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Polyoxometalate-Supported Transition Metal Complexes and Their Charge Complementarity: Synthesis and Characterization of $[M(OH)_6Mo_6O_{18}\{Cu(Phen)(H_2O)_2\}_2][M(OH)_6Mo_6O_{18}\{Cu(Phen)(H_2O)Cl\}_2]\cdot 5H_2O$ (M = Al^{3+}, Cr^{3+})

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Two Anderson-type heteropolyanion-supported copper phenanthroline complexes, $[Al(OH)_6Mo_6O_{18}\{Cu(phen)(H_2O)_2\}_2]^{1+}$ (**1c**) and $[Al(OH)_6Mo_6O_{18}\{Cu(phen)(H_2O)Cl\}_2]^{1-}$ (**1a**) complement their charges in one of the title compounds $[Al(OH)_6Mo_6O_{18}\{Cu(phen)(H_2O)_2\}_2][Al(OH)_6Mo_6O_{18}\{Cu(phen)(H_2O)Cl\}_2]\cdot 5H_2O \equiv$ [**1c**][**1a**]·5 H_2O $\equiv$ **1**. Similar charge complementarity exists in the chromium analogue, $[Cr(OH)_6Mo_6O_{18}\{Cu(phen)(H_2O)_2\}_2][Cr(OH)_6Mo_6O_{18}\{Cu(phen)(H_2O)Cl\}_2]\cdot 5\ H_2O \equiv$ [**2c**][**2a**]·5 H_2O $\equiv$ **2**. The chloride coordination to copper centers of **1a** and **2a** makes the charge difference. In both compounds, the geometries around copper centers are distorted square pyramidal and those around aluminum/chromium centers are distorted octahedral. Three lattice waters, from the formation of intermolecular O–H·····O hydrogen bonds, have been shown to self-assemble into an "acyclic water trimer" in the crystals of both **1** and **2**. The title compounds have been synthesized in a simple one pot aqueous wet-synthesis consisting of aluminum/chromium chloride, sodium molybdate, copper nitrate, phenanthroline, and hydrochloric acid, and characterized by elemental analyses, EDAX, IR, diffuse reflectance, EPR, TGA, and single-crystal X-ray diffraction. Both compounds crystallize in the triclinic space group $P\bar{1}$. Crystal data for **1**: $a = 10.7618(6)$, $b = 15.0238(8)$, $c = 15.6648(8)$ Å, $\alpha = 65.4570(10)$, $\beta = 83.4420(10)$, $\gamma = 71.3230(10)°$, $V = 2182.1(2)$ Å^3. Crystal data for **2**: $a = 10.8867(5)$, $b = 15.2504(7)$, $c = 15.7022(7)$ Å, $\alpha = 64.9850(10)$, $\beta = 83.0430(10)$, $\gamma = 71.1570(10)°$, $V = 2235.47(18)$ Å^3. In the electronic reflectance spectra, compounds **1** and **2** exhibit a broad d–d band at ~700 nm, which is a considerable shift with respect to the value of 650–660 nm for a square-pyramidal $[Cu(phen)_2L]$ complex, indicating the coordination of $[M(OH)_6Mo_6O_{18}]^{3-}$ POM anions (as a ligand) to the monophenanthroline copper complexes to form POM-supported copper complexes **1c**, **1a**, **2c**, and **2a**. The ESR spectrum of compound **1** shows a typical axial signal for a Cu^{2+} (d^9) system, and that of compound **2**, containing both chromium(III) and copper(II) ions, may reveal a zero-field-splitting of the central Cr^{3+} ion of the Anderson anion, $[Cr(OH)_6Mo_6O_{18}]^{3-}$, with an intense peak for the Cu^{2+} ion.

Introduction

Polyoxometalates have become a subject of general interest because of their potential applications in fields as diverse as catalysis, biochemical analysis, medicinal chemistry, and materials science.[1] An important advance in polyoxometalate (POM) chemistry is the polyoxoanion-supported transition metal complexes.[2] Such metal oxide-based inorganic complexes not only provide new and exciting functional materials with an interesting optical, electronic, and magnetic properties but also serve as structural models for understanding the functions of oxide-supported catalysts.[3] Keggin-type anions have mostly been used to support inorganic complexes because the charge density of the Keggin-surface oxygen

