¹⁴,¹⁵ Because the crown ether moiety has a much higher affinity for the cationic –NH₂⁺ group than the neutral –NH₂ group,¹⁶ both the size and shape of the supramolecular assemblies between H₂PDP⁺ or H₂PDP⁺ and crown ethers are strongly affected by the proton-transfer state of PPD.

Also, the change in the cation structure will modify the arrangement of the [PMo12O40]4– cluster in the crystalline state. We examined the combination of supramolecular cations between protonated PPDs and crown ethers by changing the size of the crown ethers from [12]crown-4, to [15]crown-5, to [18]crown-6 and obtained the single crystals of (H2PPD2+)2([12]crown-4)3[PMo12O40]4– (1), (HPPD+)4-([15]crown-5)3[PMo12O40]4– (2), and mixed-protonated (HPPD+)2(H2PPD2+)2([18]crown-6)3[PMo12O40]4– (CH3CN)4 (3) (Chart 1). Herein, we report the preparation and structural, optical, and magnetic properties of three new Keggin salts, in which different types of protonated states of PPD derivatives afforded unique supramolecular structures.

Experimental Section

Preparation of One-Electron-Reduced [PMo12O40]4– Salts. (H+)4[PMo12O40]3–nH2O (n = 20) and p-phenylenediamine (PPD) purchased from Tokyo Kasei Inc. were used without further purification. The crystals were grown using standard diffusion methods in an H-shaped cell (~50 mL)17 (H+)4[PMo12O40]3–nH2O (~100 mg) and PPD (50 mg)—crown ethers (200 mg) were introduced into opposite sides of the H-shaped cell, and CH3CN (distilled prior to use) was introduced into the diffusion cell slowly. After 10 days, single crystals with typical dimensions of 0.5 × 0.5 × 0.4 mm3 were obtained as black blocks. Yields of salts 1–3 were 42, 35, and 39%, respectively. The stoichiometry of the compound was determined by X-ray structural analysis and elemental analysis. Elem anal. Calcd for C64H116O60N8Mo12P (salt 1): C, 19.24; H, 3.08; N, 2.04. Found. C, 19.30; H, 2.92; N, 2.10. Calcd for C64H116O60N8Mo12P (salt 2): C, 24.48; H, 3.72; N, 3.57. Found. C, 24.60; H, 3.60; N, 3.94. Calcd for C64H116O60N8Mo12P (salt 3): C, 26.34; H, 4.12; N, 4.15. Found. C, 25.81; H, 3.78; N, 4.06. The solvent content (CH3CN) in salt 3 was determined by thermogravimetric–differential thermal analysis (TG–DTA) measurement using a Rigaku Thermo Plus TG8120 with a scanning rate of 5 K min–1 under a N2 flow. These measurements showed a ca. 4% weight loss up until 413 K, which indicates that four CH3–CH solvent molecules are present in 3.

Cyclic Voltammetry. The redox potentials of PPD and (n-BuN)N3[PMo12O40]3– were measured in anhydrous CH3CN with 0.1 M (n-BuN)BF4 as the supporting electrolyte, using Pt electrodes (working and counter electrodes) and a saturated calomel electrode (SCE) as the reference electrode. The scan rate was 20 mV s–1. (n-BuN)N3[PMo12O40]3– was prepared by a cation-exchange reaction according to the literature.39

Crystal Structure Determination. Crystallographic data (Table 1) were collected by a Rigaku Raxis Rapid diffractometer using Mo Kα (λ = 0.71073 Å) radiation from a graphite monochromator. Structural refinements were performed using the full-matrix least-squares method on F2. Calculations were performed using Crystal Structure software packages. Parameters were refined using anisotropic temperature factors except for the H atoms, and these were refined using the riding model with a fixed C–H distance of 0.95 Å.

Optical Spectra. Infrared (IR; 400–4000 cm–1) spectral measurements were carried out using KBr disks on a Perkin-Elmer Spectrum 2000 spectrophotometer with a resolution of 2 cm–1. UV–vis–near-IR spectra (350–3200 nm) were measured on KBr disks using a Perkin-Elmer Lambda-19 spectrophotometer with a resolution of 2 nm. Raman measurements were made using a Jasco RMP-210S microscope with an Ar-laser excitation source at 532 nm. The Stokes shift from the surface of single crystals was detected in a backscattering detector arrangement.

