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Article

Protonation and Methylation of an Anderson-Type Polyoxoanion $[IMo_6O_{24}]^{5-}$

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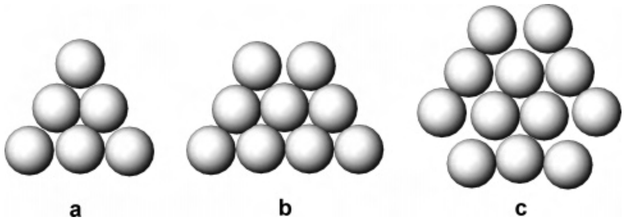
A series of protonated and methylated Anderson-type molybdoperiodates as well as the unprotonated $[IMo_6O_{24}]^{5-}$ have been synthesized and structurally characterized as tetra-*n*-butylammonium salts: $[(n\text{-}C_4H_9)_4N]_5[IMo_6O_{24}]$ [monoclinic, space group *C*2/*c*, $a = 33.6101(3)$ Å, $b = 15.2575(1)$ Å, $c = 24.0294(2)$ Å, $\beta = 126.9569(3)°$, $Z = 4$], $[(n\text{-}C_4H_9)_4N]_4[IMo_6O_{23}(OH)]$ [monoclinic, space group $P2_1/c$, $a = 9.5587(1)$ Å, $b = 24.1364(2)$ Å, $c = 18.2788(2)$ Å, $\beta = 90.1562(5)°$, $Z = 2$], $[(n\text{-}C_4H_9)_4N]_3[IMo_6O_{22}(OH)_2]\cdot 2DMF$ [monoclinic, space group $P2_1/a$, $a = 17.6105(4)$ Å, $b = 15.5432(5)$ Å, $c = 29.3316(9)$ Å, $\beta = 91.475(3)°$, $Z = 4$], $[(n\text{-}C_4H_9)_4N]_4[IMo_6O_{23}(OMe)]\cdot 3H_2O$ [orthorhombic, space group *Pbca*, $a = 17.0679(4)$ Å, $b = 25.6998(6)$ Å, $c = 20.7428(4)$ Å, $Z = 4$], $[(n\text{-}C_4H_9)_4N]_3[IMo_6O_{22}(OMe)_2]$ [monoclinic, space group $P2_1/n$, $a = 10.4009(1)$ Å, $b = 14.6658(3)$ Å, $c = 23.5395(4)$ Å, $\beta = 100.324(1)°$, $Z = 2$]. In all of these compounds, the $[IMo_6O_{24}]^{5-}$ anion is protonated or methylated selectively at O atoms shared by two Mo atoms. The results have also revealed that the protonated Anderson-type molybdoperiodates readily react with methanol in a very selective manner, while the unprotonated $[IMo_6O_{24}]^{5-}$ anion does not react with methanol under similar conditions.

Introduction

One main feature of polyoxometalates or anionic molecular oxides is that they provide structurally well-characterized surfaces formed by approximately coplanar, closest-packed O atoms. Triangular surfaces of hexametalates[1−3] and well-known Keggin anions[4] are made up of six closest-packed O atoms (**a** in the scheme below). Decavanadate[5] and decaniobate[6] have larger isosceles trapezoidal surfaces that are made up of nine closest-packed O atoms (**b**). Anderson-type anions[7,8] have yet larger surfaces where 12 almost coplanar O atoms are closest-packed to form a hexagon (**c**).



The basicity of the triangular surface is relatively well-studied. While protonation sites of the Keggin anions are still actively debated,[9] it is now generally accepted that O atoms on the sides of the triangle are more basic than those at the apexes in hexametalates.[10] X-ray and NMR studies of $[H_xCp^*TiMo_5O_{18}]^{x-3}$,[11] $[H_2Nb_6O_{19}]^{6-}$,[12] and $[HV_2W_4O_{19}]^{3-}$ [13] have revealed that the protons are attached to the O atoms on the sides in all of these cases. The results of molecular orbital (MO) calculations on hexametalates agree with those experiments.[14,15] Protonation sites of the nine-atom array of decavanadate have also been investigated by different

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research groups. However, the situation here is less unambiguous. Theoretical calculations suggested the unique O atom at the center of the trapizoid most basic.[16,17] On the other hand, X-ray structural studies of $[HV_{10}O_{28}]^{5-}$ revealed that an O atom on the side is protonated in this anion.[18,19] A total of 24 different salts of diprotonated decavanadate have been structurally characterized. In 13 of them, only the O atoms on the sides are protonated.[20−33] Both the central O atom and an O atom on the side are protonated in five of them.[25,34−37] In the other six, only the central O atoms are protonated.[30,38−42] Interestingly, only the O atoms on the sides are protonated in a hydrated 1,6-hexanediammonium salt of $[H_2V_{10}O_{28}]^{4-}$,[32] while in an unhydrated salt of the same cation, only the central O atoms are protonated.[41] These crystal structural studies of protonated decavanadate anions indicate that the protonation sites of $[V_{10}O_{28}]^{6-}$ are significantly affected by hydrogen bonding in the solid state.

Our knowledge on the protonation sites of the 12-atom hexagonal surface of Anderson-type anions is even more sketchy. The topic has never really been addressed in a systematic manner. Anderson-type anions have historically been classified in two series: those without any protons attached to the metal−oxygen framework (**A**) and those with six nonacidic protons (**B**).[43] Species with an intermediate number of protons had not been known until 1983.[44,45] All protons in the **B** series are attached to the central O atoms of the hexagonal array, and these have been assumed to be the most basic of the 12 O atoms. Bond valence calculations[46,47] on $[IMo_6O_{24}]^{5-}$ [48] and $[TeMo_6O_{24}]^{6-}$ [8] support this assumption to some extent. Thus, it has been thought that the first proton would attach to one of these central O atoms when $[IMo_6O_{24}]^{5-}$ or $[TeMo_6O_{24}]^{6-}$ is protonated.[49] However, this hypothesis has never been verified by experiments or MO calculations.

Which O atom is the most basic one in Anderson-type anions? To address this simple but interesting question, we have synthesized mono- and diprotonated species of $[IMo_6O_{24}]^{5-}$ and structurally characterized them. In the course of this study, we also found that protonated species of $[IMo_6O_{24}]^{5-}$ react with methanol in a selective manner to give methylated Anderson-type anions. Here we report the results of these studies.

