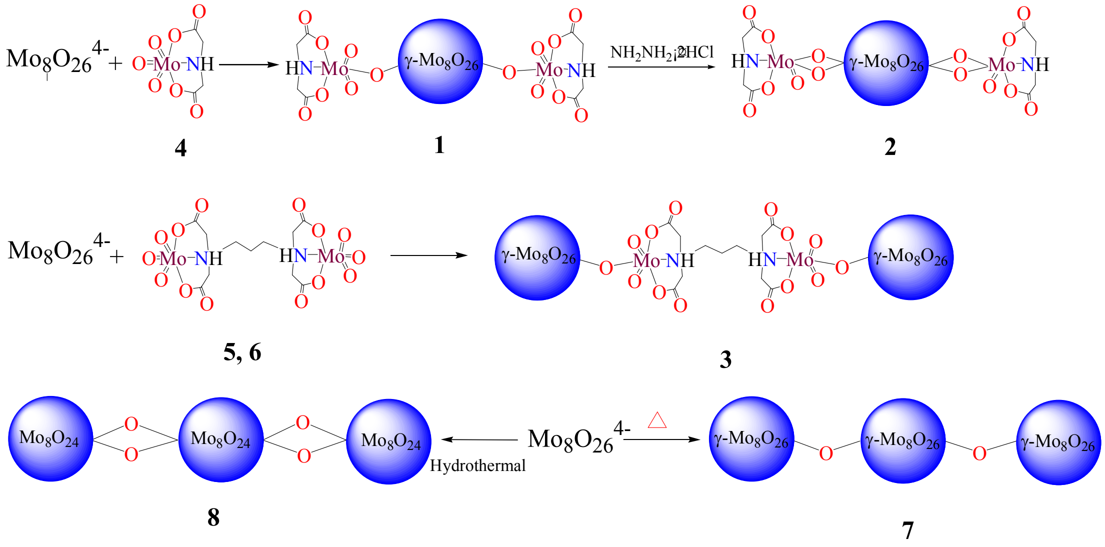
Isolated γ-Octamolybdate based complexes were investigated for Mo-ida and Mo-1,3-pdta systems in solid and solution. Selection of organic ligands, reductant and synthetic condition influence the nature of γ-octamolybdate species, while it preserves its basic structure in the different reactions. Moreover, an interesting decanuclear mixed-valence molybdate $K_8\{\gamma\text{-}Mo_8^{VI/V}O_{26}[Mo^VO_2(ida)]_2\}\cdot 12H_2O$ (***2***) with Mo_8O_{26}(VI/V) core is obtained.



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Transformations and reductions of γ-octamolybdates with their monomeric and dimeric aminopolycarboxylates

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Investigations on aminopolycarboxylato molybdates resulted in the isolations of two interesting decameric species of iminodiacetato γ-octamolybdates $(NH_4)_8\{\gamma\text{-}Mo_8O_{26}[MoO_3(ida)]_2\}\cdot6H_2O$ (**1**) (H_2ida = iminodiacetic acid) and partially reduced form $K_8\{\gamma\text{-}Mo_8^{VI/V}O_{26}[Mo^VO_2(ida)]_2\}\cdot12H_2O$ (**2**). **1** is comparable with its formal polymeric coupling form of polyaminopolycarboxylato molybdate $(NH_4)_{8n}\{\gamma\text{-}Mo_8O_{26}[Mo_2O_6(1,3\text{-}pdta)]\}_n\cdot30nH_2O$ (**3**) from 1, 3-propanediaminetetraacetate (H_4pdta = 1,3-propanediaminetetraacetic acid). The basic construction unit of iminodiacetato γ-octamolybdates was isolated as monomeric complex $(NH_4)_4[MoO_3(ida)]_2\cdot3H_2O$ (**4**). While those for propanediaminetetraacetato γ-octamolybdate are dimeric species of $(NH_4)_5[Mo_2O_6(1,3\text{-}pdta)]Cl\cdot2H_2O$ (**5**) and $K_4[Mo_2O_6(1,3\text{-}pdta)]\cdot3H_2O$ (**6**) respectively. Moreover, polymeric octamolybdates with ammonium cations $(NH_4)_{6n}(Mo_8O_{27})_n\cdot4nH_2O$ (**7**) and $(NH_4)_{4n}(Mo_8O_{26})_n$ (**8**) were obtained under heating and hydrothermal conditions respectively. Monomeric iminodiacetato molybdate **4** can be transformed to its decanuclear species **1** with $[Mo_8O_{26}]^{4-}$ anion. Mixed-valence complex **2** processes a unique deca-molybdenum core with metallic Mo(V)-Mo(V) bond [2.573(2) Å]. The complexes have been characterized by elemental analyses, spectral, X-ray structural analyses and bond valence calculations. Complexes **1**–**6** except for **3** showed obvious decomposition in solution based on solution ^{13}C NMR observations. NMR analyses revealed that $\gamma\text{-}Mo_8O_{26}$ units in **1** and **2** show effect on the carbon signals. This is attributed to the Mo–O–Mo bond between Mo_8O_{26} and MoO_3ida unit. The dimeric species **5** and **6** dissociated to free ligands in ~ 5% and ~ 27% respectively based on ^1H NMR spectra.