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atoms can be increased either by reducing some of their metal centers (e.g., Mo^{VI} to Mo^{V}) or replacing higher-valent metal centers with lower-valent metal centers (e.g., replace Mo^{VI} with V^{IV}).[4] Examples of structurally characterized discrete POM-supported transition metal complexes include $[Cu^{I}(phen)_2]_4[PMo^{VI}_8V^{IV}_6O_{42}\{Cu^{I}(phen)_2\}]\cdot H_5O_2$,[5] $[Ni(phen)_3][PMo^{VI}_9Mo^{V}_3O_{40}\{Ni(phen)\}_2]$,[5] $[Ni(2,2'\text{-bipy})_3]_{1.5}[PW^{VI}_{10}W^{V}_2O_{40}\ Ni(2,2'\text{-bipy})_2(H_2O)]\cdot 0.5H_2O$,[6] $[Co(1,10'\text{-phen})_3]_{1.5}[PMo^{VI}_{10}Mo^{V}_2O_{40}Co(1,10'\text{-phen})_2\ (H_2O)]\cdot 0.5H_2O$,[6] $[\{Ni(phen)_2\}_2(Mo_8O_{26})]$,[7] $[\{Co(phen)_2\}_2(Mo_8O_{26})]$,[7] $[Cu(phen)_2]_2[\{Cu(phen)\}_2Mo_8O_{26}]\cdot H_2O$,[8] etc. Some typical examples that have extended structures are 1D $[Ni(2,2'\text{-bpy})_2Mo_4O_{13}]$[9] and $[Cu(enMe)_2]_3[V_{15}O_{36}Cl]\cdot 2.5H_2O$,[10] 2D $[M_2(H_2N(CH_2)_2NH_2)_5][\{M(H_2N(CH_2)_2NH_2)_2\}_2V_{18}O_{42}(X)]\cdot 9H_2O$ (M = Zn, Cd; X = H_2O, Cl^-, Br^-)[11] and $[\{Cu_3\{4,7\text{-phen}\}_3\}_2Mo_{14}O_{45}]$,[12] and 3D $[\{Cu(1,2\text{-pn})_2\}_7\{V_{16}O_{38}(H_2O)\}_2]\cdot 4H_2O$,[13] $Ni(en)_3[\{Ni(en)_2\}_3V_{16}O_{38}(Cl)]\cdot 8.5H_2O$[14] and $[\{Cu(4,4'\text{-bpy})\}_4(Mo_8O_{26})]$.[15] In all of these (including discrete and extended structure-containing) compounds, the charge of the POM-linked inorganic entity is either neutral or negative; the negative charge, in most cases, is balanced by transition metal complex cations. There are few examples of POM-supported metal ions/metal complexes that act as cations; the anions, which counter balance these positive charges, are halide, acetate, hydroxyl, and POM anions. Such structurally characterized compounds are $[\epsilon\text{-}PMo_{12}O_{36}(OH)_4\{La(H_2O)_4\}_4]Br_5\cdot 16H_2O$,[16] $[Mn^{II}V^{IV}_6O_6\{(OCH_2CH_2)_2N(CH_2CH_2OH)\}_6]Cl_2$,[17] $[Ag_6(PMo_{10}V_2O_{40})](CH_3COO)\cdot 8H_2O$,[18] $[(V^{V}O_4)Mo^{VI}O_{12}O_{36}(V^{IV}O)_6][(OH)_9]\cdot 16H_2O$,[19] $K_3[\epsilon\text{-}PMo_{12}O_{36}(OH)_4\{La(H_2O)_{4.25}Cl_{0.75}\}_4][\alpha\text{-}PMo_{12}O_{40}]\cdot 28H_2O$,[16] and $[NH_4]_2[\{Gd(DMF)_7\}_2(\beta\text{-}Mo_8O_{26})][\beta\text{-}Mo_8O_{26}]$.[20] Even though, as described above, the number of POM-supported transition metal compounds is not any more limited, cases that contain POM-supported transition metal complexes both as cation and anion (as ion-pair components) are still very scarce in the literature. To our knowledge, there are only two such ion-pair compounds, reported recently: $\{[Ni(phen)_2(H_2O)]_2[Ni(phen)_2][V^{IV}_8Mo^{VI}_6Mo^{V}_2O_{40}(PO_4)]\}\{[Ni(phen)_2(H_2O)]_2[V^{IV}_8Mo^{VI}_6Mo^{V}_2O_{40}(PO_4)_2]\}\cdot 5H_2O\cdot 2EtOH$[21] and $[PMo^{VI}_6Mo^{V}_2V^{IV}_8O_{44}\{Co(2,2'\text{-bpy})_2(H_2O)\}_4][PMo^{IV}_4Mo^{V}_4V^{IV}_8O_{44}\{Co(2,2'\text{-bpy})_2(H_2O)\}_2]\cdot 4H_2O$.[5] In the former compound, the charge difference (of one) between the two ion pairs became possible because of the different numbers of phosphate anions present in the cation and anion. In the latter compound, the difference in the oxidation states of molybdenum in cation and anion makes the charge difference. In both compounds, a Keggin-type POM anion has been used to support the transition metal complexes. We report here a unique example, in which a "discrete" Anderson-type heteropolyanion-supported copper phenanthroline complex, by varying its coordination mode from "water" to "chloride", can act both as cation and anion in the same compound. Compounds **1** and **2** exhibit such charge complementarity: $[Al(OH)_6Mo_6O_{18}\{Cu(phen)(H_2O)_2\}_2][Al(OH)_6Mo_6O_{18}\{Cu(phen)(H_2O)Cl\}_2]\cdot 5\ H_2O$ ≡ [**1c**][**1a**]$\cdot 5\ H_2O$ ≡ **1**. $[Cr(OH)_6Mo_6O_{18}\{Cu(phen)(H_2O)_2\}_2][Cr(OH)_6Mo_6O_{18}\{Cu(phen)(H_2O)Cl\}_2]\cdot 5H_2O$ ≡ [**2c**][**2a**]$\cdot 5H_2O$ ≡ **2**.

No previous structural examples of transition metal complexes coordinated to "discrete" Anderson-type anions have been reported. We and others have reported the extended structures of Anderson-type heteropolyanions, linked to metal complexes including transition metals and lanthanides.[22] Another important feature of the present work is the identification of a small water cluster $(H_2O)_3$ in the crystal lattice of compounds **1** and **2**. Small water clusters have been a subject of both theoretical and experimental research as they can provide insight into the structure and characteristics of bulk water and ice.[23] In particular, the water trimer has received considerable attention with both theoretical and experimental evidence establishing a six-membered cyclic minimum energy structure.[24] In this context, we have described an acyclic water trimer, that is stabilized via

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Table 1. Crystal Data and Structural Refinement for **1** and **2**

	1	**2**
empirical formula	$C_{48}H_{66}Al_2Cl_2Cu_4Mo_{12}N_8O_{59}$	$C_{48}H_{66}Cr_2Cl_2Cu_4Mo_{12}N_8O_{59}$
fw	3229.39	3279.43
temp (K)	298(2)	298(2)
wavelength (Å)	0.71073	0.71073
cryst syst, space group	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$
unit cell dimensions		
a (Å)	10.7618(6)	10.8867(5)
b (Å)	15.0238(8)	15.2504(7)
c (Å)	15.6648(8)	15.7022(7)
α (deg)	65.4570(10)	64.9850(10)
β (deg)	83.4420(10)	83.0430(10)
γ (deg)	71.3230(10)	71.1570(10)
vol ($Å^3$)	2182.1(2)	2235.47(18)
Z, $density_{calcd}$ ($mg\ m^{-3}$)	1, 2.458	1, 2.436
abs coeff (mm^{-1})	2.805	2.948
F(000)	1562	1584
crystal size (mm^3)	0.154 × 0.35 × 0.194	0.2 × 0.12 × 0.2
θ range for data collection (deg)	1.43−28.28	1.43−28.30
reflns collected/unique	25459/10206	25837/10342
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/parameters	10206/0/686	10342/0/634
GOF on F^2	1.064	1.021
final R indices [$I > 2\sigma(I)$]	R1 = 0.0288	R1 = 0.0287
	wR2 = 0.0783	wR2 = 0.0736
R indices (all data)	R1 = 0.0298	R1 =0.0320
	wR2 = 0.0791	wR2 = 0.0758
largest diff. peak, hole (e $Å^{-3}$)	1.091, −1.138	0.877, −0.610

noncovalent supramolecular interactions with POM-supported copper(II) phenanthroline complexes in the crystals of compounds **1** and **2**.

Experimental Section

General Consideration. All chemical were purchased from commercial sources and used without further purification. Compounds **1** and **2** were synthesized from aqueous solutions and characterized by elemental analyses, IR, UV−vis, ESR, TGA, and powdered XRD and unambiguously by single-crystal X-ray analysis. Microanalytical (C, H, N) data were obtained with a FLASH EA 1112 Series CHNS Analyzer. EDAX analyses were performed using Philips XL 30 SEM equipment. The IR spectra (with KBr pellet) were recorded in the range of 400−4000 cm^{-1} on a JASCO FT/IT-5300 spectrometer. UV−vis spectra were recorded using a 3101 PC/UV/VIS-NIR Philips spectrometer equipped with a diffuse reflectance accessory. The solid powders of **1** and **2** were spread over grease on a glass plate, and the diffuse reflectance spectra obtained were then Kubelka−Munk corrected for the grease (on glass plate) background. The ESR spectra were recorded on a (JEOL) JES FA200 spectrometer at liquid nitrogen temperature. The powdered X-ray diffraction data were collected on a Philips PW 3710 diffractometer. The TGA analysis of compound **1** was performed on a Shimadzu DTG-50 analyzer under an argon atmosphere at a heating rate of 3 °C min^{-1}.