Magnetic Susceptibility. The magnetic susceptibility was measured using a Quantum Design model MPMS-5 SQUID magnetometer for polycrystalline samples. The applied magnetic field was 1 T for all measurements.

ESR. Temperature-dependent ESR spectra were measured using a JEOL JES FA-100 spectrometer equipped with a temperature control system (Oxford ESR900 cryostat). The single crystals were attached to a support on a quartz sample holder. The g values of the ESR signals were corrected at the third and fourth reference signals of MnO. All ESR signals were fitted using the Lorentzian line shape.

Results and Discussion

Preparation of Salts 1–3. The stoichiometries and protonation states of PPD derivatives for salts 1–3 were determined as H2PPD2+2([12]crown-4)3[PMo12O40]4– (1), (HPPD+)4-([15]crown-5)3[PMo12O40]4– (2), and (HPPD+)2(H2PPD2+)2([18]crown-6)3[PMo12O40]4– (CH3CN)4 (3), from the elemental analysis, X-ray crystal structural analysis, and IR spectra. The changes in the protonated states of PPD modified the structures of the supramolecular cations and cluster arrangements (see below). Further, the absolute magnitude of the magnetic susceptibilities of salts 1–3 were in accordance with the formation of the one-electron-reduced [PMo12O40]4– species. Although one electron was transferred from PPD to [PMo12O40]3– during the formation of the crystal lattice, no oxidized species of PPD were included in the structure. However, protons were transferred from H+ [PMo12–O40]– to PPD, which generated HPPD+ or H2PPD2+ in [PMo12O40]4– via complexation with the crown ether moieties. Slow diffusion between (H+)3[PMo12–O40]– and PPD–crown ethers in CH3CN yielded both the proton- and electron-transfered states in salts 1–3. We discuss the crystal formation from the viewpoints of electron- and proton-transfer processes in solution.19,20

Upon crystallization, the color of the mother liquor changed from yellow to black-violet by the slow diffusion

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of (H\textsuperscript+)\textsubscript{2}([PMo\textsubscript{12}O\textsubscript{40}]\textsuperscript{3-}) and PPD in CH\textsubscript{3}CN over 2–3 days, and then black single crystals of salts 1–3 were obtained as one-electron-reduced mixed-valence [PMo\textsubscript{12}O\textsubscript{40}]\textsuperscript{3-} salts. Because the crown ethers are electrochemically inert, electron transfer from the electron donor of PPD to the electron acceptor of [PMo\textsubscript{12}O\textsubscript{40}]\textsuperscript{3-} yielded the one-electron-reduced [PMo\textsubscript{12}O\textsubscript{40}]\textsuperscript{4-} state. The electron-accepting and -donating abilities of [PMo\textsubscript{12}O\textsubscript{40}]\textsuperscript{3-} and PPD were evaluated from cyclic voltammetry in CH\textsubscript{3}CN. 19 Reversible two-step, one-electron transfer from typical electron donors to [PMo\textsubscript{12}O\textsubscript{40}]\textsuperscript{3-} were observed at the half-wave reduction potentials of \(E_{1/2}^{0.394}\) V and \(E_{1/2}^{0.394}\) V at 298 K, respectively, whereas \(E_{1/2}^{0.394}\) V and \(E_{1/2}^{0.394}\) V were observed at the half-wave oxidation potentials of \(E_{1/2}^{0.421}\) and \(E_{1/2}^{0.421}\) in the A unit. The average thermal parameter of the C atoms in the B unit. The result strongly suggested that the rotation of the phenyl ring around the long axis of HPPD\textsuperscript{+} is expected.

The highly acidic properties of (H\textsuperscript+)\textsubscript{2}([PMo\textsubscript{12}O\textsubscript{40}]\textsuperscript{3-})–have been reported in solution,\textsuperscript{14} and the monoprotonated HPPD\textsuperscript{+} state can be expected to coexist in equilibrium with H\textsubscript{2}PPD\textsuperscript{2+} under the crystalization conditions because both HPPD\textsuperscript{+} and H\textsubscript{2}PPD\textsuperscript{2+} have the possibility of being included as counter-cations of the [PMo\textsubscript{12}O\textsubscript{40}]\textsuperscript{4+} anion species.\textsuperscript{12}–\textsuperscript{18} Crystallographically independent cationic radicals of PPD or their protonated species were not incorporated into the crystals.