Introduction

Polyoxoanions of molybdenum attracted much interests due to their diverse structures and their significant applications in catalysts, materials sciences, biology, and industrial analysis.[1] Octamolybdate $[Mo_8O_{26}]^{4-}$ is one of the important branch of the molybdenum polyoxoanions in acidic condition, which has been observed as eight isomers including *α*-, *β*-, *γ*-, *δ*-, *ε*-, *ζ*-, *η*-, and *θ*–Mo_8O_{26}. These octameric isomers are easily transformed each other under mild environmental modifications mainly studied by structural analyses.[2]

In the other aspect, a number of inorganic-organic hybrid complexes with attractive size, structure, charge and property have been reported.[1b,3] For example, polyoxometalate (POM)-based frameworks were reported using different octamolybdate isomers (Mo_8) and copper-organic fragments or organic units.[4] A series of supramolecular assemblies were reported as catalysts for the epoxidation of olefin with *tert*-butyl hydroperoxide as the oxidant.[5] High dimensional *γ*-octamolybdates were synthesized based on the step-wise synthetic method.[6] Among the polyoxoanions, *γ*-$[Mo_8O_{26}]^{4-}$ was regarded as an useful blocks to construct various types of hybrid compounds with one-, two-, or three dimensional structures.[6-7] While, until now, only limited examples of isolated *γ*-$[Mo_8O_{26}]^{4-}$ compounds were obtained due to the difficulty of the synthetic control and the rational design.[6-7] Furthermore, their conversions and transformations are rare reported, especially the gap between solid state and solution studies.

High oxidation state molybdenum(VI) can be reduced by appropriate method to give low valence molybdates (such as +4, +5), which extends the research scope of molybdates. In Mo(V) chemistry, $[Mo_2O_4]^{2+}$ moiety is an magic block to construct novel polyoxomolybdates.[8] Moreover, mixed-valent molybdates have been prepared by partial reduction.[8a,9] For instance, novel mixed-valent "shrink-wrapped" POM $[H_2Mo_{16}O_{52}]^{10-}$ and an unusual small octamolybdate $[Mo^V{}_4Mo^{VI}{}_4O_{24}]^{4-}$ in partially reduced form were obtained in aqueous and nonaqueous solvents.[9d,9e] However, investigations on the small mixed-valence units are still in the primary state and will attract more and more interest.

To better understand the octamolybdate based complexes, the basic built unit (Mo_8O_{26}) and aminopolycarboxylic acids (such as ida and pdta) were applied to synthesize different aggregates in this work. In the reactions, their precursor as monomeric Mo-ida and dimeric Mo-pdta were successful isolated. The influence of Mo_8O_{26} on Mo-ida species in solution was systematically discussed with solution ^{1}H and ^{13}C NMR techniques.

Experimental

Materials and instrumentation

All chemicals were analytical reagents and used without further purification. Nanopure-quality water was used throughout this work. Infrared spectra were recorded as Nujol mulls between KBr plates using a Nicolet 200 FT-IR spectrometer. Electronic spectra in water were recorded on a UV 2501 spectrophotometer. Elemental analyses were performed using EA 1110 elemental analyzers. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV 500 NMR spectrometer with D_2O using DSS (sodium 2, 2-dimethyl-2-silapentane-5-sulfornate) as internal reference. EPR spectra were analysed by a Bruker ER-200D-RC spectrometer using crystalline samples at room temperature. pH value was determined by PHB-8 digital pH meter.

Synthesis

Synthesis of $(NH_4)_8\{\gamma\text{-}Mo_8O_{26}[MoO_3(ida)]_2\}\cdot 6H_2O$ (1). Hydrogen peroxide (5.0 mL) was added to a mixture of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (5.32 g, 4.3 mmol), iminodiacetic acid (2.66 g, 20.0 mmol) and water (80 mL). The pH value was adjusted to 5.0 with ammonium hydroxide (5.0 M). The solution was refluxed at 60 °C for 12 h. After that, the solution was filtered and evaporated at room temperature. Yellow crystals obtained after standing for one week were collected and washed by 50% ethanol and 95% ethanol. Yield: 4.6 g (77%). Anal. Found: C, 5.1; H, 2.7; N, 6.8. Calc. for $C_8H_{54}Mo_{10}N_{10}O_{46}$: C, 4.8; H, 2.7; N, 7.1. UV-Vis: 296 nm. IR (KBr): ν_{as}(C=O) 1615$_{vs}$; ν_s(C=O) 1389$_{vs}$; ν(Mo=O) 939$_{vs}$, 897$_{vs}$; ν_{as}(MoO$_b$Mo) 834$_s$, 804$_s$; ν_s(MoO$_b$Mo) 697$_s$, 600$_s$. ^{1}H NMR δ_H (500 MHz, D_2O, ppm): 3.704(C**H**$_2$). ^{13}C NMR δ_C (D_2O, ppm): 182.66 (**C**O$_2$)$_\beta$, 59.45 (**C**H$_2$).

Synthesis of $K_8\{Mo_8O_{26}[MoO_2(ida)]_2\}\cdot 12H_2O$ (2). Potassium molybdate pentahydrates (1.64 g, 5.0 mmol) and iminodiacetic acid (0.665 g, 5.0 mmol) were dissolved in 10 mL of water. Hydrazine hydrochloride (0.263 g, 2.5 mmol) was added to give a dark green solution. The solution was kept stirring for about 7 h until it changed to deep red. Then the pH value of the solution was adjusted to 4.5 with potassium hydroxide (5.0 M). The solution was kept in a refrigerator for one week to give deep red crystals, which were filtered off and washed with ethanol to give **2**. Yield: 0.5 g (45%). Anal. Found: C, 4.1; H, 1.7; N, 1.5. Calc. for $C_8H_{34}K_8Mo_{10}N_2O_{50}$: C, 4.2; H, 1.5; N, 1.3. UV-Vis: 299 nm. IR (KBr): ν_{as}(C=O) 1629$_{vs}$; ν_s(C=O) 1388$_{vs}$; ν_{as}(MoO$_b$Mo) 849$_s$; ν_s(MoO$_b$Mo) 676$_s$, 600$_s$. ^{1}H NMR δ_H (500 MHz, D_2O, ppm): 3.890 (C**H**$_2$). ^{13}C NMR δ_C (D_2O, ppm): 182.48 (**C**O$_2$)$_\beta$, 59.10 (**C**H$_2$).