Synthesis of $[Al(OH)_6Mo_6O_{18}\{Cu(phen)(H_2O)_2\}_2][Al(OH)_6Mo_6O_{18}\{Cu(phen)(H_2O)Cl\}_2]\cdot 5H_2O$ (1). One gram of hydrous aluminum chloride, $AlCl_3\cdot 6H_2O$ (4.14 mmol), was dissolved in 50 mL of distilled water to which a 100 mL aqueous solution containing 1.5 g of sodium molybdate, $Na_2MoO_4\cdot 2H_2O$ (6.20 mmol), and 10 mL of glacial acetic acid were added with stirring at room temperature. 1,10′-Phenanthroline, $C_{12}H_8N_2\cdot H_2O$ (0.2 g, 1 mmol), dissolved in a mixture of 50 mL of water and 50 mL of methanol, was added to the resulting reaction mixture, followed by the addition of 0.7 g of $Cu(NO_3)_2\cdot 3H_2O$ (2.9 mmol). The pH of this solution was adjusted to 2.6 with concentrated HCl, stirred for 10 min and filtered to a 250 mL conical flask, which was kept open for one week at room temperature. Blue block-shaped crystals of **1**, precipitated during this time, were filtered, washed with water, and dried at room temperature. Yield: 0.79 g (47% based on Mo). Anal. Calcd for $C_{48}H_{66}Al_2Cl_2Cu_4Mo_{12}N_8O_{59}$: C, 17.85; H, 2.06; N, 3.47; Cl, 2.19. Found: C, 16.95; H, 2.11; N, 3.45; Cl, 2.28%. IR (KBr, cm^{-1}): 3325br, 1626m, 1582m, 1518m, 1493w, 1425m, 1344w, 1222w, 1145m, 1107m, 940s, 900s, 775m, 648s-br, 440w.

Synthesis of $[Cr(OH)_6Mo_6O_{18}\{Cu(phen)(H_2O)_2\}_2][Cr(OH)_6Mo_6O_{18}\{Cu(phen)(H_2O)Cl\}_2]\cdot 5H_2O$ (2). One gram of chromic chloride, $CrCl_3\cdot 6H_2O$ (3.75 mmol), was dissolved in 50 mL of water, to which 100 mL of an aqueous solution containing 3.5 g of $Na_2MoO_4\cdot 2H_2O$ (14.46 mmol) and 10 mL of glacial acetic acid were added. 1,10′-Phenanthroline (0.2 g, 1 mmol) was dissolved in a mixture containing 50 mL of water and 50 mL of methanol, to which 0.7 g of $Cu(NO_3)_2\cdot 3H_2O$ (2.9 mmol) was subsequently added. This reaction mixture was added to the first reaction mixture. The pH of the resulting reaction mixture was then adjusted to 2.6 with concentrated HCl, and it was boiled until its temperature reached 90 °C. It was then filtered into a 250 mL conical flask, and the filtrate was kept closed at room temperature. The blue blocks of **2** were obtained within one week. Yield: 0.62 g (16% based on Mo). Anal. Calcd for $C_{48}H_{66}Cr_2Cl_2Cu_4Mo_{12}N_8O_{59}$: C, 17.58; H, 2.03; N, 3.42; Cl, 2.16. Found: C, 17.37; H, 2.11; N, 3.39; Cl, 2.31. IR (KBr, cm^{-1}): 3328br, 1626m, 1577m, 1518m, 1492w, 1425m, 1344w, 1221w, 1145m, 1105m, 937s, 893s, 775m, 640s-br, 439w.

Synthesis of $[Cu(phen)_2(H_2O)](NO_3)_2$. $[Cu(phen)_2(H_2O)](NO_3)_2$ was synthesized by a published method.[25] 1,10-Phenanthroline (3.96 g, 20 mmol) was dissolved in 30 mL of methanol, and this mixture was added to 30 mL of an aqueous solution containing 2.41 g of

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$Cu(NO_3)_2 \cdot 3H_2O$ (10 mmol). The green crystals appeared within a day and were filtered, washed with water, and recrystallized from a water−methanol mixture. This compound was characterized by IR, UV−vis spectroscopy, and CHN analysis. These results are consistent with the reported data.[25] Anal. Calcd: C, 50.93; H, 3.20; N, 14.84. Found: C, 50.85, H, 3.35, N, 14.16. IR (KBr, cm^{-1}): 3211br, 1608m, 1585m, 1521s, 1429w, 1386s, 1311br, 1105m, 1039m, 852s, 788m, 721s, 648w, and 434m.

X-ray Analyses. Crystallography. Data were measured at 298(2) K on a Bruker SMART APEX CCD area detector system [λ(Mo Kα) = 0.71073 Å], graphite monochromator, 2400 frames were recorded with an ω scan width of 0.3°, each for 8 s, a crystal−detector distance of 60 mm, and a collimator of 0.5 mm. The data were reduced using SAINTPLUS,[26] the structure was solved using SHELXS-97,[27] and it was refined using SHELXL-97.[28] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms on the phenanthroline rings were introduced on calculated positions and included in the refinement riding on their respective parent atoms. The hydrogen atoms of some of the solvent water molecules were located in the differential Fourier maps, and their positions were refined using isotropic thermal parameters. For compound **2**, the hydrogen atoms are not located in its crystal structure analysis. A summary of the crystallographic data and structural determination for **1** and **2** is provided in Table 1. Selected bond lengths and angles for the compounds **1** and **2** are provided in the Supporting Information.

Results and Discussion

Synthesis. The majority of POM-supported transition metal complexes, reported earlier, have been synthesized hydrothermally.[5,17,19,21] We have isolated compounds $[Al(OH)_6Mo_6O_{18}\{Cu(phen)(H_2O)_2\}_2][Al(OH)_6Mo_6O_{18}\{Cu(phen)(H_2O)Cl\}_2] \cdot 5H_2O$ (**1**) and $[Cr(OH)_6Mo_6O_{18}\{Cu(phen)(H_2O)_2\}_2][Cr(OH)_6Mo_6O_{18}\{Cu(phen)(H_2O)Cl\}_2] \cdot 5\ H_2O$ (**2**) using a simple wet synthesis. The synthesis is performed in a mixed aqueous−organic medium. We propose the following synthesis scheme (eqs 1−5) for the formation of compounds **1** and **2** (see Experimental Section) ($C_{12}H_8N_2$ = 1,10′-phenanthroline = phen).

$$6[MoO_4]^{2-} + M^{3+}\ (M = Al, Cr) + 6H^+ \rightarrow [M(OH)_6Mo_6O_{18}]^{3-} \quad (1)$$

$$Cu^{2+} + phen + H_2O/\text{organic solvent} \rightarrow [Cu(phen)(H_2O)_n(\text{organic solvent})_{4-n}]^{2+} \quad (2)$$

$$2[Cu(phen)(H_2O)_n(\text{organic solvent})_{4-n}]^{2+} + [M(OH)_6Mo_6O_{18}]^{3-} \rightarrow [M(OH)_6Mo_6O_{18}\{Cu(phen)(H_2O)_2\}_2]^{1+}\ (\mathbf{1c}/\mathbf{2c}) + 2nH_2O/\text{organic solvent} \quad (3)$$

$$2[Cu(phen)(H_2O)_n(\text{organic solvent})_{4-n}]^{2+} + [M(OH)_6Mo_6O_{18}]^{3-} + 2Cl^- \rightarrow [M(OH)_6Mo_6O_{18}\{Cu(phen)(H_2O)Cl\}_2]^{1-}\ (\mathbf{1a}/\mathbf{2a}) + 3nH_2O/\text{organic solvent} \quad (4)$$

$$[M(OH)_6Mo_6O_{18}\{Cu(phen)(H_2O)_2\}_2]^{1+} + [M(OH)_6Mo_6O_{18}\{Cu(phen)(H_2O)Cl\}_2]^{1-} + 5H_2O \rightarrow [M(OH)_6Mo_6O_{18}\{Cu(phen)(H_2O)_2\}_2][M(OH)_6Mo_6O_{18}\{Cu(phen)(H_2O)Cl\}_2] \cdot 5H_2O \quad (5)$$