### Table 1. Selected Crystal Parameter of Salts 1–3

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<td>2543(6)</td>
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<td>40 485</td>
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<td>22 278</td>
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<td>(σ(I))</td>
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<td>R\textsuperscript{1}, R\textsuperscript{2}</td>
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<td>0.043</td>
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<tr>
<td>R\textsuperscript{3}(F\textsuperscript{2})</td>
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<td>0.064</td>
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<tr>
<td>GOF</td>
<td>1.29</td>
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\( R = \sum||F_o|| - |F_c||/\sum|F_o| \) and \( R_{w} = \sum(\sum(\sum|F_o| - |F_c|)^2)/(\sum(\sum(\sum|F_o|)^2))^{1/2}. \)
in the A unit. It has been observed that the O atoms present in the crown ether interact strongly with the cationic $-\text{NH}_3^+$ group, as has often been observed, through H-bonded type interactions, while the affinity between the O atoms of the crown ether and the neutral $-\text{NH}_3$ group is low; this demonstrates the electrostatic nature of the interaction. As such, it can be seen that coordination between the five O atoms of $[15]$crown-5 and HPPD$^+$ occurred at the $-\text{NH}_3^+$ group of HPPD$^+$; the upper and lower N sites of HPPD$^+$ in Figure 1b were $-\text{NH}_2$ and $-\text{NH}_3^+$ moieties, respectively.

Both the HPPD$^+$ and H2PPD$^{2+}$ cations were confirmed in salt 3 as a HPPD$^+$($[18]$crown-6) A unit and a sandwich-type H3PPD$^{3+}$($[18]$crown-6) B unit (Figure 1c). The dihedral angles between the mean $\pi$ plane of the phenyl ring and the mean O$_6$ plane of $[18]$crown-6 in the A and B units were 97° and 99°, respectively. Therefore, the long axes of the HPPD$^+$ and H3PPD$^{3+}$ molecules were almost normal to the O$_6$ plane of $[18]$crown-6. Both HPPD$^+$ and H2PPD$^{2+}$, under Bronsted acid–base equilibrium during crystallization, were introduced into the crystal to realize a closed-packing structure of cations and anions.

The strength of N–H$^+–\text{O}$ hydrogen-bonded interactions of the cations in salts 1–3 was evaluated from the average N–O distance ($d_{\text{N–O}}$) between the $-\text{NH}_3^+$ group of HPPD$^+$ or H2PPD$^{2+}$ and the O atoms of crown ethers. The average $d_{\text{N–O}}$ distances in salts 1–3 were 2.89, 2.88, and 2.92 Å, respectively, whose distances were similar to each other. The H-bonded supramolecular cation structures in salts 1–3 were constructed from similar magnitudes of N–H$^+–\text{O}$ hydrogen-bonded interactions.22

**Packing Structures.** The sandwich-type H2PPD$^{2+}$($[12]$-crown-4)$_2$ units were arranged between $[\text{PMo}_{12}\text{O}_{40}]^{4–}$ clusters along the $a$ and $b$ axes (Figure 2a), where effective intermolecular interactions between cations and anions were not observed within the limit of van der Waals interactions. Parts b and c of Figure 2 show a polyhedral representation of the $[\text{PMo}_{12}\text{O}_{40}]^{4–}$ clusters forming the lattice in the $ab$ and $bc$ planes, respectively. Within the $ab$ plane, a two-dimensional (2D) layer of $[\text{PMo}_{12}\text{O}_{40}]^{4–}$ clusters was observed. Within the $ab$ plane, the P–P distances ($d_{\text{P–P}}$) between the nearest-neighboring $[\text{PMo}_{12}\text{O}_{40}]^{4–}$ clusters along the $a$ axis ($d_{\text{P–P}} = 12.1$ Å) were ca. 1 and 2 Å shorter than those along the $b$ axis ($d_{\text{P–P}} = 13.1$ Å) and along the $-a + b$ axis ($d_{\text{P–P}} = 13.7$ Å). The most effective intercluster interaction was observed along the $a$ axis, which formed a one-dimensional (1D) chain of $[\text{PMo}_{12}\text{O}_{40}]^{4–}$ clusters. The 1D cluster chains were connected through two kinds of

intercluster interactions along the $b$ and $-a + b$ axes, forming the 2D layer within the $ab$ plane.