Synthesis of $(NH_4)_{8n}\{\gamma\text{-}Mo_8O_{26}[Mo_2O_6(1,3\text{-}pdta)]\}_n\cdot 30nH_2O$ (3). The complex was prepared as reported with modification.[10] We provide a wider pH range to get **3** and the molar ratio is different. Ammonium molybdate tetrahydrates (1.70 g, 1.4 mmol) and propanediaminetetraacetic acid (0.30 g, 1.0 mmol) were dissolved in 40 mL of water with continuous stirring. The pH value of the mixture was adjusted to 3.0-4.5 with the addition of 2.0 M HCl. The solution was refluxed at 70 °C for about 13 h. Then the solution was filtered and evaporated at room temperature. Prism crystals obtained after standing for one week were collected and washed with 50% ethanol and 95% ethanol respectively. IR and analyses of structural parameters show the product as $(NH_4)_{8n}\{\gamma\text{-}Mo_8O_{26}[Mo_2O_6(1,3\text{-}pdta)]\}_n\cdot 30nH_2O$ reported.[10]

Synthesis of $(NH_4)_4[MoO_3(ida)]_2\cdot 3H_2O$ (4). A mixture of ammonium molybdate tetrahydrates (5.32 g, 4.3 mmol), iminodiacetic acid (5.59 g, 42.0 mmol) and 80 mL water was adjusted to pH 4.5 with the addition of dilute ammonium hydroxide. The mixture was refluxed at 60 °C for 12 h. After cooling to room temperature, the solution was filtered and evaporated at room temperature. Colorless crystals standing for two weeks were collected and washed with 50% ethanol and 95% ethanol respectively. Yield: 7.2 g (62%). Anal. Found: C, 14.3; H, 4.6; N, 12.9. Calc. for $C_8H_{32}Mo_2N_6O_{17}$: C, 14.2; H, 4.8; N, 12.4. IR (KBr): ν_{as}(C=O) 1619$_{vs}$; ν_s(C=O) 1340$_m$, 1399$_{vs}$; ν(Mo=O) 887$_s$, 836$_{vs}$. ^{1}H NMR (500MHz, D_2O, ppm): δ_H 3.694 (C**H**$_2$); ^{13}C NMR δ_C (D_2O, ppm): 182.47 (**C**O$_2$)$_\beta$, 59.18 (**C**H$_2$).

Transformation from 4 to 1. A mixture of **4** (1.9 g, 5.0 mmol) and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (1.2 g, 1.0 mmol) in 20 mL of water was stirred at room temperature for 1 h. Two drops of 30% hydrogen peroxide were added to the mixture with stirring. The solution was then filtered and evaporated at room temperature. Yellow crystals of **1** obtained after standing for two weeks were collected and washed with 50% ethanol and 95% ethanol respectively. (Yield: 70%)

Transformation from 1 to 4. A mixture of **1** (9.93 g, 5.0 mmol), iminodiacetic acid (1.33 g, 10.0 mmol) and 20 mL water was adjusted to pH 4.5 with the addition of dilute ammonium hydroxide and then was refluxed at 60 °C for 12 h. After cooling to room temperature, the solution was kept in a refrigerator for one week to give colorless crystals. The crystals were collected and washed with 95% ethanol. Analysis of structural parameters shows the product as **4**.

Synthesis of $(NH_4)_5[Mo_2O_6(1,3\text{-}pdta)]Cl\cdot 2H_2O$ (5) and $K_4[Mo_2O_6(1,3\text{-}pdta)]\cdot 3H_2O$ (6). Ammonium molybdate tetrahydrates (1.31 g, 4.0 mmol) was added to a mixture of propanediaminetetraacetic acid (0.61 g, 2.0 mmol), water (15 mL) and ammonium hydroxide (5.0 M, 1.5 mL). The solution was stirred at room temperature for half hour. The mixture (pH

= 7.2) was filtered and evaporated to about 10 mL. Colorless crystals of **5** were obtained after standing for several days were collected and washed with 95% ethanol. Yield: 0.77 g (51%). Anal. Found: C, 17.5; H, 5.0; N, 12.8. Calc. for $C_{11}H_{38}Mo_2N_7O_{16}Cl$: C, 17.6; H, 5.1; N, 13.0. IR (KBr): ν_{as}(C=O) 1647_{vs}; ν_s(C=O) 1472_m, 1405_{vs}, 1384_{vs}; ν(Mo=O) $940_{s,}$ $854_{b};$. ^{1}H NMR δ_H (500MHz, D_2O, ppm): 3.72-3.85 (4H, m), 3.31-3.48 (8H, m), 2.15 (2H, m); ^{13}C NMR δ_C (500MHz, D_2O, ppm): 180.7 and 173.1 (**C**O_2), 60.0-65.3 (**C**H_2CO_2), 56.4 (**C**H_2N), 21.8 and 21.7 (CH_2**C**H_2CH_2). Similarly, compound **6** was obtained with a yield of 0.86 g (54%). Anal. Found: C, 16.4; H, 2.7; N, 3.3. Calc. for $C_{11}H_{20}Mo_2N_2O_{17}K_4$: C, 16.5; H, 2.5; N, 3.5. IR (KBr): ν_{as}(C=O) 1651_{vs}; ν_s(C=O) 1409_s, 1386_{vs}; ν(Mo=O) $894_{vs,}$ $859_{vs};$. ^{1}H NMR δ_H (500MHz, D_2O, ppm): 3.71-3.82 (4H, m), 3.27-3.51 (8H, m), 2.15 (2H, m); ^{13}C NMR δ_C (500 MHz, D_2O, ppm): 180.7 and 173.4 (**C**O_2), 60.0-65.3 (**C**H_2CO_2), 55.6 and 56.4 (**C**H_2N), 22.2 and 21.7 (CH_2**C**H_2**C**H_2).