Experimental Section

Reagents, Solvents, and General Procedures. The following were purchased from commercial sources and used without further purification: $Na_2MoO_4{\cdot}2H_2O$, $HIO_4{\cdot}2H_2O$, concentrated aqueous HCl and P_2O_5 (Kishida), MoO_3 (Nakarai), $[(n\text{-}C_4H_9)_4N]Br$ (Tokyo Kasei), and 10% aqueous $[(n\text{-}C_4H_9)_4N]OH$ (Tokyo Kasei or Wako). Dimethylformamide (DMF), diethyl ether, and ethyl acetate (Wako) were dried over 4-Å molecular sieves. Methanol (Wako) and deuterated acetonitrile (ISOTEC) were dried over 3-Å molecular sieves. Acetonitrile (Kishida) was routinely dried over 3-Å molecular sieves. $[(n\text{-}C_4H_9)_4N]_4[\alpha\text{-}Mo_8O_{26}]$ was prepared according to the literature.[50]

Analytical Procedures. Elemental analyses were performed by Toray Research Center Inc., Shiga, Japan. IR spectra were recorded from mineral oil (Nujol) mulls between KRS plates on a Shimadzu FTIR-8400 spectrometer. Absorptions are described as follows: very strong (vs), strong (s), medium (m), weak (w), and shoulder (sh). NMR spectra were recorded on a Varian Inova spectrometer. ^1H NMR spectra were recorded at 299.966 MHz and referenced internally against tetramethylsilane. ^{13}C NMR spectra were recorded at 75.434 MHz and referenced against the 116.53 ppm peak of solvent CD_3CN.

Preparation of $[(n\text{-}C_4H_9)_4N]_5[IMo_6O_{24}]$. Method 1. To the solution of the monoprotonated compound $[(n\text{-}C_4H_9)_4N]_4[IMo_6O_{23}(OH)]$ (0.10 g, 4.9×10^{-5} mol) in 1 mL of CH_3CN was added 0.13 mL of a 10% aqueous $[(n\text{-}C_4H_9)_4N]OH$ solution (5.0×10^{-5} mol). The mixed solution was left to stir for 2 h before 27 mL of ethyl acetate was added. The mixture was then allowed to stand at ambient temperature for 18 h. The colorless plate-shaped crystals that formed were collected by filtration and dried in vacuo over

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P_2O_5 for 3 h to yield 0.078 g (3.4×10^{-5} mol, 70% on Mo) of analytically pure compound. Anal. Calcd for $C_{80}H_{180}N_5IMo_6O_{24}$: C, 41.80; H, 7.89; N, 3.05; I, 5.52; Mo, 25.0. Found: C, 41.43; H, 7.93; N, 3.18; I, 5.20; Mo, 24.8. IR (Nujol, 400−1000 cm^{-1}): 419 (w), 469 (m), 495 (w), 525 (w), 562 (w), 621 (s), 680 (vs), 721 (m), 735 (m), 789 (w), 886 (s), 906 (s), 927 (s).

Preparation of $[(n\text{-}C_4H_9)_4N]_5[IMo_6O_{24}]$. Method 2. MoO_3 (0.75 g, 5.2 mmol), $HIO_4{\cdot}2H_2O$ (0.17 g, 0.75 mmol), and 10% aqueous $[(n\text{-}C_4H_9)_4N]OH$ (10 mL, 3.9 mmol) were mixed and left to stir overnight. After removal of the undissolved solids by filtration, the filtrate was evaporated to dryness in vacuo. The powder thus obtained was further dried in vacuo over P_2O_5 for 10 h. This crude product (1.6 g) was dissolved in 5 mL of acetonitrile, and 37 mL of ethyl acetate was added to the solution with stirring. The mixed solution was allowed to stand at ambient temperature overnight. Colorless microcrystals that formed were collected by filtration and dried in vacuo over P_2O_5 for 4 h to yield 1.1 g (0.48 mmol, 64% based on I) of the product. The material obtained by this method gave satisfactory elemental analysis (C, H, and N) and IR spectra identical with those of the material obtained by method 1.

Preparation of $[(n\text{-}C_4H_9)_4N]_4[IMo_6O_{23}(OH)]$. Method 1. $Na_2MoO_4{\cdot}2H_2O$ (5.31 g, 21.9 mmol) was dissolved in 25.2 mL of 1.04 M HCl (26.2 mmol). $HIO_4{\cdot}2H_2O$ (1.00 g, 4.39 mmol) was added to this acidic solution with stirring to produce a colorless precipitate. The mixture was stirred for 5 min before it was heated to 50 °C and was allowed to stir for an additional 5 min at this temperature, during which period the precipitate dissolved. A solution of $[(n\text{-}C_4H_9)_4N]Br$ (5.66 g, 17.6 mmol, in 5 mL of water) was then added with vigorous stirring to cause immediate formation of a white precipitate, which turned pale yellow upon further stirring. After the mixture was stirred for 20 min at 50 °C, the pale-yellow precipitate was collected by filtration, washed with 3 × 20 mL of water, and dried in vacuo over P_2O_5 for 6 h to yield 2.06 g of a crude product. A total of 0.30 g of this crude product was dissolved in 3 mL of acetonitrile, and the solution was filtered to remove a small amount of insoluble material. Diethyl ether was added to the filtrate to the point of saturation (ca. 11.0 mL). The mixture was then heated briefly with a heat gun to obtain a clear solution, and the solution was allowed to stand at ambient temperature for 16 h. The block-shaped crystals that formed were collected by filtration and dried in vacuo over P_2O_5 for 5 h to yield 0.15 g of analytically pure compound (7.3×10^{-5} mol, 14% on Mo). Anal. Calcd for $C_{64}H_{145}N_4IMo_6O_{24}$: C, 37.36; H, 7.10; N, 2.72; I, 6.17; Mo, 28.0. Found: C, 37.25; H, 7.10; N, 2.27; I, 6.33; Mo, 27.2. IR (Nujol, 400−1000 cm^{-1}): 431 (w), 477 (m), 497 (w), 535 (m), 568 (w), 599 (m), 621 (w), 639 (m), 661 (m), 676 (sh), 695 (s), 722 (s), 796 (w), 896 (s), 914 (s), 936 (s).

Preparation of $[(n\text{-}C_4H_9)_4N]_4[IMo_6O_{23}(OH)]$. Method 2. To a solution of the nonprotonated compound $[(n\text{-}C_4H_9)_4N]_5[IMo_6O_{24}]$ (0.20 g, 8.7×10^{-5} mol, in 2.0 mL of CH_3CN) was added 0.08 mL of 1.0 M HCl (8×10^{-5} mol). The mixed solution was stirred for 15 min before 13 mL of ethyl acetate was added to the solution. The colorless microcrystals that formed were collected by filtration and dried in vacuo over P_2O_5 for 6 h to yield 0.11 g (5.3×10^{-5} mol, 61%) of the product. The crystals thus obtained gave satisfactory elemental analysis (C, H, and N) and IR spectra identical with those of the material obtained by method 1.