On the basis of our own experience[22b−d] and that of others in the synthesis of Anderson-type POM compounds,[29] we used MCl_3 (M = Al^{3+} and Cr^{3+}) in aqueous sodium molybdate solution to generate in situ Anderson-type heteropolyanion $[M(OH)_6Mo_6O_{18}]^{3-}$ (eq 1). The isolated compounds (**1** and **2**) contain monophenanthroline copper complexes, and thereby, the formation of a solvated monophenanthroline copper complex is proposed (eq 2). The reaction of the Anderson heteropolyanion with 2 equiv of solvated monophenanthroline copper complex produces the cationic components **1c** and **2c** (eq 3), and the reaction of the Anderson anion with the solvated monophenanthroline copper complex and chloride anion in a 1:2:2 ratio results in the formation of the anionic components **1a** and **2a** (eq 4) of the ion-pair complexes **1** and **2**, respectively. In the final (ion-pairing) step (eq 5), each of the ion-pair compounds, **1** and **2**, crystallizes with five water molecules.

Crystals of both compounds **1** and **2** gave satisfactory elemental analyses. The number of Al, Cu, and Cl sites revealed by single-crystal X-ray structure analysis is consistent with the result of the EDAX analysis, which gave an average value of Al/Cu/Cl ≈ 1:2:1 for compound **1**. Similarly, EDAX analysis gave the ratio of Cr/Cu/Cl as ∼1:2:1 for compound **2**.

Description of the Crystal Structures. The crystal structure of **1** shows the abundance of a polyoxometalate-supported copper(II)-bis(aqua)-phenanthroline complex, $[Al(OH)_6Mo_6O_{18}\{Cu(phen)(H_2O)_2\}_2]^{1+}$, **1c**, as a cation and the same polyoxometalate-supported copper(II)-aqua-chloro-phenanthroline complex, $[Al(OH)_6Mo_6O_{18}\{Cu(phen)(H_2O)Cl\}_2]^{1-}$, **1a**, as an anion as shown in Figure 1. The cation **1c** is formed by an Anderson-type anion $[Al(OH)_6Mo_6O_{18}]^{3-}$ coordinated to two $[Cu(phen)(H_2O)_2]^{2+}$ complexes through the terminal oxygen atoms of two nonadjacent MoO_6 octahedra. Similarly, the coordination of $[Al(OH)_6Mo_6O_{18}]^{3-}$ to two $[Cu(phen)(H_2O)Cl]^{1+}$ results in the formation of the **1a** anion. As the structures of other Anderson anions,[29] the present cluster anion $[Al(OH)_6Mo_6O_{18}]^{3-}$ has a B-type Anderson structure consisting of seven edge-shared octahedra, six of which are Mo octahedra arranged hexagonally around the central Al^{3+} octahedron (Figure 1). The hydrogen atoms of the hydroxyl groups around the Al^{3+} ions are located from difference Fourier maps, and their positions were refined. The molybdenum−oxygen distances in **1c** and **1a** can be grouped into four sets: molybdenum−terminal oxygen ($Mo-O_t$), 1.68−1.73 Å; molybdenum−oxygen linked to copper ($Mo-O_t$), 1.70−1.72 Å; molybdenum−bridging oxygen ($Mo-O_b$), 1.89−1.97 Å; and molybdenum−

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(26) *SAINT: Software for the CCD Detector System*; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1998.

(27) Sheldrick, G. M. *SHELXS-97, Program for Structure Solution*; University of Göttingen: Göttingen, Germany, 1997.

(28) Sheldrick, G. M. *SHELXL-97, Program for Crystal Structure Analysis*; University of Göttingen: Göttingen, Germany, 1997.

(29) Kondo, H.; Kobayashi, A.; Sasaki, Y. *Acta Crystallogr*. **1980**, *B36*, 661. (b) Lee, U.; Ichida, H.; Kobayashi, A.; Sasaki, Y. *Acta Crystallogr*. **1980**, *C40*, 5. (c) Schmidt, K. J.; Schrobilgen, G. J. *Acta Crystallogr*. **1986**, *C42*, 1115. (d) Nomiya, K.; Takahashi, T.; Shirai, T.; Miwa, M. *Polyhedron* **1987**, *6*, 213. (e) Lee, H. Y.; Park, K. M.; Lee, U. *Acta Crystallogr*. **1980**, *C47*, 1959. (f) Lee, U. *Acta Crystallogr*. **1994**, *C50*, 1657.

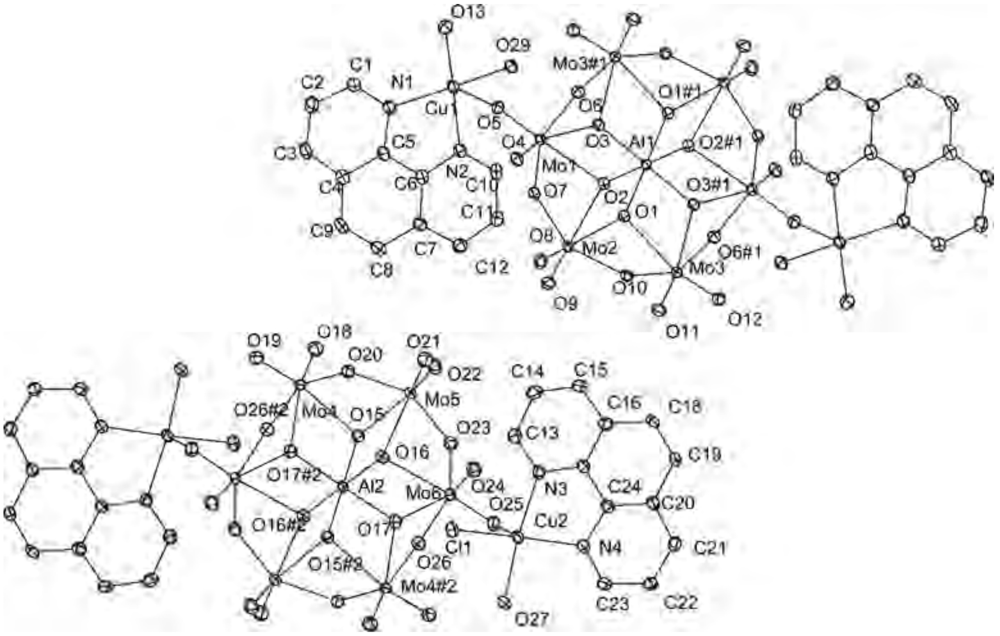

Figure 1. Thermal ellipsoidal plot of $[Al(OH)_6Mo_6O_{18}\{Cu(phen)(H_2O)_2\}_2][Al(OH)_6Mo_6O_{18}\{Cu(phen)(H_2O)Cl\}_2] \equiv$ [**1c**][**1a**] in **1**: (top) cation **1c** and (bottom) anion **1a**. The atoms with additional labels #1 and #2 are related to each other by the following symmetry operations: #1 $-x + 2, -y + 1, -z$; #2 $-x + 3, -y - 1, -z + 1$.