The $[\text{PMo}_{12}\text{O}_{40}]^{4-}$ clusters of salt 2 were observed on the lattice points, while the (HPPD$^+$)([15]crown-5) cations A and B formed an antiparallel dimer arrangement around the center of the unit cell (Figure 3a). Alternate arrangements of (HPPD$^+$)([15]crown-5) A and B units were observed along the $a$ and $b$ axes, which formed the cation layer within the $ab$ plane. The cation dimer was surrounded by eight nearest-neighboring $[\text{PMo}_{12}\text{O}_{40}]^{4-}$ clusters in the crystal. The inter-cluster distances along the $a$ axis ($d_{P-P}$) 13.6 Å were ca. 1 and 2 Å shorter that those along the $b$ axis ($d_{P-P}$) 14.6 Å and the $-a + b$ axis ($d_{P-P}$) 15.6 Å, respectively. The 1D arrangement of the $[\text{PMo}_{12}\text{O}_{40}]^{4-}$ clusters along the $a$ axis dominated intercluster interaction in salt 2. However, the shortest intercluster distance was 1.5 Å longer than that in compound 1, suggesting that the intercluster interactions in 2 were decreased by increasing of the size of the crown ether from [12]crown-4 to [15]crown-5.

The sandwich-type (H$_2$PDP$^+$)([18]crown-6)$_2$ cations of salt 3 were observed on the lattice points (Figure 4), while two (HPPD$^+$)([18]crown-6) cations existed at around the center of the unit cell. The most effective intercluster interaction was observed along the $a$ axis with $d_{P-P}$ of 14.2 Å, the distance of which was 0.4 and 0.7 Å shorter than those along the $b$ and $c$ axes, respectively. Because the intercluster distances in salt 3 were 1–2 Å longer than those in salt 1, each Keggin cluster was isolated to each other because of the large size of the [18]crown-6 molecules separating the $[\text{PMo}_{12}\text{O}_{40}]^{4-}$ clusters in salt 3.

**Electronic Spectra of Salts 1–3.** The electronic states of $[\text{PMo}_{12}\text{O}_{40}]^{4-}$ in salts 1–3 were evaluated by UV–vis–near-IR–IR spectra of the solid (Figure 5). The yellow (H$^+$)$_3[\text{PMo}_{12}\text{O}_{40}]^{3-}$ did not show the d–d transition (spectrum iv in Figure 5) due to the (4d)$^0$ electronic structure of the Mo$^{VI}$ ions. The electronic absorptions at 32 and 46 $10^3$ cm$^{-1}$ have been assigned to the metal–ligand charge-transfer electronic excitation from the doubly occupied oxo orbitals to the unoccupied d orbitals of Mo$^{VI}$ (23). On the other hand, the electronic spectra of salts 1–3 showed broad absorption in the vis–near-IR–IR energy region. Because the octahedral coordination of six O atoms to a Mo ion splits the d orbitals into $t_{2g}$ and $e_g$ orbitals, whose energy separation was usually larger than $10 \times 10^3$ cm$^{-1}$, the low-energy absorption in salts 1–3 was assigned to the intervalence transition from Mo$^{V}$ to Mo$^{VI}$ through the Mo–O–Mo bond within the cluster and the d–d transitions of Mo$^{VI}$ octahedrally coordinated.
dra.9,23,24 Because the terminal Mo–O distance (d_t) of the [PMo_12O_40] cluster was shorter than the inner (d_i) and bridging Mo–O distances (d_b), the [MoO_4] octahedra were rather too distorted to cause further splitting of the d orbitals. Therefore, the complex and broad electronic absorption bands were observed at an energy below ~18 × 10^3 cm^{-1}.9