Preparation of $[(n\text{-}C_4H_9)_4N]_4[IMo_6O_{23}(OH)]$. Method 3. To a solution of the diprotonated compound $[(n\text{-}C_4H_9)_4N]_3[IMo_6O_{22}(OH)_2]$ (0.20 g, 0.10 mmol) in 2.0 mL of CH_3CN was added 0.25 mL of 10% aqueous $[(n\text{-}C_4H_9)_4]OH$ (0.10 mmol). After removal of a small amount of yellow precipitate that formed by filtration, 30 mL of ethyl acetate was added to the filtrate. The mixture was then allowed to stand at ambient temperature overnight. Colorless microcrystals that formed were collected by filtration and dried in vacuo over P_2O_5 for 8 h to yield 0.078 g (0.038 mmol, 37%) of the product. The compound thus obtained gave satisfactory elemental analysis (C, H, and N) and IR spectra identical with those of the material obtained by method 1.

Preparation of $[(n\text{-}C_4H_9)_4N]_3[IMo_6O_{22}(OH)_2]{\cdot}2DMF$. Method 1. To a solution of $[(n\text{-}C_4H_9)_4N]_3[IMo_6O_{22}(OMe)_2]$ (1.0 g, 0.54 mmol, in 12.5 mL of DMF) was added 1.17 mL of water. The solution was stirred for 1 h before 85 mL of ethyl acetate was added. The mixture was stirred for 1 min, and the microcrystals that appeared were collected by filtration and dried in vacuo for 8 h to yield 0.53 g (0.29 mmol, 50%) of the compound. Anal. Calcd for $C_{54}H_{124}N_5IMo_6O_{26}$: C, 33.06; H, 6.37; N, 3.57; I, 6.47; Mo, 29.3. Found: C, 33.01; H, 6.45; N, 2.90; I, 6.58; Mo, 29.4. IR (Nujol, 400−1000 cm^{-1}): 471 (m), 479 (m), 487 (sh), 530 (m), 566 (m), 620 (w), 637 (w), 668 (s), 700 (s), 718 (sh), 742 (m), 880 (w), 906 (s), 922 (s), 944 (s). Single crystals suitable for X-ray structural analysis were obtained by dissolving 0.10 g of the microcrystals in 1.25 mL of DMF, adding 5 mL of ethyl acetate, removing a small amount of solids that formed by filtration, and allowing the filtrate to stand at ambient temperature. Block-shaped crystals appeared in 3 h.

Preparation of $[(n\text{-}C_4H_9)_4N]_3[IMo_6O_{22}(OH)_2]{\cdot}2DMF$. Method 2. To a solution of the monoprotonated compound $[(n\text{-}C_4H_9)_4N]_4[IMo_6O_{23}(OH)]$ (0.20 g, 9.7×10^{-5} mol) in 2.0 mL of DMF was added 0.09 mL of 1.0 M HCl (9×10^{-5} mol). The mixed solution was stirred for 15 min before 12 mL of ethyl acetate was added to the solution. The colorless microcrystals that formed were collected by filtration and dried in vacuo over P_2O_5 for 7 h to yield 0.12 g (6.1×10^{-5} mol, 63%) of the product. The material obtained by this method gave satisfactory elemental analysis (C, H, and N) and IR spectra identical with those of the material obtained by method 1.

Preparation of $[(n\text{-}C_4H_9)_4N]_4[IMo_6O_{23}(OMe)]{\cdot}H_2O$. $[(n\text{-}C_4H_9)_4N]_4[IMo_6O_{23}(OH)]$ (0.10 g, 4.9×10^{-5} mol) was dissolved in 1.5 mL of methanol, and the solution was allowed to stand at ambient temperature for 4 h. A small amount of colorless precipitate that formed was filtered off, and 3.2 mL of diethyl ether was added to the filtrate. The solution was then allowed to stand for 18 h. The colorless block-shaped crystals that formed were collected by filtration and dried in vacuo over P_2O_5 for 1.5 h to yield 0.025 g of analytically pure compound (1.2×10^{-5} mol, 25%). Anal. Calcd for $C_{65}H_{149}N_4IMo_6O_{25}$: C, 37.36; H, 7.19; N, 2.68; I, 6.07; Mo, 27.5. Found: C, 37.52; H, 7.29; N, 2.56; I, 6.20; Mo, 27.3. IR (Nujol, 400−1000 cm^{-1}): 475 (m), 494 (w), 538 (m), 567 (w), 600 (m), 637 (m), 667 (s), 673 (s), 696 (vs), 721 (s), 894 (vs), 913 (vs), 935 (s). ^1H NMR (CD_3CN): δ (ppm) 0.97 (t, $CH_3CH_2CH_2CH_2N$), 1.47 (m, $CH_3CH_2CH_2CH_2N$), 1.66 (m, $CH_3CH_2CH_2CH_2N$), 3.19 (m, $CH_3CH_2CH_2CH_2N$), 4.15 (s, CH_3O).

Preparation of $[(n\text{-}C_4H_9)_4N]_3[IMo_6O_{22}(OMe)_2]$. Method 1. $Na_2MoO_4{\cdot}2H_2O$ (3.20 g, 13.2 mmol) was dissolved in 17.7 mL of 1.05 M HCl (18.6 mmol). $HIO_4{\cdot}2H_2O$ (0.500 g, 2.19 mmol) was added to this solution. The mixture was stirred for 5 min, during which time colorless precipitates formed. It was further stirred for 15 min at 70−75 °C to yield a clear solution. A solution of $[(n\text{-}C_4H_9)_4N]Br$ (2.83 g, 8.78 mmol, in 5 mL of water) was then added to the solution, and the resulting slurry was allowed to stir at 70 °C for 30 min. The mixture was filtered, and the pale-yellow solids collected were dried in vacuo over P_2O_5 for 12 h to yield 3.31 g of crude $[(n\text{-}C_4H_9)_4N]_4[IMo_9O_{32}(OH)(OH_2)_3]$.[51] A total of 0.43 g of