Table 1 Crystallographic data and stureture refinements for compounds **1**—**7** except for **3**.

	1	**2**	**4**	
Empirical formula	$C_8H_{54}Mo_{10}N_{10}O_{46}$	$C_8H_{34}K_8Mo_{10}N_2O_{50}$	$C_8H_{32}Mo_2N_6O_{17}$	
Fw (g/mol)	1986.01	2246.57	676.28	
Temperature (K)		173(2)		
Space group	$P\,2_1/n$	$P\,\bar{1}$	$P\,\bar{1}$	
a (Å)	10.5418(5)	10.3517(4)	6.7791(3)	
b (Å)	16.8661(8)	11.2044(3)	12.8945(6)	
c (Å)	14.0774(7)	11.3559(8)	14.1217(7)	
α (°)	90.0	95.776(2)	109.542(1)	
β (°)	92.525(1)	95.670(3)	90.903(1)	
γ (°)	90.0	92.794(3)	103.527(1)	
V (Å^3)	2500.5(2)	1301.72(7)	1125.08(9)	
Z	2	2	2	
F(000)	1920	1076	684	
D_c (g/cm^3)	2.638	2.866	1.996	
Crystal size (mm^3)	0.15 × 0.10 × 0.10	0.25 × 0.20 × 0.10	0.34 × 0.23 × 0.17	
θ range (°)	1.89 -26.00	2.70-27.00	1.54-26.00	
GOF on F^2	1.113	0.872	1.050	
R_1 [$I > 2\sigma(I)$]	0.0453	0.0226	0.0310	
wR_2 [$I > 2\sigma(I)$]	0.0964	0.0633	0.0774	
$R_1{}^a$ (all data)	0.0531	0.0291	0.0324	
$wR_2{}^b$ (all data)	0.1003	0.0670	0.0786	
Largest diff/hole(e/Å^3)	1.023and -0.611	1.176 and -1.003	0.707 and -0.642	
	5	**6**	**7**	**8**
Empirical formula	$C_{11}H_{38}Mo_2N_7O_{16}Cl$	$C_{11}H_{20}Mo_2N_2O_{17}K_4$	$H_{32}Mo_8N_6O_{31}$	$H_{16}Mo_8N_4O_{26}$
Fw (g/mol)	751.81	800.57	1379.84	1255.66
Temperature (K)		173(2)		
Space group	$P\,2_1/c$	$P\,\bar{1}$	$P\,2_1/n$	$P\,\bar{1}$
a (Å)	7.1046(1)	6.780(1)	9.5129(6)	8.2533(9)
b (Å)	15.0877(4)	12.993(2)	11.3042(6)	8.305(1)
c (Å)	25.2185(5)	14.072(2)	14.865(1)	10.205(1)
α (°)	90	104.66(1)	90	104.69(1)
β (°)	91.879(2)	90.48(1)	107.488(7)	105.91(1)
γ (°)	90	94.98(1)	90	109.50(1)
V (Å^3)	2701.8(1)	1194.2(3)	1524.6(2)	586.4(1)
Z	4	2	2	2
F(000)	1528	792	1316	593
D_c (g/cm^3)	1.848	2.226	3.006	3.601
Crystal size (mm^3)	0.25 × 0.20× 0.10	0.20 × 0.05 × 0.04	0.12 × 0.12 ×0.10	0.20 × 0.05 ×0.03
θ range (°)	2.82−27.50	2.99−25.99	2.87−26.00	3.01−25.00
GOF on F^2	0.696	0.542	1.068	1.007
$R_1{}^a$ [$I > 2\sigma(I)$]	0.0445	0.0378	0.0490	0.0384
$wR_2{}^b$ [$I > 2\sigma(I)$]	0.1307	0.0828	0.0892	0.0816
R_1 (all data)	0.0532	0.0766	0.0781	0.0495
wR_2 (all data)	0.1428	0.0955	0.1123	0.0883
Largest diff/hole(e/Å^3)	1.387 and -1.080	1.339 and -0.549	1.112 and -1.329	1.254 and -1.189

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]^{1/2}$.