internal oxygen common to two molybdenum atoms and the aluminum atom ($Mo-O_c$), 2.26−2.36 Å. In both cation **1c** and anion **1a**, the Anderson anions act as bidentate ligands, each coordinating two copper phenanthroline complexes. In **1c**, the copper is coordinated by two nitrogen atoms from phenanthroline ligand (Cu(1)−N(1) = 1.991(3) Å, Cu(1)−N(2) = 2.003(3) Å), two water molecules (Cu(1)−O(13) = 2.000(2) Å, Cu(1)−O(29) = 1.975(2) Å), and a terminal oxygen atom from the Anderson anion (Cu(1)−O(5) = 2.2490(19) Å) to complete a roughly square-pyramidal geometry around copper. Similarly, in the case of anion **1a**, the copper square pyramid is defined by two nitrogen coordination from the phenanthroline ligand (Cu(2)−N(3) = 2.001(3) Å, Cu(2)−N(4) = 2.002(2) Å), one water ligation (Cu(2)−O(27) = 1.983(2) Å), one chloride coordination (Cu(2) −Cl(1) = 2.2636(8) Å), and one terminal oxygen atom from the Anderson anion (Cu(2)−O(25) = 2.253(2) Å) (see Figure 1). In both cases, the terminal oxygen atom (from the Anderson anion) occupies the apical position. In **1c** and **1a**, the copper ions are well separated, with a Cu(1)⋯Cu(1) separation of 12.51 Å in **1c** and a Cu(2)⋯Cu(2) separation of 11.28 Å in **1a**. A relatively shorter distance (8.09 Å) between Cu(1) (of **1c**) and Cu(2) (of **1a**) manifests the intermolecular interactions as shown in Figure 2. Indeed, Cu(1) (of **1c**) and Cu(2) (of **1a**) interact via hydrogen bonding interactions involving lattice waters (that include a supramolecular water trimer) and copper-coordinated water molecules (vide infra).

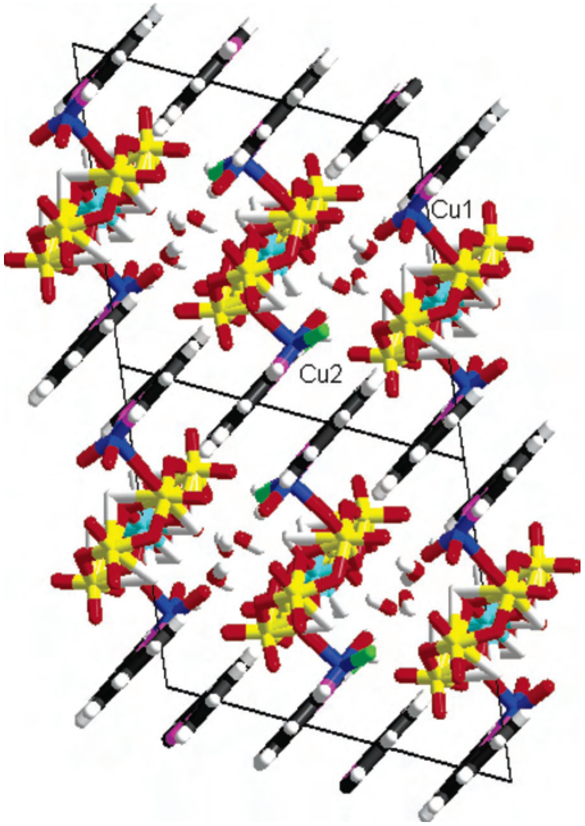

Figure 2. Packing diagram (wire-frame representation) of **1** (4 × 4 cells). Cu(1) is from **1c** and Cu(2) from **1a**. Color code: Al, cyan; Mo, yellow; O, red; Cu, blue; N, purple; Cl, green; C, dark gray; H, white.

Single crystal X-ray diffraction analyses revealed that compounds **1** and **2** are isostructural and thereby the unit cell dimensions, volumes, other related data for structure determinations vary only slightly (Table 1). Notable differences are observed in $M-O_c$ ($M = Al^{3+}$ and Cr^{3+}, $O_c = OH^{1-}$) bond distances in compounds **1** and **2**, respectively (Tables 2 and 3 in Supporting Information). The $Al-O_c$ distances fall in the range of 1.879−1.925 Å, whereas the $Cr-O_c$ bond lengths vary from 1.977 to 1.987 Å. The bond valence-sum calculations indicate that Al and Cr sites are in +3 oxidation states and that all Mo sites are in +6 oxidation states. That the O_c atoms, attached to central Al^{3+}/Cr^{3+}, are

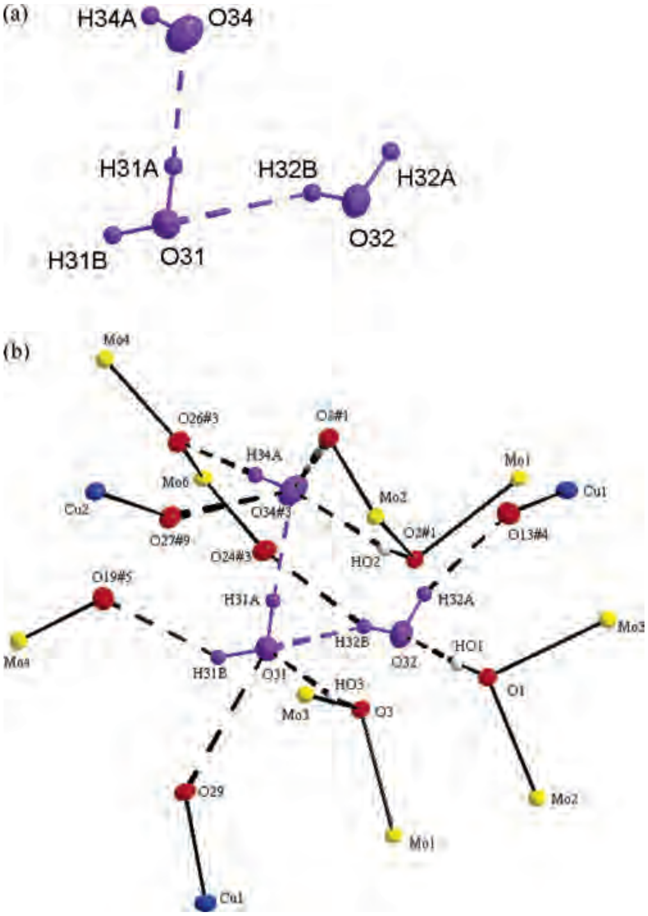

Figure 3. (a) Hydrogen-bonded water trimer (shown in violet). (b) Hydrogen bonding situation describing the water trimer (shown in violet) and its peripheral hydrogen bonding sites. Color code: Mo, yellow; O, red; Cu, blue; H, white. Atoms with additional labels #1, #3, #4, #5, and #9 are related to each other by the following symmetry operations: #1 $-x + 2$, $-y + 1$, $-z$; #3 $-x + 3$, $-y$, $-z$; #4 $x + 1$, y, z; #5 $-x + 2$, $-y$, $-z$; #9 $x - 1$, $y + 1$, $z - 1$.

in protonated forms is also strongly supported by bond valence sum calculations.