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this material was dissolved in 15 mL of methanol, and the solution was filtered to remove a small amount of solids left undissolved. The crystals that appeared after allowing the filtrate to stand at ambient temperature for 24 h were collected by filtration and dried in vacuo over P_2O_5 for 12 h to yield 0.15 g of $[(n\text{-}C_4H_9)_4N]_3[IMo_6O_{22}(OMe)_2]$ (8.1×10^{-5} mol, 28% based on Mo). Anal. Calcd for $C_{50}H_{114}N_3IMo_6O_{24}$: C, 32.56; H, 6.23; N, 2.28; I, 6.9; Mo, 31.2. Found: C, 32.10; H, 6.20; N, 2.03; I, 7.2; Mo, 30.9. IR (Nujol mull, 1050−400 cm^{-1}): 1013 (m), 943 (vs), 925 (vs), 907 (vs), 892 (m), 880 (w), 750 (s), 733 (s), 701 (vs), 666 (s), 641 (m), 624 (m), 556 (vs), 478 (m), 473 (m). ^1H NMR (CD_3CN): δ (ppm) 0.97 (t, $C\mathit{H}_3CH_2CH_2CH_2N$), 1.37 (m, $CH_3C\mathit{H}_2CH_2CH_2N$), 1.62 (m, $CH_3CH_2C\mathit{H}_2CH_2N$), 3.11 (m, $CH_3CH_2CH_2C\mathit{H}_2N$), 4.30 (s, $C\mathit{H}_3O$), 4.31 (s, $C\mathit{H}_3O$).[52] ^{13}C NMR (CD_3CN): δ (ppm) 12.21 ($\mathit{C}H_3CH_2CH_2CH_2N$), 18.64 ($CH_3\mathit{C}H_2CH_2CH_2N$), 22.74 ($CH_3CH_2\mathit{C}H_2CH_2N$), 5761 ($CH_3CH_2CH_2\mathit{C}H_2N$), 69.39 (s, $\mathit{C}H_3O$), 69.62 (s, $\mathit{C}H_3O$).

Preparation of $[(n\text{-}C_4H_9)_4N]_3[IMo_6O_{22}(OMe)_2]$. Method 2. $[(n\text{-}C_4H_9)_4N]_4[\alpha\text{-}Mo_8O_{26}]$ (0.50 g, 0.23 mmol) was added to 13 mL of methanol, and the mixture was stirred for 20 min to obtain a clear solution. $HIO_4 \cdot 2H_2O$ (0.071 g, 0.31 mmol) was dissolved in this molybdate solution. After 5 min of stirring, white microcrystals appeared. The mixture was then heated in an oil bath (60 °C) with stirring for 10 min, and the clear solution obtained was allowed to stand at ambient temperature for 24 h. Block-shaped crystals that formed were collected by filtration and dried in vacuo over P_2O_5 for 12 h to yield 0.44 g of the product (0.24 mmol, 78%). The material obtained by this method gave satisfactory elemental analysis (C, H, and N). Its IR and ^1H NMR spectra were identical with those for the material obtained by method 1.

Crystal Structure Determinations. All of the crystals used for the structure determinations were prepared as mentioned above but without the final drying. Single-crystal diffraction data for $[(n\text{-}C_4H_9)_4N]_5[IMo_6O_{24}]$, $[(n\text{-}C_4H_9)_4N]_4[IMo_6O_{23}(OH)]$, $[(n\text{-}C_4H_9)_4N]_3[IMo_6O_{22}(OH)_2] \cdot 2DMF$, and $[(n\text{-}C_4H_9)_4N]_4[IMo_6O_{23}(OMe)] \cdot 3H_2O$ were measured on a Rigaku Mercury CCD diffractometer and were processed with the HKL2000 package.[53] Data for $[(n\text{-}C_4H_9)_4N]_3[IMo_6O_{22}(OMe)_2]$ were measured on a Bruker SMART CCD system. All of the structures were solved by the direct methods and refined by full-matrix least squares using the *SHELX-97* program suite.[54]

An asymmetric unit of $[(n\text{-}C_4H_9)_4N]_5[IMo_6O_{24}]$ contains a half of a $[IMo_6O_{24}]^{5-}$ anion with the I atom located at the center of symmetry, two $[(n\text{-}C_4H_9)_4N]^+$ cations at general positions, and a half of a $[(n\text{-}C_4H_9)_4N]_5^+$ cation with the N atom on the twofold axis. The ratio of the number of anions to that of cations, $^1/_2$ to $^5/_2$, is compatible with that of the unprotonated hexamolybdoperiodate anion. All of the non-H atoms were refined in anisotropic modes, and the H atoms were treated with riding models.

In the crystal of $[(n\text{-}C_4H_9)_4N]_4[IMo_6O_{23}(OH)]$, an asymmetric unit contains a half of a hexamolybdoperiodate anion with the I atom at the center of symmetry and two $[(n\text{-}C_4H_9)_4N]^+$ cations at general positions. The ratio of the number of anions to that of cations is $^1/_2$ to 2, which requires an attachment of one proton to the anion. Bond valence sum (BVS) calculation[46,47] revealed that Ob2 shows a BVS of 1.6, which is significantly smaller than those of the other two Ob atoms (1.9 and 1.8). Therefore, Ob2 was concluded to be protonated at a probability of 50%. All of the non-H atoms were refined in anisotropic modes, and the H atoms of the cations were treated with riding models. The H atom on Ob2 could not be located.

An asymmetric unit of the crystal of $[(n\text{-}C_4H_9)_4N]_3[IMo_6O_{22}(OH)_2] \cdot 2DMF$ contains halves of hexamolybdoperiodate anions with the I atoms at the centers of symmetry at (0, 0, 0) and (0, 0, $^1/_2$). It also contains three $[(n\text{-}C_4H_9)_4N]^+$ cations and two DMF molecules at general positions. The charge neutrality condition requires that each anion is doubly protonated. The BVS calculation suggested the possible protonation sites as Ob2A and Ob2B for the two independent anions. The BVS value for these atoms is 1.4, while other Ob atoms show a BVS value of 2.0. A difference Fourier synthesis showed residual electron densities assignable to the H atom attached to Ob2A and Ob2B. They were included in the structure factor calculation with their positional parameters fixed and their displacement parameters set to 1.5 times the equivalent isotropic displacement parameters of their parent O atoms. H atoms of the cations and DMF molecules were treated by riding models. Two terminal methyl groups of $[(n\text{-}C_4H_9)_4N]^+$ cations are disordered. All of the non-H atoms except for the disordered ones were refined in anisotropic modes.

An asymmetric unit of $[(n\text{-}C_4H_9)_4N]_4[IMo_6O_{23}(OMe)] \cdot 3H_2O$ contains a half of a hexamolybdoperiodate anion with the I atom at the center of symmetry and two $[(n\text{-}C_4H_9)_4N]^+$ cations at general positions. In the proximity of Ob2, a methyl group was found. The charge neutrality condition based on the cation/anion ratio does not allow the methyl group to fully occupy the site. Therefore, its occupancy was set to 50%. In its proximity, the residual electron density was observed, which was interpreted as a water molecule of crystallization that occupies the site when the methyl group is absent. There is another water molecule at a general position; thus, the total number of water molecules of crystallization per anion is three. All of the non-H atoms were refined in the anisotropic mode. H atoms of the cations were treated with riding models, while those of water molecules and the methyl group were not located.