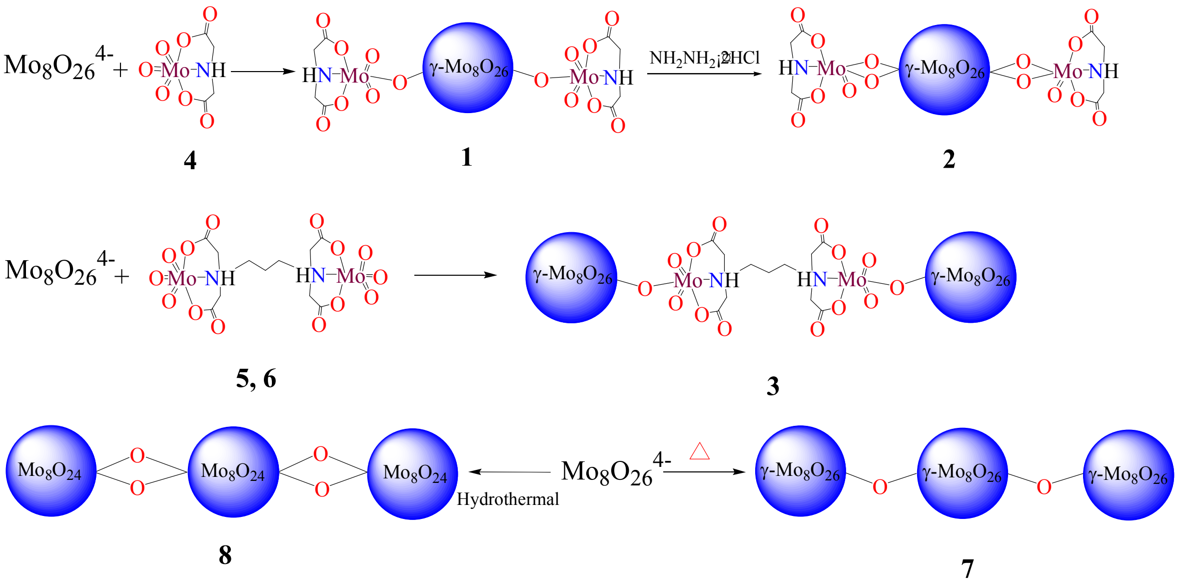
Transformation from 5 to 3. A mixture of **5** (0.75 g, 1.0 mmol) and $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (1.20 g, 1.0 mmol) in 10 mL of water was stirred at room temperature for 0.5 h. The pH value of the solution was adjusted to 4.0 with the addition of dilute ammonium hydroxide. The resulting solution was refluxed at 70 °C for 20 h. After cooling to room temperature, the solution was filtered and evaporated at room temperature to give product **3**.

Synthesis of $(NH_4)_{6n}(Mo_8O_{27})_n{\cdot}4nH_2O$ (7). Ammonium molybdate tetrahydrates (1.24 g, 1.0 mmol) and ethylenediaminediacetic acid (0.42 g, 1.0 mmol) were dissolved in 30 mL of water with continuous stirring for 1.5 h. The pH value of the mixture was adjusted to 4.5–5.0 with the addition of 4.0 M ammonium hydroxide. The resulting solution was refluxed at 90 °C for 12 h. After cooling to room temperature, the solution was filtered and evaporated at room temperature. Yellow crystals of **7** obtained after standing for several days were collected and washed with 50% ethanol and 95% ethanol (0.74 g, yield 63%). IR (KBr): ν(Mo=O) 942_{vs} cm^{-1}. Anal. Found: H, 2.2; N, 6.1. Calc. for $H_{32}N_6Mo_8O_{31}$: H, 2.3; N, 6.1.

Synthesis of $(NH_4)_{4n}(Mo_8O_{26})_n$ (8). A mixture of ammonium molybdate tetrahydrates (1.24 g, 1.0 mmol), and 1,3-propanediaminetetraacetic acid (0.31 g, 1.0 mmol) in 15 mL water were were sealed into a 25 mL teflon-lined stainless steel vessel, and heated at 160 °C for 60 h. The mixture was cooled to room temperature for 40 h. Colorless crystalline materials were separated. The solids were washed with water, and dried in air. The yield of **8** was 59 % (0.64 g). IR (KBr): ν(Mo=O) 950_{vs} cm^{-1}. Anal. Found: H, 1.3; N, 4.5. Calc. for $H_{16}N_4Mo_8O_{26}$: H, 1.3; N, 4.5.

X-Ray crystallography

Crystals of suitable quality for the subsequent X-ray diffraction studies were obtained as transparent prisms or rhombohedral blocks by slow evaporation of the related solution. The resulting crystals were sealed in capillary to prevent loss of water molecules. Crystal data for **1** ~ **8** except for **3** were collected on an Oxford CCD diffractometer with graphite monochromate Mo-Kα (λ = 0.71073 Å) radiation at 173 K. Empirical absorption corrections were applied using the SADABS program. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the Shelxl crystallographic software package. Hydrogen atoms were included at geometrically calculated positions with thermal parameters derived from the parent atoms, except those bonded to the water molecules and ammonium hydrogen. The water and ammonium hydrogen atoms were located in the difference map and included at these sites, with a fixed isotropic displacement factor of U(H) = $1.2U_{eq}$(O). Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition numbers 987093 to 987099 for **1**—**8** except for **3**. Crystallographic data for **1**—**8** except for **3** are summarized in Table 1.



Scheme 1. Schematic view for the transformations and reductions of Mo_8 based complexes.

Results and discussion

Preparation of the Complexes

The syntheses of **1**–**8** were performed from potassium molybdate pentahydrates or ammonium molybdate tetrahydrates as molybdenum source with related aminopolycarboxylic ligands (ida and 1,3-pdta). Iminodiacetic and propanediaminetetraacetic acids are both multidentate chelates. They show different features to construct Mo_8-based complexes which were shown in Scheme 1. Previous studies had demonstrated that pH value is one of the crucial factors for the formation of octamolybdates in aqueous condition. Octamolybdate [$Mo_8O_{26}^{4-}$] is formed from its heptamolybdate precursor [$Mo_7O_{24}^{6-}$] in acidic condition.[11] The pH value of the γ-Mo_8O_{26} based complexes synthesized in this work was in the range of 3−5. Moreover, the molar ratio of Mo:ligand is also an important factor for the preparation of Mo_8-based complexes. Excess molybdates in the synthesis drive the formation of Mo_8 moiety.