Table 2. Geometrical Parameters of Hydrogen Bonds (Å, deg) Involved in the Supramolecular Construction of the Water Trimer and its Surronding (in **1**)[a]

D−H⋯A[b]	*d*(D−H)	*d*(H⋯A)	*d*(D⋯A)	∠(DHA)
O(32)−H(32B)⋯O(31)	0.66(5)	2.50(6)	2.986(4)	133(6)
O(31)−H(31A)⋯O(34)#3	0.85(5)	1.99(5)	2.8164(4)	163(4)
O(1)−H(O1)⋯O(32)	0.91(4)	1.80(5)	2.705(3)	178(4)
O(32)−H(32A)⋯O(13)#4	0.94(7)	2.05(6)	2.920(3)	154(5)
O(3)−H(O3)⋯O(31)	0.78(4)	1.94(4)	2.716(3)	168(4)
O(31)−H(31B)⋯O(19)#5	0.87(6)	2.31(6)	2.999(3)	137(5)
O(2)#1−H(O2)⋯O(34)#3	0.75(4)	2.07(5)	2.784(3)	159(5)
O(34)#3−H(34A)⋯O(26)#3	0.85(4)	1.85(4)	2.706(3)	176(4)
O(32)−H(32B)⋯O(24)#3	0.66(5)	2.31(6)	2.878(3)	145(6)
O(34)⋯O(8)#1			2.999(3)	
O(34)⋯O(27)#9			3.021(3)	
O(31)⋯O(29)			2.984(3)	

[a] D = donor; A = Acceptor. [b] Atoms with additional labels #1, #3, #4, #5, and #9 are related to each other by the symmetry operations specified in the caption of Figure 3.

Water Trimer. There are five crystal/lattice water molecules per formula unit of **1** and **2**. In compound **1**, these are O(30), O(31), O(32), O(33), and O(34). Both hydrogen atoms of the O(30), O(31), and O(32) waters are located; O(33) and O(34) waters are located, each with one hydrogen atom. Among these, three crystal water molecules (O(31), O(32), and O(34)) interact among themselves forming an acyclic water trimer (a small water cluster) as shown in Figure 3a. The water trimer is formed in a clock-wise manner (in terms of proton donation): O(32) water donates one of its H(32B) proton to water O(31), which in turn donates its H(32A) proton to the water O(34). In this context, we must mention that, theoretical calculations have established a six-membered minimum energy cyclic water trimer, which is chiral and undergoes two types of degenerate structural rearrangements. The O⋯O separations have been calculated to be 2.83 and 2.91 Å for the minimum and lowest transition-state structures, respectively.[24a] The cyclic supramolecular $(H_2O)_3$ cluster has not only been identified (in liquid water) experimentally by various spectroscopic methods including infrared VRT (vibration−rotation−tunneling) spectroscopy[24c,d] but the ability of three water molecules to form a cyclic trimer has also been observed crystallographically in the solid state of the complex hydrate {[2,2,2]cryptand-2H}-$[CoCl_4]\cdot 1.5H_2O$.[30] The existence of the present acyclic water trimer (Figure 3a) in the crystal lattices of **1** and **2**, which is as such energetically unfavorable, can be justified by its supramolecular hydrogen-bonding interactions with its surrounding, that include the copper-coordinated water and oxygen atoms (terminal and bridging) of the Anderson anions (Figure 3b). As shown in Figure 3b, the water trimer is hydrogen bonded to all of its possible sites, and the resulting steric constraints decide the conformation of the present acyclic water trimer. Interestingly, two water oxygens, O(31) and O(34), of the water trimer have a formal coordination number of five, and the O(32) water oxygen has a formal coordination number of three. The hydrogen bonding parameters for the water trimer and its association with its surrounding is presented in Table 2. One hydrogen atom (H(32B)) of the O(32) water of the water trimer undergoes bifurcating hydrogen bonding by accepting lone pairs of electrons from O(31) water (part of the water trimer) and O(24) water (a terminal oxygen atom of the Anderson polyanion). This justifies the value of the angle ∠O(32)−H(32B)−O(31) of the water trimer (133°) as given in Table 2. The surroundings of the water trimer, which stabilizes such a high-energy acyclic conformation, include four bridging oxygen atoms (O(1), O(2), O(3), and O(26)), three terminal oxygen atoms (O(8), O(19), and O(24)) of the Anderson polyanions, and three copper-coordinated water molecules (O(13), O(29), and O(27)), as shown in Figure 3b. Even though the water trimer is hydrogen bonded to three copper-coordinated water molecules, it is logical to identify these three water molecules (O(31), O(32), and O(34)) as a supramolecular water trimer (not a water hexamer) because these three waters are not at all involved in covalent interactions and are solely hydrogen bonded to its periphery. Contributions from the peripheral hydrogen-bonding sites (terminal and bridging oxygen atoms of the Anderson anions and copper-coordinated waters), which play an important role in the existence of this acyclic small water cluster $(H_2O)_3$, can be

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(30) MacGillivray, L. R.; Atwood, J. L. *J. Am. Chem. Soc.* **1997**, *119*, 2592.