An asymmetric unit of $[(n\text{-}C_4H_9)_4N]_3[IMo_6O_{22}(OMe)_2]$ contains a half of a $[IMo_6O_{22}(OMe)_2]^{3-}$ anion with the I atom at the center of symmetry and a $[(n\text{-}C_4H_9)_4N]^+$ cation at a general position and another $[(n\text{-}C_4H_9)_4N]^+$ cation with its N atom located 0.2 Å from a center of symmetry. The occupancy for the latter cation was set to 0.5. Two terminal methyl groups of the former cation and one of the γ-methylene groups of the latter cation are disordered. H atoms of the methyl group of the anion were fixed at the difference Fourier peak position with the isotropic displacement parameter set to 1.5 times its parent C atom. The H atoms of the cations were treated with the riding models. Atoms in the anion, nondisordered atoms in the first cation, and the central five atoms of the second cation were refined with anisotropic displacement parameters.

Crystallographic parameters are summarized in Table 1. Selected bond distances in $[(n\text{-}C_4H_9)_4N]_5[IMo_6O_{24}]$, $[(n\text{-}C_4H_9)_4N]_4[IMo_6O_{23}(OH)]$, $[(n\text{-}C_4H_9)_4N]_3[IMo_6O_{22}(OH)_2] \cdot 2DMF$, $[(n\text{-}C_4H_9)_4N]_4[IMo_6O_{23}(OMe)] \cdot 3H_2O$, and $[(n\text{-}C_4H_9)_4N]_3[IMo_6O_{22}(OMe)_2]$ are listed in Table 2. The structures of $[IMo_6O_{24}]^{5-}$ and $[IMo_6O_{22}(OMe)_2]^{3-}$ are shown in Figures 1 and 2, respectively. The structures of $[IMo_6O_{23}(OH)]^{4-}$, $[IMo_6O_{22}(OH)_2]^{3-}$, and $[IMo_6O_{23}(OMe)]^{4-}$ are shown in Figures S1−S3 of the Supporting Information.

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(52) The ^1H NMR spectrum of $[(n\text{-}C_4H_9)_4N]_3[IMo_6O_{22}(OMe)_2]$ gives two peaks assignable to the methyl groups of the anion in roughly a 2:1 ratio, although they are equivalent in the solid state. Partial hydrolysis of the $[IMo_6O_{22}(OMe)_2]^{3-}$ anion to form the monomethylated $[IMo_6O_{23}(OMe)]^{4-}$ anion is one possible explanation but has been excluded because the monomethylated anion gives a single peak with a chemical shift different from both of those peaks. The intensity ratio of those peaks does not change with the concentration of the compound or the amount of methanol in solution either. Hindered rotation of the methyl groups is another possible explanation but has also been rejected because they give two peaks in roughly a 2:1 ratio even in the ^{13}C NMR spectra. We currently have no solid explanation for this observation.

(53) Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276A*, 307.

(54) Sheldrick, G. M. *SHELX97*, *Program for the Crystal Structure Analysis*; University of Göttingen: Göttingen, Germany, 1997.

Table 1. Crystallographic Data for $[(n\text{-}C_4H_9)_4N]_5[IMo_6O_{24}]$ (**1**), $[(n\text{-}C_4H_9)_4N]_4[IMo_6O_{23}(OH)]$ (**2**), $[(n\text{-}C_4H_9)_4N]_3[IMo_6O_{22}(OH)_2]\cdot 2DMF$ (**3**), $[(n\text{-}C_4H_9)_4N]_4[IMo_6O_{23}(OMe)]\cdot 3H_2O$ (**4**), and $[(n\text{-}C_4H_9)_4N]_3[IMo_6O_{22}(OMe)_2]$ (**5**)

	1	**2**	**3**	**4**	**5**
empirical formula	$C_{80}H_{180}IMo_6N_5O_{24}$	$C_{64}H_{145}IMo_6N_4O_{24}$	$C_{54}H_{124}IMo_6N_5O_{26}$	$C_{65}H_{153}IMo_6N_4O_{27}$	$C_{50}H_{114}IMo_6N_3O_{24}$
fw	2298.83	2057.38	1962.12	2125.45	1843.98
space group	*C*2/*c*	*P*2$_1$/*c*	*P*2$_1$/*a*	*Pbca*	*P*2$_1$/*n*
a/Å	33.6101(3)	9.5587(1)	17.6105(4)	17.0679(4)	10.4009(1)
b/Å	15.2575(1)	24.1364(2)	15.5432(5)	25.6998(6)	14.6658(3)
c/Å	24.0294(2)	18.2788(2)	29.3316(9)	20.7428(4)	23.5395(4)
β/deg	126.9569(3)	90.1562(5)	91.475(3)	90	100.324(1)
V/Å^3	9846.7(1)	4217.1(1)	8026.1(4)	9098.7(3)	3532.5(1)
Z	4	2	4	4	2
T/K	123(2)	120(2)	120(2)	120(2)	83(2)
λ/Å	0.71073	0.71073	0.71073	0.71073	0.71073
ρ_{calcd}/g cm^{-3}	1.551	1.620	1.624	1.552	1.734
μ/mm^{-1}	1.123	1.300	1.364	1.210	1.541
$R\ [F_o^2 > 2\sigma(F_o^2)]^a$	0.0189	0.0346	0.0588	0.0410	0.0343
R_w [all data]^b	0.0502^c	0.0936^d	0.1842^e	0.1278^f	0.0791^g

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = (F_o^2 + 2F_c^2)/3$. [c] $a = 0.0166$, $b = 3.0844$. [d] $a = 0.0506$, $b = 0$. [e] $a = 0.0938$, $b = 0$. [f] $a = 0.0712$, $b = 4.0953$. [g] $a = 0$, $b = 12.4895$.