Molybdenum iminodiacetato system was investigated in aqueous solution by potentiometric, IR, UV, NMR and the other spectrophotometric techniques before.[12] According to previous investigations, iminodiacetato molybdate(VI) complexes were considered to exist with Mo:ida molar ratio of 1:1 in solution. Three iminodiacetato molybdates $M_2[MoO_3(ida)]\cdot xH_2O$ (M = Li, Na or K)[13] have been isolated and structurally determined. The potassium, sodium and lithium cations in the complexes show interesting aromatic activities. In this work, deca-nuclear iminodiacetato molybdate (VI) **1** containing γ-Mo_8O_{26} cluster was obtained from the reaction of potassium molybdate and iminodiacetic acid in the presence of small amount of hydrogen peroxide. Complex **4** can also be obtained from **1** with the addition of ammonium molybdate. The molar ratio of Mo: ida in **1** is unprecedented 5:1 because of the embedded γ-Mo_8O_{26} cluster. As the structure described below, the anion of **1** was constructed through one γ-Mo_8O_{26} core connected to two mononuclear MoO_3ida moieties. Iminodiacetato ligand in MoO_3ida moiety coordinates to molybdenum atoms through one amino nitrogen and two carboxy oxygen atoms as a tridentate chelate. Here, the monomeric complex **4** was also isolated as the precursor for **1**, which was obtained from the reaction of ammonium heptamolybdate and iminodiacetic acid with the Mo-ida molar ratio of ~ 1:1.

Reaction of potassium molybdate and iminodiacetic acid with excess hydrazine hydrochloride afford partially reduced product **2**. As the structure described below, γ-Mo_8O_{26} core in **2** connects each MoO_2ida moiety through the two shared oxygen atoms. It is inferred that there would be a full reduced iminodiacetato molybdenum(V) complex with $[Mo_2O_4]^{2+}$ core. However, attempt to isolate full reduced product was unsuccessful.

Compared to iminodiacetic acid, propanediaminetetraacetic acid can be considered as a coupling product of the two iminodiacetato groups, which provides hexadentate chelation and is expected to produce plentiful types of propanediaminetetraacetato molybdenum(VI) species. Compound **3** was prepared by utilizing 1,3-pdta and ammonium molybdate tetrahydrates as starting materials with excess 1,3-pdta. We found the suitable pH value is in the range of 3.0 - 4.5, which is a little wider than that reported previously.[10] In the anion structure of **3**, each γ-Mo_8O_{26} unit octamolybdate linked by $[Mo_2O_6(1,3\text{-pdta})]^{4-}$ to form meso-helical chains. While in dimeric molybdates, complexes **5** and **6** with the anion $[Mo_2O_6(1,3\text{-pdta})]^{4-}$ were identified as the precursors of **3**. Reduction of the mixture of molybdate and 1,3-pdta did not produce the mixed-valence complex like Mo-ida system.

The preparation of polyoxomolybdate **7** was promoted by the existence of ethylenediaminediacetic acid. The pH value and reaction temperature are crucial for the formation of **7**. Higher pH value or lower temperature leads to separation of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ after standing a few days. In addition, complex **8** was afforded by using hydrothermal condition in the presence of propanediaminetetraacetic acid.

Description of the Structures

(a) Structure Description of 1 and 3.

Decamer **1** consists of ammonium cations, deca-nuclear molybdenum iminodiacetato anions and lattice water molecules. The deca-nuclear molybdate anion is built by one γ-Mo_8O_{26} core and two MoO_3ida units [Figure 1]. The unique [γ-Mo_8O_{26}]$^{4-}$ anion consists of six distorted {MoO_6} and two distorted {MoO_5} pentahedra with four kinds of O atoms: two μ_4–O, four μ_3–O, six μ_2–O, and fourteen O_t. γ–Mo_8O_{26} core is symmetrically linked by two MoO_3ida units through two bridging oxygen atoms with Mo–O_b–Mo 2.089(2) Å. The structure of MoO_3ida unit is the same as the complex **4** discussed below. The bond distance in **1** [Mo–O_{c1} 2.211(5), Mo–O_{c2} 2.212(4) and Mo–N 2.285(5) Å] is close to those in **4** [Mo–O_{c1} 2.202(2), Mo–O_{c2} 2.226(2) and Mo–N 2.306(2) Å]. Hydrogen bonds are found to exist in complex **2** [Figure S3].

In the anion of **3**, [γ-Mo_8O_{26}]$^{4-}$ moiety connects to [O_5Mo_2(pdta)Mo_2O_5] unit through bridging oxo atoms to form infinite chains. The structure of [O_3Mo(pdta)MoO_3] unit is similar to those of **5** and **6**. The bond distance of the oxo bridge between [γ-Mo_8O_{26}]$^{4-}$ moiety and [O_3Mo(pdta)MoO_3] unit in polymer **3** [Mo–O_b–Mo 1.825(7) Å] is shorter than that of isolated decamer **1** [Mo–O_b–Mo 2.089(2) Å].

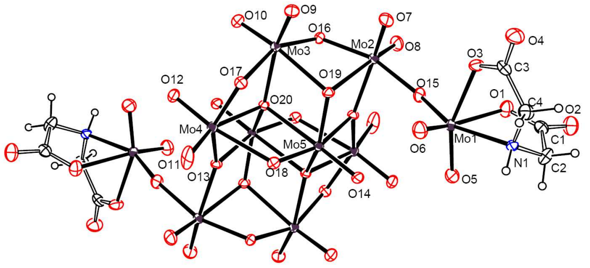


Figure 1. Perspective view of the anion structure of $(NH_4)_8\{\gamma\text{-}Mo_8O_{26}[MoO_3(ida)]_2\}\cdot 6H_2O$ (**1**).