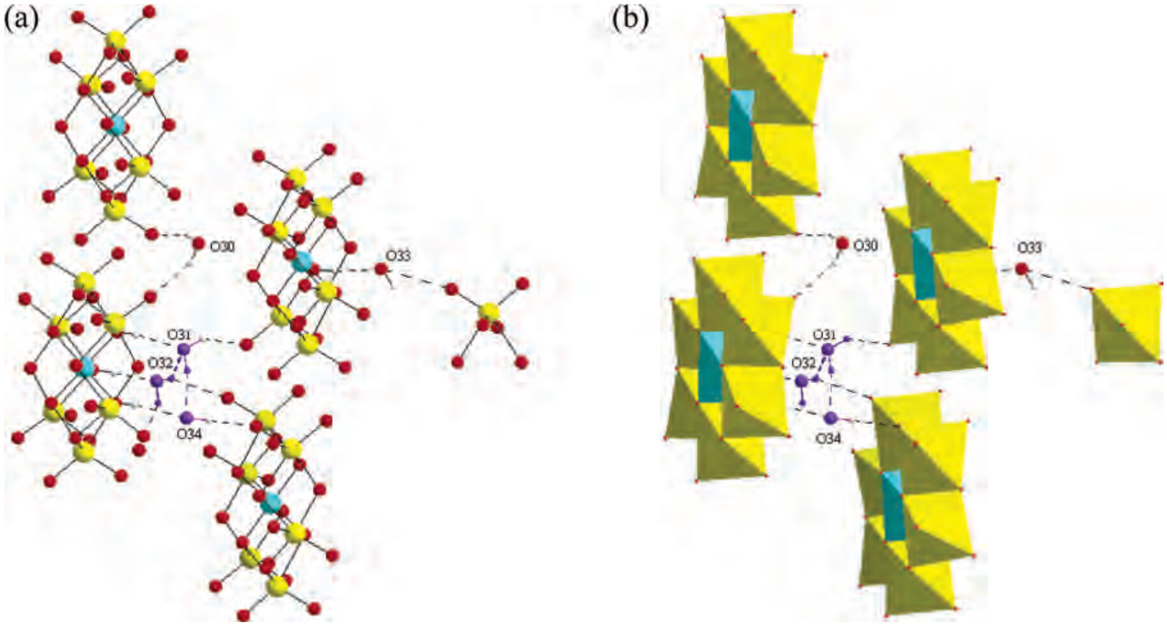

Figure 4. Linking the Anderson heteropolyanion via O−H···O hydrogen bonds that involve solvent waters including water trimer (shown in violet): (a) ball-and-stick representation and (b) polyhedral representation. Color code: Al, cyan; Mo, yellow; O, red; H, white.

realized by the fact that some of the H-bond contacts to the peripheral surroundings of the water trimer are even shorter than those in intrawater trimer (see Table 2 and Figure 3b). In the crystal, the water trimer and the other two lattice waters (O(30) and O(33)) are extensively hydrogen bonded with their surrounding heteropolyanions resulting in an intricate hydrogen-bonding supramolecular network as shown in Figure 4.

Spectroscopy. In the IR spectrum of compound **1**, the peaks at 940, 900, 775, 648, and 440 cm^{-1} are attributed to the vibration modes ν(Mo−O$_t$), ν(Mo−O$_b$), and ν(Mo−O$_c$) of the Anderson anion $[Al(OH)_6Mo_6O_{18}]^{3-}$. Features at 1626, 1582, 1518, 1493, 1425, 1344, 1222, 1145, and 1107 cm^{-1} are characteristic absorptions of the copper-coordinated phenanthroline ligands. The IR spectrum of compound **2** is comparable to that of 1 showing the presence of $[Cr(OH)_6Mo_6O_{18}]^{3-}$ and phenanthroline ligands in **2**. A broad band around 3325 cm^{-1} in the IR spectra of both compounds could be ascribed to the absorptions of coordinated- and lattice-water molecules.

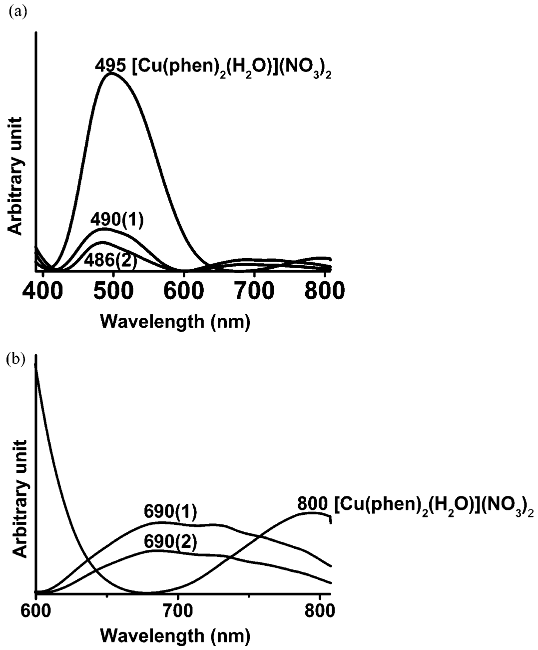

Figure 5. Diffuse reflectance electronic spectra of **1**, **2**, and $[Cu(phen)_2(H_2O)]NO_3$: (a) 400−800 nm region and (b) 600−800 nm region.

The electronic reflectance spectra of compounds **1** and **2** are presented in Figure 5, and they are similar to one another, giving a band maximum at ca. 490 nm and a relatively low energy band at around 700 nm. The geometry around the copper centers in compounds **1** and **2** is distorted square pyramidal. Copper(II) (bis)phenanthroline/bipyridine complexes with metal geometry close to square pyramid generally show a broad peak in their electronic spectra at ~650−660 nm,[31] whereas those with the trigonal bipyramidal (tbp) CuN$_4$L chromophore show a single broad band in their electronic spectra at ~800 nm, as shown by the known tbp complex[25] $[Cu(phen)_2(H_2O)]NO_3$ in Figure 5. The d−d bands for compounds **1** and **2**, which were supposed to appear at around 650−660 nm (because of square-pyramidal geometry around copper), shift to ~700 nm (appearing as broad bands). We believe that this shift to a low-energy region is the result of the coordination of $[M(OH)_6Mo_6O_{18}]^{3-}$ POM anions to the copper center of aquo/chloro-copper monophenanthroline complexes in **1** and **2**. For a given geometry and a metal center, the magnitude of the Δ value (crystal-field splitting) increases as one goes from left to right in a spectrochemical series of different ligands.[32] The position of the phenanthroline ligand is much at the right side of the spectrochemical series. Therefore, it is logical to argue that these POM anions,

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[31] (a) Harrison, W. D.; Kennedy, D. M.; Power, M.; Sheahan, R.; Hathaway, B. J. *J. Chem. Soc., Dalton Trans.* **1981**, 1556. (b) Tokii, T.; Watanabe, N.; Nakashima, M.; Muto, Y.; Morooka, M.; Ohba, S.; Saito, Y. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 364.

[32] Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry, Principles of Structure and Reactivity*, 4th ed.; Addison-Wesley Publishing Company: New York, 2000; p 405.

$[M(OH)_6Mo_6O_{18}]^{3-}$ (as ligands), should occupy the left-side positions (compared to the phenanthroline ligand) in the spectrochemical series (if a new spectrochemical series including such POM anions as ligands is made) because their coordination to the copper center (via terminal oxygen atoms) of the aquo/chloro-copper monophenanthroline complexes leads to a low-energy region shift of the d−d band. The band around 490 nm for the POM-excluded compound $[Cu(phen)_2(H_2O)]NO_3$ can be assigned to the intramolecular charge-transfer (CT) band of the Cu(phen) cation (Figure 5a). These intramolecular CT bands for Cu(phen) cations in compounds **1** and **2** have also appeared in the same region (around 490 nm) as shown in Figure 5a. Thus, the intramolecular CT transitions for the Cu(phen) cations are not affected by coordination of POM heteropolyanion $[M(OH)_6Mo_6O_{18}]^{3-}$ to the copper center of the Cu(phen) cations. The POM anion $[Al(OH)_6Mo_6O_{18}]^{3-}$ itself (without copper coordination) does not exhibit any band in the region of 400−800 nm. The chromium analogue compound $[Cr(OH)_6Mo_6O_{18}]^{3-}$ (without copper coordination) shows a band at ~545 nm, which could be obscured by the intramolecular CT transition of the Cu(phen) cations in the electronic reflectance spectrum of compound **2** as shown in Figure 5a (See the Supporting Information for the electronic reflectance spectra of $La[Al(OH)_6Mo_6O_{18}]\cdot 11H_2O$ and $La[Cr(OH)_6Mo_6O_{18}]\cdot 11H_2O$).[33]