IR and Raman Spectra of Salts 1–3. The protonated states of the PPD derivatives and the electronic states of [PMo_12O_40] in salts 1–3 were evaluated from the vibrational spectra (Figure 6). The N–H stretching modes (v_{N–H}) of −NH_2 and −NH_3 have been typically observed at 3500–3300 and 3130–3030 cm^{-1}, respectively, while the N–H deformation modes (δ_{N–H}) of −NH_2 and −NH_3 were observed at around 1650–1560 and 1600 cm^{-1}, respectively.25 In general, the energy of the vibrational bands of the −NH_2 group was higher than that of the −NH_3 group. The cation structure of (H_2PPD_2)+([12]crown-4)_2 in salt 1 may exhibit the vibrational bands of −NH_3 only, while the IR spectra of salts 2 and 3 were expected to show both the −NH_3 and −NH_2 vibrational modes simultaneously. The v_{N–H} mode of the −NH_2 group was not observed in the energy region around 3400 cm^{-1} for salt 1, while those in salts 2 and 3 were clearly confirmed at 3418 and 3370 cm^{-1}, respectively (Figure 6a). The disappearance of the v_{N–H} mode of the −NH_2 group in salt 1 was consistent with the formation of the sandwich-type cation structure of (H_2PPD_2)+([12]crown-4)_2. The v_{N–H} modes of the −NH_3 groups of HPPD^+ and H_2PPD^2+ in salts 1–3 were observed as broad bands with two transmittance maxima observed at 2870 and 2910 cm^{-1}.

The absorptions at 1516 and 1470 cm^{-1} were assigned to the aromatic C=C stretching mode (v_{C=C}) of the phenyl ring, and those around 1100 cm^{-1} were related to the C–O–C stretching mode of the crown ethers. The δ_{N–H} mode of the −NH_3 groups for H_2PPD^2+ in salt 1 was observed at 1597 cm^{-1}, while the δ_{N–H} mode of the −NH_2 group in salts 2 and 3 appeared at 1625 cm^{-1} accompanied by a shoulder of the δ_{N–H} vibrational mode of the −NH_3 group at around 1600 cm^{-1}. Because salts 2 and 3 showed δ_{N–H} modes of both the −NH_3 and −NH_2 groups, the monoprotonated HPPD^+ cations were included in the salts.

Characteristic vibrational bands of (H^+)[PMo_12O_40]^3− in the IR spectrum (iv in Figure 6) were observed at 1065 and 962 cm^{-1}, which were assigned to the asymmetric coupling mode of ν_{p–O}/ν_{Mo–O} and asymmetric ν_{Mo–O} modes, respectively.26 The asymmetric ν_{Mo–O} modes for salts 1–3 were observed at 946, 946, and 947 cm^{-1}, respectively, whose energy was ca. 15 cm^{-1} red-shifted from the [PMo_12O_40]^3− cluster by one-electron reduction. The red shifts of the asymmetric ν_{Mo–O} mode in the reduced Keggin cluster have already been reported,27 and the force constant of the Mo–O stretching mode was found to decrease by the introduction of one electron into the cluster due to electron delocalization on the cluster framework.

In the Raman spectrum of (H^+)[PMo_12O_40]^3−, the symmetric and asymmetric ν_{Mo–O} modes were observed at 989 and 977 cm^{-1}, respectively (spectrum iv in Figure 6b).26b The Raman spectra of salts 1–3 showed sharp symmetric vibrational modes at 995, 995, and 993 cm^{-1}, respectively. The symmetric ν_{Mo–O} mode of salts 1–3 was ca. 7 cm^{-1} red-shifted through the one-electron reduction of the Keggin cluster. Although the vibrational modes found around 820 cm^{-1} are related to the PPD derivatives, a clear correlation between the energy of these bands and the protonated states was not observed.