(b) Structure Description of 2.

X-ray structural analysis reveals that complex **2** consists of potassium cations, deca-nuclear mixed-valence molybdenum anions and lattice water molecules. The perspective view of the anion is given in Figure 2. The deca-nuclear molybdenum anion of **2** can be regarded as the coupling of one γ-Mo_8O_{26} core and two symmetric [O_2MoO(ida)] unit linked by four μ_2 bridging oxygen atoms, in which two terminal oxo atoms in the γ-Mo_8O_{26} isomer serve as bridging atoms because of the partially reduced molybdenum(V) atoms. It is also worth noting that the two $[Mo^{5+}{}_2O_4]^{2+}$ units are formed in this anion. The short bond distance [Mo1–Mo2 2.573(2) Å] indicates that Mo–Mo bonds is in the reported range.[14] The bond distances of bridging oxygen atoms with molybdenum(V) atoms [Mo(1)–O(5) 1.924(2) Å, Mo(1)–O(6) 1.923(2) Å, Mo(2)–O(5) 1.948(2) Å, Mo(2)–O(6) 1.942(2) Å] are averaged compared with those from **1** [Mo(1)–O(15) 1.821(4) Å, Mo(2)–O(15) 2.008(4) Å]. While the Mo–N bond distance in **2** is longer than those in **1** and **4**.

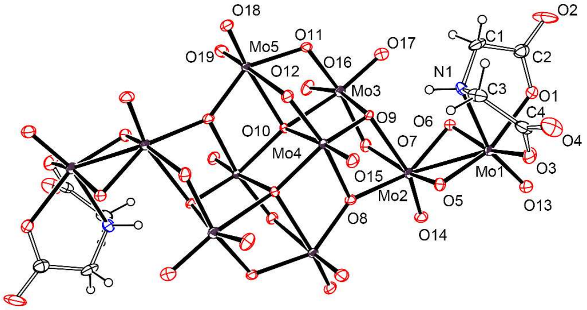


Figure 2. Perspective view of the anion structure of $K_8\{\gamma\text{-}Mo_8O_{26}[MoO_2(ida)]_2\}\cdot 12H_2O$ (**2**).

(c) Structure Descriptions of 4 ~ 6.

Complex **4** consists of ammonium cations, molybdenum–iminodiacetate anion and solvent waters. The molybdenum-iminodiacetate adduct is in 1:1 stoichiometric ratio. Ammonium cations in **4** do not show aromatic activity as those in $M_2[MoO_3(ida)]\cdot xH_2O$ (M = Na or K)[13]. Each molybdenum atom is octahedrally surrounded by three terminal oxygen atoms and a tridentate iminodiacetate ligand, which binds through two deprotonated β-carboxy oxygen atoms and one nitrogen atom. The perspective view of the anion is presented in Figure 3. The molybdenum coordination with iminodiacetate is pentagonal bipyramidal, similar to those found in the other carboxylate ligand molybdates. The Mo–N bond distance is 2.306(2) Å. The average carboxylate-molybdenum distance is 2.214(2) Å. Comparing with the other M-ida (M = metal) species, the Mo−N bond distance and Mo–O_c are in the reported range [Table S2]. The water molecules and ammonium cations are hydrogen bonded to carboxylate oxygen atoms. The perspective view of the 3D structure of complex **4** can be drawn in Figure S5.

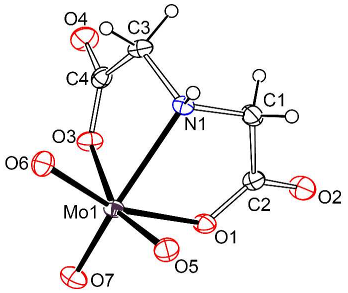


Figure 3. Perspective view of the anion structure of$(NH_4)_4[MoO_3(ida)]_2\cdot 3H_2O$ (**4**).

The analyses reveal that complexes **5** and **6** both consist of a molybdenum–propanediaminetetraacetate adduct in 2:1 stoichiometric ratio because of hexadentate chelation of propanediaminetetraacetate acid [Figure 4]. The coordination mode of molybdenum atoms in **5** and **6** are the same as **4**. Each molybdenum atom is octahedrally coordinated by three terminal oxo groups and a tridentate iminodiacetate group of pdta ligand, which binds through the nitrogen atom and two μ-O carboxylates. The Mo–N bonds in **5** and **6** are similar in the range of 2.34-2.35 Å, small longer than that of complex **4**.

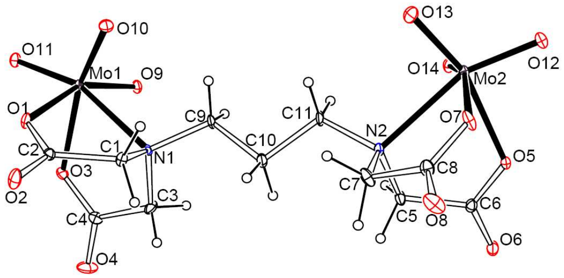


Figure 4. Perspective view of the anion structure of $K_4[Mo_2O_6(1,3\text{-}pdta)]\cdot 3H_2O$ (**6**).

(d) Structure Description of 7 and 8.