Table 2. Selected Distances in $[(n\text{-}C_4H_9)_4N]_5[IMo_6O_{24}]$ (**1**), $[(n\text{-}C_4H_9)_4N]_4[IMo_6O_{23}(OH)]$ (**2**), $[(n\text{-}C_4H_9)_4N]_3[IMo_6O_{22}(OH)_2]\cdot 2DMF$ (**3**), $[(n\text{-}C_4H_9)_4N]_4[IMo_6O_{23}(OMe)]\cdot 3H_2O$ (**4**), and $[(n\text{-}C_4H_9)_4N]_3[IMo_6O_{22}(OMe)_2]$ (**5**)

			3			
	1	**2**	anion A	anion B	**4**	**5**
I1−Oc1	1.8833(8)	1.8895(12)	1.891(4)	1.893(3)	1.887(2)	1.885(2)
I1−Oc2	1.8888(8)	1.8927(12)	1.901(4)	1.899(4)	1.899(2)	1.9056(19)
I1−Oc3	1.8919(8)	1.8900(12)	1.886(4)	1.882(3)	1.888(2)	1.8936(19)
Mo1−Ob1	1.9238(8)	1.9309(12)	1.957(4)	1.931(4)	1.930(2)	1.964(2)
Mo1−Ob3^a	1.9351(9)	1.9514(13)	1.935(4)	1.965(4)	1.944(2)	1.962(2)
Mo1−Oc1	2.3478(8)	2.3369(13)	2.310(4)	2.327(4)	2.340(2)	2.352(2)
Mo1−Oc3^a	2.3186(8)	2.3259(12)	2.353(4)	2.329(3)	2.331(2)	2.357(2)
Mo1−Ot1	1.7132(9)	1.7158(13)	1.697(4)	1.701(4)	1.707(3)	1.703(2)
Mo1−Ot2	1.7125(10)	1.7105(13)	1.701(4)	1.709(4)	1.713(3)	1.706(2)
Mo2−Ob1	1.9202(9)	1.9180(13)	1.872(4)	1.890(4)	1.897(3)	1.880(2)
Mo2−Ob2	1.9280(9)	1.9969(14)	2.040(4)	2.044(4)	2.002(3)	2.086(2)
Mo2−Oc1	2.3655(8)	2.2970(13)	2.375(4)	2.300(4)	2.376(2)	2.334(2)
Mo2−Oc2	2.3295(8)	2.3167(13)	2.278(4)	2.306(4)	2.300(2)	2.289(2)
Mo2−Ot3	1.7145(9)	1.7108(13)	1.701(4)	1.700(4)	1.706(3)	1.707(2)
Mo2−Ot4	1.7142(9)	1.7108(14)	1.699(4)	1.694(4)	1.702(3)	1.705(2)
Mo3−Ob2	1.9278(8)	2.0057(13)	2.040(4)	2.047(4)	2.012(2)	2.089(2)
Mo3−Ob3	1.9336(9)	1.9234(13)	1.890(4)	1.860(4)	1.893(2)	1.879(2)
Mo3−Oc2	2.3415(9)	2.3097(13)	2.295(4)	2.282(3)	2.298(2)	2.267(2)
Mo3−Oc3	2.3329(8)	2.3119(13)	2.311(4)	2.345(4)	2.350(2)	2.310(2)
Mo3−Ot5	1.7141(10)	1.7078(14)	1.702(4)	1.709(4)	1.698(3)	1.713(2)
Mo3−Ot6	1.7102(9)	1.7071(14)	1.702(4)	1.695(4)	1.708(3)	1.709(2)
Ob2−C0					1.605(9)	1.451(4)

[a] Located at the symmetry position related with the original site with the inversion center at I1.

Results and Discussion

The dimethylated Anderson-type anion $[IMo_6O_{22}(OMe)_2]^{3-}$ was first isolated as a $[(n\text{-}C_4H_9)_4N]^+$ salt soluble in polar aprotic solvents in moderate yield by reacting Na_2MoO_4, HIO_4, and $[(n\text{-}C_4H_9)_4N]Br$ in an acidic aqueous solution and dissolving the compound thus obtained in methanol.[51] Later we found out that the same compound can be synthesized in a simpler way and in much higher yield (~80%) by reacting HIO_4 with $[\alpha\text{-}Mo_8O_{26}]^{4-}$ in methanol.

$$3[\alpha\text{-}Mo_8O_{26}]^{4-} + 4HIO_4 + 8MeOH \rightarrow 4[IMo_6O_{22}(OMe)_2]^{3-} + 6H_2O$$

Hydrolysis of this anion led to formation of the diprotonated anion $[IMo_6O_{22}(OH)_2]^{3-}$.[55] The reaction is reversible. ^1H NMR spectra revealed that 90% of the diprotonated anion turned back into the dimethylated anion when 30 equiv of methanol was added to a CD_3CN solution of $[IMo_6O_{22}(OH)_2]^{3-}$.

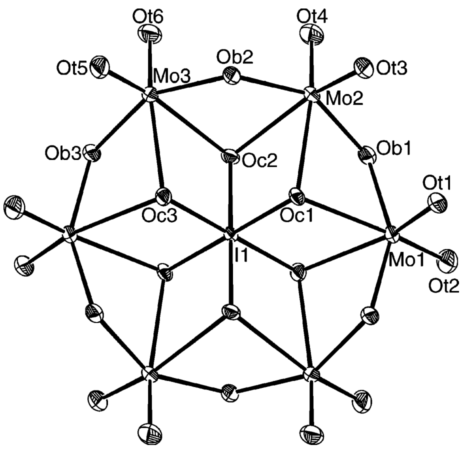

Figure 1. Structure of $[IMo_6O_{24}]^{5-}$. Displacement ellipsoids are drawn to encompass 50% probability levels.

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(55) Khenkin, A. M.; Neumann, R. *Adv. Synth. Catal.* **2002**, *344*, 1017.

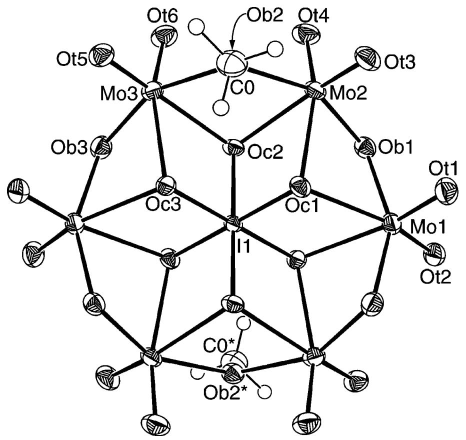

Figure 2. Structure of [IMo$_6$O$_{22}$(OMe)$_2$]$^{3-}$. Displacement ellipsoids are drawn to encompass 50% probability levels. Atoms labeled with an asterisk are related to those without an asterisk by the crystallographic inversion center at I1.