Magnetic Susceptibilities of Salts 1–3. Figure 7 shows the χ_{mol} vs T (left scale) and χ_{mol}T vs T (right scale) plots of salt 2 in the temperature range from 2 to 300 K. The temperature-dependent magnetic susceptibilities of salts 1 and 3 were also similar to that of salt 2. The χ_{mol}T vs T plot of salt 2 was in accordance with the Curie–Weiss behavior, whose Curie constant was 0.322 emu K mol^{-1}. This value was slightly decreased from the calculated Curie constant of 0.355 emu K mol^{-1} with g = 1.945. Although the C = 0.325 emu K mol^{-1} value of salt 3 was similar to that of salt 2, the magnetic susceptibility of salt 1 (C = 0.258 emu K mol^{-1}) was appreciably reduced from that of the free spin. The suppression of magnetic susceptibility in salt 1 may be

due to (i) spin–orbit coupling of the distorted MoV octahedron, (ii) antiferromagnetic interaction between [PMO12O40]4− clusters, or (iii) a slight change in the protonated state of the crystal.

When the excess protons were introduced or removed from the ideal stoichiometry of (H2PPD)2{[12]crown-4}4− [PMO12O40]4−, the number of the S = 1/2 spin on the cluster should be modified. About a 20% fluctuation of the H+ stoichiometry of (H+)4+{[12]crown-4}4− [PMO12O40]4− leads to an increase in the free spin value to 0.25 emu K mol−1. Although a distinct change of the protonated states and electronic structures could not be identified from both the vibrational and electronic spectra, the possibility of a slight change in the protonated state of salt 1 should not be completely disregarded at present. The antiferromagnetic interactions between [PMO12O40]4− clusters are also expected to reduce the C value of salt 1. In the crystal, the 2D layer and effective intercluster interactions of the [PMO12O40]4− clusters were observed. The intercluster distance in salt 1 was ca. 1–2 Å shorter than those in salts 2 and 3, which should increase the magnetic exchange interactions between the [PMO12O40]4− clusters in salt 1. Although the lowest unoccupied molecular orbital coefficients at terminal O atoms of the Keggin structure were quite significantly small,25 intercluster antiferromagnetic exchange energy is expected to reduce the magnetic susceptibility of salt 1 and remains a possibility of the spin–orbit coupling of the MoV octahedron within the cluster.

The magnitude of the spin–orbit coupling constant (λ) for the second and third transition-metal ions is usually larger than that for the first transition-metal ions because of the d-electron broadening, which decreases the absolute magnitude of the magnetic susceptibility. The magnetic susceptibility including the spin–orbit coupling constant is expressed for the ground-state symmetry of the [MoVO6] octahedron (2T2) as

\[
\chi_{\text{mol}} = \frac{N_A d^4 B}{3 k_B T} \left[ 2 + \frac{3 \lambda}{k_B T} \exp \left( -\frac{3 \lambda}{2 k_B T} \right) \right]
\]

Table 2. Average Mo–O Distances and Spin–Orbit Coupling Constant (λ) in Salts 1–3

<table>
<thead>
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<th>2</th>
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<td>0.325</td>
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<tr>
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<td>+347</td>
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<td>d3 Å</td>
<td>2.39</td>
<td>2.48</td>
<td>2.45</td>
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</table>

* The shape of the [MoO6] octahedron was evaluated from Mo–O distances of terminal Mo–O (d1), bridging Mo–O–Mo (d2), and anionic Mo–PO43− (d3).

where \( N_A \), \( \mu_B \), and \( k_B \) are Avogadro’s number, the Bohr magneton, and Boltzmann’s constant, respectively. The magnitude of λ is +155 cm−1 for a free spin and depends on a structural distortion of the [MoVO6] octahedron, where a large distortion of the octahedron decreased the λ value.29 Table 2 summarizes the Curie constant (C) and spin–orbit coupling constant (λ) calculated from eq 1 of salts 1–3 together with the average Mo–O distances of terminal Mo–O (d1), bridging Mo–O–Mo (d2), and anionic Mo–PO43− (d3) in the [MoO6] octahedron.