The room-temperature ESR spectrum of **1** shows the axial feature (as expected for a square-pyramidal Cu^{2+} center) with $g_{\parallel} = 2.29$ and $g_{\perp} = 2.08$. At liquid nitrogen temperature, the spectrum remains same (see Supporting Information for ESR spectra of **1** and **2**). Even though two different copper complexes, **1c** and **1a** (which differ in the chloride and water coordinations to the copper centers), are present in compound **1**, a single average ESR spectrum appears in its solid-state instead of a complex feature from two different complexes. This could be the result of the weak O−H···O type hydrogen-bond interactions between two different copper centers (Cu(1) and Cu(2), see Figure 2) from **1c** and **1a**, respectively, throughout the crystal lattice in its solid state. The ESR parameters are in good agreement with those of Cu^{2+} (d^9) systems in the literature.[34] The ESR spectrum of compound **2**, which has two different paramagnetic centers (Cr^{3+} and Cu^{2+} ions), shows features both from Cr(III) and Cu(II) centers. The geometries around both Cr(III) centers in compound **2** are distorted octahedral; more specifically both are tetragonally deformed (considering $Cr-O_c$ distances with respective esd values, Table 3 in the Supporting Information). For an octahedral Cr^{3+} ($3d^3$, ^4F, $L = 3$, $S = {}^3/_2$), a situation results from a possible zero-field splitting. Thus, the chromium centers of compound **2** show an anisotropic axial signal with $g_{\parallel} = 4.3$ and $g_{\perp} = 1.08$. These ESR data (for a central octahedral Cr^{3+} center of an Anderson heteropolyanion in compound **2**) are consistent with those for other reported Anderson polyanions containing a central octahedral chromium(III) center.[35] A central intense feature (at $g \approx 2$) in the ESR spectrum of **2** is the result of the presence of copper square pyramids in **2**. These findings indicate the absence of strong exchange coupling between Cu(II) and central Cr(III) spins because of the bulkiness of the polyanion.

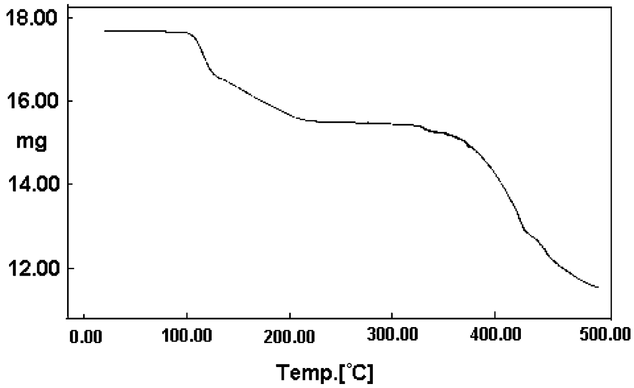

Figure 6. Thermogravimetric (TG) curve for compound **1**.

TG Analysis. TGA performed on $[Al(OH)_6Mo_6O_{18}\{Cu(phen)(H_2O)_2\}_2][Al(OH)_6Mo_6O_{18}\{Cu(phen)(H_2O)Cl\}_2]\cdot 5H_2O \equiv [\mathbf{1c}][\mathbf{1a}]\cdot 5H_2O \equiv \mathbf{1}$ showed a sharp weight loss (6.17%) at around 120 °C; this corresponds to the loss of 11 water molecules (5 lattice waters + 6 copper-coordinated water molecules) per formula unit of **1**. The second loss (5.6%) was observed between ~130 and 220 °C, which corresponds to the loss of 12 hydroxyl groups and two chloride anions. The decomposition of organic components (phenanthroline ligands) starts around 300 °C. At ~500 °C, the total loss is 36%, which corresponds to the loss of 11 water molecules, 12 hydroxyl groups, two chloride anions, and 4 phenanthroline ligands. The TG curve for compound **1** is shown in Figure 6.

Conclusions

We have described an intriguing example where a polyoxometalate-supported transition metal complex $[M(OH)_6Mo_6O_{18}\{Cu(phen)(H_2O)_2\}_2]^{1+}$, **1c** (or **2c**), acts as a cation and the same POM-supported metal complex with chloride coordination to the copper center (replacing a water molecule), $[M(OH)_6Mo_6O_{18}\{Cu(phen)(H_2O)Cl\}_2]^{1-}$ **1a** (or **2a**), acts as an anion in a new type of POM-based ion-pair compound $[M(OH)_6Mo_6O_{18}\{Cu(phen)(H_2O)_2\}_2]^{1+}[M(OH)_6Mo_6O_{18}\{Cu(phen)(H_2O)Cl\}_2]^{1-}\cdot 5H_2O$ **1** (or **2**). This charge complementarity is a rare and unique example in POM chemistry. We have shown the coordination of a chloride anion to a POM-supported copper phenanthroline complex; therefore, it may be possible to extend this chemistry by choosing other halides or pseudo-halides.

An energetically unfavorable acyclic water trimer, consisting exclusively of solvent water molecules, is identified in the crystal lattices of **1** and **2**. The peripheral hydrogen-bonding sites of the Anderson anion supported aquo/chloro-copper monophenanthroline complexes seem to play an

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[33] Shivaiah, V.; Das, S. K. Unpublished results.

[34] Tyagi, S.; Hathaway, B. J. *J. Chem. Soc., Dalton Trans.* **1983**, 2693.

[35] (a) Golhen, S.; Ouahab, L.; Grandjean, D.; Molinie, P. *Inorg. Chem.* **1998**, *37*, 1499. (b) Ouahab, L.; Golhen, S.; Yoshida, Y.; Saito, G. *J. Cluster Sci.* **2003**, *14*, 193.

important role in stabilizing such an acyclic supramolecular water trimer.

The coordination of Anderson polyanions, $[M(OH)_6Mo_6O_{18}]^{3-}$ (as ligands), to the copper centers of aquo/chlorocopper monophenanthroline complexes, in forming square-pyramidal copper complexes **1c**, **1a**, **2c**, and **2a** in compounds **1** and **2**, respectively, is reflected in their electronic reflectance spectra, which show a considerable shift of a characteristic d−d band for a typical square-pyramidal $[Cu(phen)_2L]$ complex to a low-energy region. This predicts that Anderson-type heteropolyanions (as ligands) may occupy their positions at the left side, with respect to the positions of phenanthroline/bipyridine ligands in a spectrochemical series of different ligands (including Anderson anion-type ligands), in a square-pyramidal geometry for a given transition metal.

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Supporting Information Available: Eight figures related to crystal structures of compounds **1** and **2**, a table of hydrogen bond distances for the water trimer and its association with its surrounding in the crystal of compound **2**, X-ray powder diffraction patterns (simulated and experimentally obtained) for compounds **1** and **2**, a figure featuring the diffuse reflectance spectra of $La[Al(OH)_6Mo_6O_{18}]\cdot 11\,H_2O$ and $La[Cr(OH)_6Mo_6O_{18}]\cdot 11\,H_2O$, tables for selected bond lengths and bond angles in compounds **1** and **2**, and complete X-ray crystallographic files in CIF format for compounds **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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