The protons of [IMo$_6$O$_{22}$(OH)$_2$]$^{3-}$ are acidic enough to be removed by a base. The reaction of [IMo$_6$O$_{22}$(OH)$_2$]$^{3-}$ with 1 equiv of [(n-C$_4$H$_9$)$_4$N]OH yielded the monoprotonated anion [IMo$_6$O$_{23}$(OH)]$^{4-}$. When [IMo$_6$O$_{23}$(OH)]$^{4-}$ was further reacted with [(n-C$_4$H$_9$)$_4$N]OH in a 1:1 ratio, the nonprotonated anion [IMo$_6$O$_{24}$]$^{5-}$ was obtained. The monoprotonated anion can also be synthesized directly from Na$_2$MoO$_4$ and HIO$_4$ by reacting them in an acidic aqueous solution and adding [(n-C$_4$H$_9$)$_4$N]Br to the solution. However, attempts to obtain the nonprotonated anion [IMo$_6$O$_{24}$]$^{5-}$ in an analogous manner failed. We ended up with [α-Mo$_8$O$_{26}$]$^{4-}$ in those attempts. Instead, we have been able to synthesize [IMo$_6$O$_{24}$]$^{5-}$ by reacting MoO$_3$ and HIO$_4$ in aqueous [(n-C$_4$H$_9$)$_4$N]OH.

$$6\mathrm{MoO_3} + \mathrm{HIO_4} + 5[(n\text{-}\mathrm{C_4H_9})_4\mathrm{N}]\mathrm{OH} \rightarrow [(n\text{-}\mathrm{C_4H_9})_4\mathrm{N}]_5[\mathrm{IMo_6O_{24}}] + 3\mathrm{H_2O}$$

The reaction of HCl with [IMo$_6$O$_{24}$]$^{5-}$ and [IMo$_6$O$_{23}$(OH)]$^{4-}$ yielded [IMo$_6$O$_{23}$(OH)]$^{4-}$ and [IMo$_6$O$_{22}$(OH)$_2$]$^{3-}$, respectively, as expected. On the other hand, attempts to further protonate the anion by reacting [IMo$_6$O$_{22}$(OH)$_2$]$^{3-}$ with HCl or CCl$_3$COOH have so far been unsuccessful.

When [IMo$_6$O$_{22}$(OH)$_2$]$^{3-}$ was reacted with methanol, the dimethylated anion [IMo$_6$O$_{22}$(OMe)$_2$]$^{3-}$ formed as mentioned above. However, no formation of methylated species was observed by ^{1}H NMR when methanol was added to a CD$_3$CN solution of the nonprotonated anion. When methanol was added to a CD$_3$CN solution of the monoprotonated anion [IMo$_6$O$_{23}$(OH)]$^{4-}$, only the formation of the monomethylated anion [IMo$_6$O$_{23}$(OMe)]$^{4-}$ was observed. The ^{1}H NMR experiments showed that all of the monoprotonated anion in solution turned into the monomethylated species when 7 equiv of methanol was added, but formation of the dimethylated anion was not observed even after this much methanol was added to the solution. When 1 equiv of HCl was added to the CD$_3$CN solution of [IMo$_6$O$_{23}$(OMe)]$^{4-}$, on the other hand, the peak for the monomethylated anion disappeared from the ^{1}H NMR spectra and a new peak assignable to [IMo$_6$O$_{22}$(OH)(OMe)]$^{3-}$ appeared at 4.28 ppm. When methanol was added to this solution, this peak at 4.28 ppm disappeared with the formation of [IMo$_6$O$_{22}$(OMe)$_2$]$^{3-}$. These results strongly suggest that [IMo$_6$O$_{24}$]$^{5-}$ should first be protonated before it reacts with methanol to form methylated Anderson-type anions. Unfortunately, attempts to isolate [IMo$_6$O$_{22}$(OH)(OMe)]$^{3-}$ have not been successful.

X-ray crystallographic experiments confirmed that all protonated and methylated anions maintain the Anderson-type metal−oxygen framework. X-ray crystallography also confirmed that the bond distances and angles of the [IMo$_6$O$_{24}$]$^{5-}$ anion in the current tetrabutylammonium salt are comparable to those observed previously for the potassium salt, although the [IMo$_6$O$_{24}$]$^{5-}$ anion in the tetrabutylammonium salt more closely approximates its maximum possible symmetry $\bar{3}m$.[48] The O atoms of an Anderson-type anion can be classified into three groups: terminal O atoms that are bonded to only one Mo atom (Ot), bridging O atoms that bridge two Mo atoms (Ob), and triply bridging O atoms that connect two Mo atoms and the central heteroatom (Oc). X-ray structural analyses revealed that only Ob atoms are methylated in both [IMo$_6$O$_{23}$(OMe)]$^{4-}$ and [IMo$_6$O$_{22}$(OMe)$_2$]$^{3-}$. The methyl groups stick out from the surface of the Anderson-type anion almost at right angles (see Figures 2 and S3 of the Supporting Information). It is worth noting that there are no terminal methoxy groups in the structures unlike in [Mo$_8$O$_{24}$(OCH$_3$)$_4$]$^{4-}$, where both terminal and bridging O atoms are methylated.[56] The Oc sites are not methylated either. Selective methylation of the doubly bridging O atom was also observed in the direct methylation of [PMo$_{12}$O$_{40}$]$^{3-}$ by trimethyloxonium.[57]

The X-ray structural study also revealed that the protons in [IMo$_6$O$_{22}$(OH)$_2$]$^{3-}$ are attached to Ob2 O atoms. Protonation at these O atoms is consistent with anomalously long Mo−Ob2 bonds (Table 2). There exist two DMF molecules in close proximity to each [IMo$_6$O$_{22}$(OH)$_2$]$^{3-}$ anion in the crystal. The distance between the O atom of the DMF molecule and Ob2A is 2.550(6) Å. That between Ob2B and the O atom of the DMF molecule is 2.569(6) Å. These short distances are indicative of hydrogen bonding. Although the acidic proton of [IMo$_6$O$_{23}$(OH)]$^{4-}$ was not located by X-ray diffraction, its location can be reasonably inferred from a comparison of bond lengths in the nonprotonated and protonated anions and BVS calculations.[46,47] The bonds to Ob2 are unusually long in the [IMo$_6$O$_{23}$(OH)]$^{4-}$ anion (see Table 2), and the apparent valence of this O atom is anomalously small (1.6). This identifies the Ob2 atom as the protonation site also for [IMo$_6$O$_{23}$(OH)]$^{4-}$.

Both [IMo$_6$O$_{22}$(OH)$_2$]$^{3-}$ and [IMo$_6$O$_{22}$(OMe)$_2$]$^{3-}$ anions closely conform to their maximum possible symmetry $2/m$. The [IMo$_6$O$_{23}$(OH)]$^{4-}$ and [IMo$_6$O$_{23}$(OMe)]$^{4-}$ anions have also come up with an apparent $2/m$ symmetry because of the disorder. To discern systematic variations in the Mo−O and I−O bond lengths that are attributable to [IMo$_6$O$_{24}$]$^{5-}$ protonation and methylation, the $\bar{3}m$ averaged bond lengths of [IMo$_6$O$_{24}$]$^{5-}$ are subtracted from the corresponding $2/m$ averaged bond lengths of protonated and methylated anions (Chart 1).