The distortion of the [MoO6] octahedron was evaluated from Mo–O distances of d1, d2, and d3. In salt 1, the average distances of d1, d2, and d3 were 1.66, 1.90, and 2.39 Å, respectively, which were within the same range of previously reported reduced Keggin structures of [Fe(C5Me5)2]4− [PMO12O40]4− and [tetrathiafulvalene]6 (tetraethylammonium)− ([H+]2[PMO12O40]4−).26,27c Because the terminal d1 of salt 1 was ca. 0.3 and 0.7 Å shorter than the bridging d2 and anionic d3, the [MoO6] octahedron was distorted to form an ideal octahedron. Although the lengths of d1 and d3 for salts 1–3 were observed within a similar range, the length of d2 for salt 1 (2.39 Å) was about 0.1 Å shorter than those of salts 2 (2.48 Å) and 3 (2.45 Å). Therefore, the structural distortion of the [MoO6] octahedron for salt 1 was smaller than those of salts 2 and 3. Both the spin–orbit coupling on the MoV octahedron and antiferromagnetic interaction between [PMO12O40]4− clusters play an important role in reducing the absolute magnitude of the magnetic susceptibility in salt 1.

Spin Dynamics in the [PMO12O40]4− Cluster. The formation of one-electron-reduced [PMO12O40]4− clusters was confirmed by temperature-dependent magnetic susceptibilities of salts 1–3. One 4d electron on the [PMO12O40]4− cluster was delocalized on the cluster at room temperature from the appearance of an interfacial transition at ~8 × 103 cm−1 in the electronic spectra, which suggested delocalization of a S = 1/2 spin of the MoV ion on the cluster.9 Figure 8a shows the ESR spectra of a polycrystalline sample of salt 2 at 5, 50, and 80 K. Because the π spin of PPD derivatives was not detected in salts 1–3 from ESR spectra, the closed-shell cation structures of HPPD+ and H2PPD2+ were confirmed.


A Lorentzian-type ESR spectrum at $g = 1.946$ and a line width ($\Delta H$) of 4.73 mT was observed at 5 K, while the $g$ value and $\Delta H$ at 80 K were observed at 1.945 and 8.17 mT, respectively. Weak hyperfine structures around both sides of the central signal at $g = 1.946$ were due to the two isotopes of $^{99}$Mo and $^{95}$Mo species with a nuclear spin of $I = 5/2$. The intensity of the ESR signals of salt 2 followed the Curie–Weiss law, which was consistent with the temperature-dependent magnetic susceptibility. Figure 8b shows the temperature-dependent $g$ values (left scale) and $\Delta H$ (right scale) of salt 2. The $g$ values showed the temperature-independent behavior from 4 to 100 K, while an abrupt enhancement of the $\Delta H$ values was observed by increasing the temperature at around 60 K. The magnitude of $\Delta H$ at 100 K (12.89 mT) was about 3 times larger than that at 50 K (4.00 mT), and the change in $\Delta H$ has been discussed from a motional freedom of one $S = 1/2$ spin on a reduced $[\text{PMo}_{12}\text{O}_{40}]^{4-}$ cluster. The temperature-dependent $\Delta H$ values of the Keggin cluster were composed of the sum of temperature-independent $\Delta H_0$ and temperature-dependent $\Delta H_T$ as expressed in eq 2, where the $\Delta H_T$ term is proportional to the hopping frequency ($\nu_T$) of the $S = 1/2$ spin between the nearest-neighbor Mo sites:30

$$\Delta H = \Delta H_0 + \Delta H_T = \Delta H_0 + C\nu_T$$  \hspace{1cm} (2)

The $\nu_T$ term can be further expressed by Mott’s hopping frequency as31

$$\nu_T = \nu_0 \exp(-2\alpha R) \exp(-E_0/k_B T)$$  \hspace{1cm} (3)

where $\alpha$, $R$, and $E_0$ are the tunneling factor, nearest-neighbor Mo–Mo distance, and activation energy of spin dynamics, respectively. Because $\nu_0$, $\alpha$, and $R$ are constants, the $\Delta H$ vs $T^{-1}$ plots yield $E_0$ of spin dynamics within the reduced $[\text{PMo}_{12}\text{O}_{40}]^{4-}$ cluster (Figure 8c). The $E_0$ value was 0.015 eV for salt 2 in the temperature range from 60 to 120 K, which was similar to those previously reported.9a The spin in the cluster was localized at a specific MoV site in the temperature range below 60 K, while the spin had a motional freedom among the 12 Mo sites above 60 K.

**Summary**

Supramolecular cation structures between protonated PPD derivatives of HPPD$^{+}$ and/or H$_2$PPD$^{2+}$ and crown ethers of [12]crown-4, [15]crown-5, and [18]crown-6 were introduced into the one-electron-reduced $\alpha$-[PMo$_{12}$O$_{40}$]$^{4-}$ Keggin salts. Three new Keggin salts of (H$_2$PPD$^{+}$)$_3$[(12)crown-4]$_2$-[PMo$_{12}$O$_{40}$]$^{4-}$ (1), (HPPD$^+$)$_3$[(15)crown-5]$_4$[PMo$_{12}$O$_{40}$]$^{5-}$ (2), and (HPPD$^+$)$_2$[(18)crown-6]$_4$[PMo$_{12}$O$_{40}$]$^{6-}$ (CH$_3$CN)$_3$ (3) were successfully obtained by the electron- and proton-transfer processes between the electron donor (proton acceptor) of PPD and the electron acceptor (proton donor) of the (H$^+$)$_3$[PMo$_{12}$O$_{40}$]$^{3-}$ clusters. The cation structure in salt 1 was the sandwich-type (H$_2$PPD$^{2+}$)([12]crown-4)$_2$, while in salt 2 was the monoprotonated 1:1 (HPPD$^+$)([15]crown-5) adduct. The mono- and diprotonated states of (HPPD$^+$)([18]crown-6) and (H$_2$PPD$^{2+}$)([18]crown-6)$_2$ coexisted in salt 3. Because the coordination affinity of the O atoms of crown ethers for the amino group was negligible in general, the sandwich-type coordination corresponded to the formation of the H$_3$PPD$^{2+}$ state in salts 1 and 3, and the 1:1 adduct between HPPD$^+$ and crown ethers was formed in salts 2 and 3. The Brønsted acid/base equilibrium and formation of a closed-packing structure in the crystals yielded different types of cationic structures and molecular assemblies in salts 1–3. A 2D layer of [PMo$_{12}$O$_{40}$]$^{4-}$ clusters was observed in salt 1, in which 1D [PMo$_{12}$O$_{40}$]$^{3-}$ chains were connected through interchain interactions. On the other hand, the clusters in salts 2 and 3 were isolated from each other. By an increase in the size of the crown ethers, the magnitude of intercluster interactions decreased in the order of [12]crown-4, to [15]crown-5, to [18]crown-6 because of an increase in the cation volume in the crystals. The crystals were fundamentally constructed from the electrostatic interaction between [PMo$_{12}$O$_{40}$]$^{3-}$ tetravalent anions and supramolecular cations. The crystal densities of salts 1–3 decreased in the order of the size of the crown ethers, and CH$_3$CN molecules were introduced into salt 3 in order to fill the crystal space. Therefore, the cation size of (H$_2$PPD$^{2+}$)-([12]crown-4)$_2$ was just fitted to the formation of a closed-packing structure of [PMo$_{12}$O$_{40}$]$^{4-}$ tetravalent anions in the...
crystal. One-electron-reduced $\alpha$-[PMo$_{12}$O$_{40}$]$^{4-}$, bearing one $S = \frac{1}{2}$ spin, was confirmed by the temperature-dependent magnetic susceptibilities of salts 1–3. The electronic absorption spectra of salts 1–3 revealed the intervalence optical transition between the pentavalent Mo$^V$ and hexavalent Mo$^VI$ ions within the cluster. In addition, temperature-dependent ESR spectra of salt 2 showed delocalization of the $S = \frac{1}{2}$ spin on the cluster above 60 K. The localization–delocalization spin transition was observed at 60 K by a temperature-dependent line width of the ESR spectra. The controls of spin dynamics and intervalence electron transfer within the reduced Keggin clusters have the potential of forming novel electrical and magnetic materials of an organic–inorganic hybrid molecular system.

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**Supporting Information Available:** Crystal data (CIF) of salts 1–3, selected bond lengths, temperature-dependent magnetic susceptibilities of salts 1 and 3, cyclic voltammetry, XRD, and TG–DTA chart of salt 3. This material is available free of charge via the Internet at http://pubs.acs.org.

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