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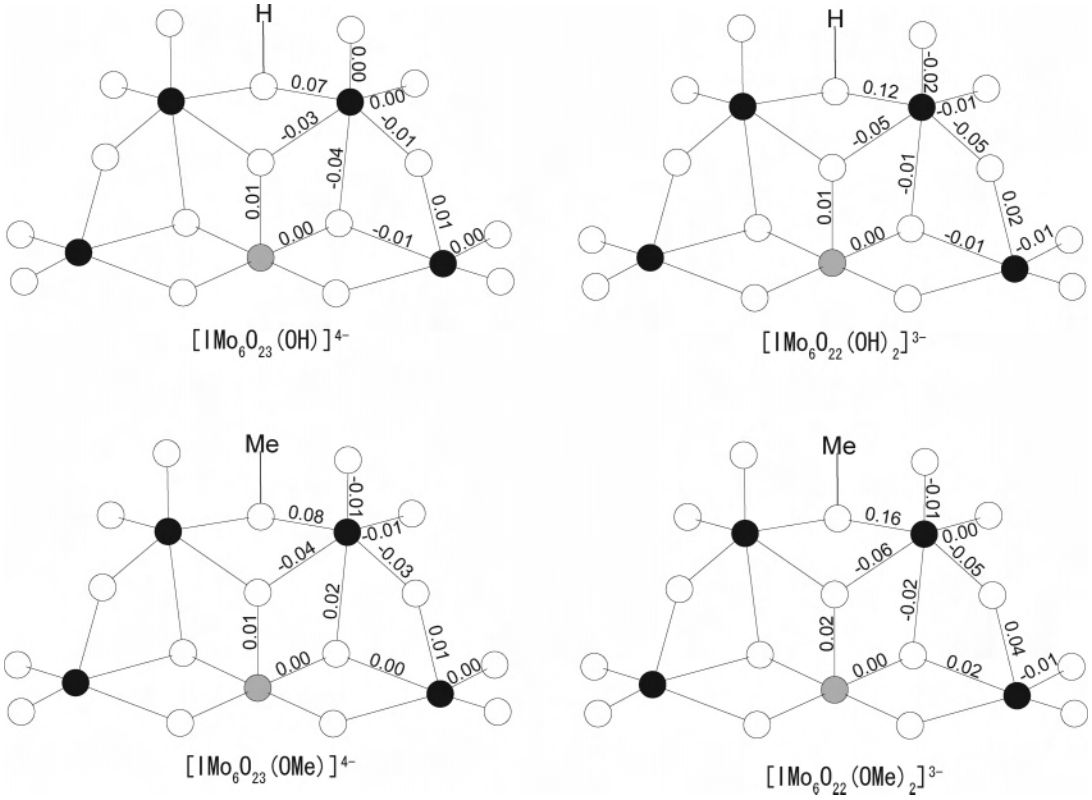
(56) McCarron, E. M.; Harlow, R. L. *J. Am. Chem. Soc.* **1983**, *105*, 6179.
(57) Knoth, W. H.; Harlow, R. L. *J. Am. Chem. Soc.* **1981**, *103*, 4265.

Chart 1



$[IMo_6O_{23}(OH)]^{4-}$ $[IMo_6O_{22}(OH)_2]^{3-}$

$[IMo_6O_{23}(OMe)]^{4-}$ $[IMo_6O_{22}(OMe)_2]^{3-}$

In the cases for $[CpTiW_5O_{18}]^{3-}$ and $[Cp^*TiMo_5O_{18}]^{3-}$, protonation clearly induced a pattern of trans bond length alternation throughout their structures.[11,58] However, such a nonlocal trans influence of protonation is not observed unambiguously in the current anions. Instead, a cis influence is observed for $[IMo_6O_{23}(OH)]^{4-}$. The Mo−Ob2 bonds are elongated by protonation as mentioned above. Four Mo−Oc bonds that are cis to the elongated bonds are significantly shortened. The cis influence is also observed in $[IMo_6O_{22}(OH)_2]^{3-}$. Here the bonds that connect the Mo atoms and the Oc2 atom that faces the protonated Ob2 are shortened by as much as 0.05 Å on average. However, the changes of the other Mo−Oc bonds are not very significant. Protonation has little effect on the I−Oc bonds. The lengths of the I−Oc bonds in both $[IMo_6O_{23}(OH)]^{4-}$ and $[IMo_6O_{22}(OH)_2]^{3-}$ are virtually the same as those in the unprotonated anion.

Methylation has a more pronounced effect on the Anderson framework. In $[IMo_6O_{22}(OMe)_2]^{3-}$, the Mo−Ob2 bonds are lengthened by as much as 0.16 Å. Here the trans bond length alternation pattern is clearly visible up to Mo1, where competing effects of two different methyl groups crash. The trans influence is less pronounced in the monomethylated $[IMo_6O_{23}(OMe)]^{4-}$ anion, where the trans bond length alternation is not observable beyond Ob1 and Ob3. The cis influence of methylation is visible for both monomethylated and dimethylated anions. The Mo−O bonds to Oc2 that faces the methylated O atom are significantly shortened in both cases.

The current study has established that Ob atoms are the most basic O atoms in the $[IMo_6O_{24}]^{5-}$ anion, contrary to the previous assumption. Because the reaction conditions employed to protonate $[IMo_6O_{24}]^{5-}$ are less demanding than those used to protonate $[Nb_2W_4O_{19}]^{4-}$,[13] $[CpTiW_5O_{18}]^{3-}$,[54] and $[Cp^*TiW_5O_{18}]^{3-}$,[11] the Anderson-type $[IMo_6O_{24}]^{5-}$ anion should at least be as basic as those polyoxometalates. This, in turn, suggests that it would be feasible to prepare organometallic adducts where organometallic cations are supported on the Anderson-type anion.

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Supporting Information Available: Crystallographic data for $[(n\text{-}C_4H_9)_4N]_5[IMo_6O_{24}]$, $[(n\text{-}C_4H_9)_4N]_4[IMo_6O_{23}(OH)]$, $[(n\text{-}C_4H_9)_4N]_3[IMo_6O_{22}(OH)_2]\cdot 2DMF$, $[(n\text{-}C_4H_9)_4N]_4[IMo_6O_{23}(OMe)]\cdot 3H_2O$, and $[(n\text{-}C_4H_9)_4N]_3[IMo_6O_{22}(OMe)_2]$ and perspective drawings of the $[IMo_6O_{23}(OH)]^{4-}$ (Figure S1), $[IMo_6O_{22}(OH)_2]^{3-}$ (Figure S2), and $[IMo_6O_{23}(OMe)]^{4-}$ (Figure S3) anions. This material is available free of charge via the Internet at http://pubs.acs.org.

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