Single-crystal X-ray diffraction analysis reveals that the structure of **7** is composed of discrete $[Mo_8O_{27}]^{6-}$ anions connected in network by NH_4^+ cations and waters hydrogen-bonding interactions. In this anion, $[\gamma\text{-}Mo_8O_{26}]^{4-}$ are linked together by sharing bridging oxygen atoms [Mo(2)–O(7) 1.887(8) Å] to form one dimensional $[Mo_8O_{27}]^{6-}$ chains as shown in Figure 5a. In **8**, adjacent monomers in $[Mo_8O_{24}]_n{}^{4-}$ are connected through four sharing oxides. These chains are shown in Figure 5b.

(e) Discussion of the Mo_8O_{26} Based Complexes

γ-Mo_8O_{26} unit was decorated and constructed in different way mainly depending on the nature of organic ligands. The reaction conditions such as pH value, temperature and Mo concentration are supposed to take into account.[15] However, it is difficult to rationally design a specific Mo_8-based compound until now. Previously, carboxylate and nitrogen groups of organic ligand bind to γ-Mo_8O_{26} as monodentate coordination observed in the octamolybdate derivates $[Mo_8O_{26}(L)_2]^{4-}$, in which two ligands are attached symmetrically to Mo(VI) ions.[14b,16] Furthermore, flexible organic amine ligands help to build 3D supramolecular framework in transition-metal complexes (such as Cu, Ni) modified with octamolybdate.[17] In this work, iminodiacetate does not directly bind to γ-Mo_8O_{26} cluster with deprotonated β-carboxy oxygen atom or nitrogen atom. They are unique that they bounded to capping $[MoO_4]$ tetrahedral and linked to γ-Mo_8O_{26} using bridging O atoms to form dacamolybdate. The bridging O atoms are offered by the terminal atoms of their precursors. As for the mixed-valent decamolybdate **2**, four reduced Mo(V) atoms make its structure different from **1**. However, we failed to prepare the other mixed-valent molybdate analogs by using different amount of reducing agents. The reason why only four specific Mo(VI) atoms are reduced in decamolybdate **2** needs to be further explored.

Hexadentate EDTA (H_4EDTA = Ethylenediaminetetraacetic acid) has the similar function to assemble decamolybdates as complex **3**. To explore the smaller aminopolycarboxylic ligand, ethylenediaminediacetic acid and several reaction conditions were tried, no ethylenediaminediacetato Mo_8 unit contained complex was isolated except for complex **7**. In that, $[Mo_8O_{27}]^{6-}$ anion applies sharing oxygen atoms to connect γ-Mo_8O_{26} moiety, which may be ascribed to the steric hindrance of the ligand.

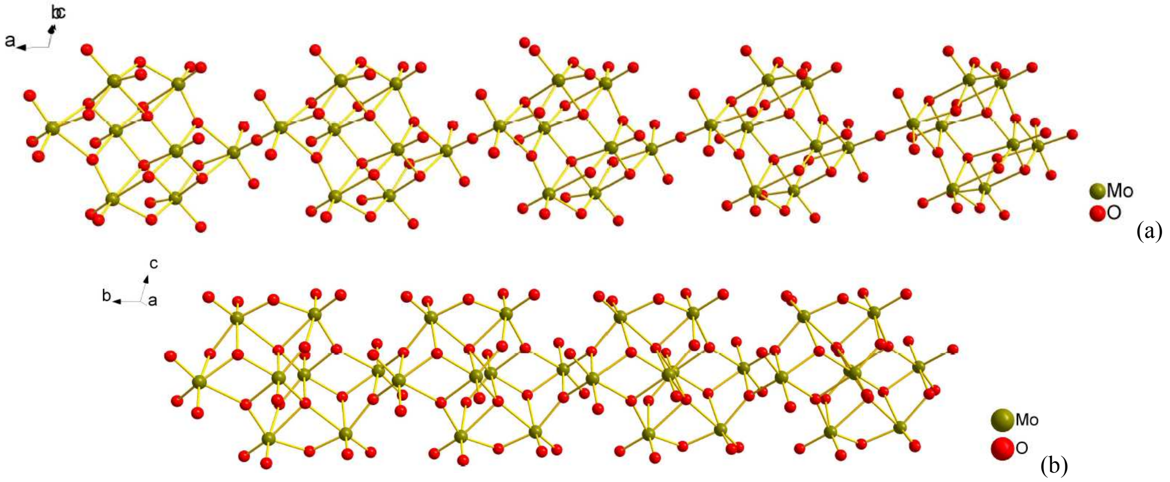


Figure 5. (a) The 1D chain of $(NH_4)_{6n}(Mo_8O_{27})_n$·4nH₂O (**7**, top). (b) The 1D chain of $(NH_4)_{4n}(Mo_8O_{26})_n$ (**8**, bottom).

IR and UV Spectra

The infrared spectra of **1**, **2** and **4** show strong and sharp absorption bands for the carboxylate groups of the coordinated iminodiacetate ligand as shown in Figure S1. Antisymmetric stretching vibrations ν_{as}(COO) appear between 1635 and 1622 cm^{-1}. The corresponding symmetric stretches ν_s(COO) appear between 1405 and 1382 cm^{-1}. The frequencies of the coordinated carboxylates are shifted to lower wavenumbers compared to those of the free ligands of H_2ida. These observations are in accord with the formation of a chelate ring and the bridge mode of the iminodiacetate ligand. The bands around 900 cm^{-1} for **1**, **2** and **4** can be attributted to Mo=O stretching vibration. The bands around 700 cm^{-1} of complexes **1** and **2** observed are due to the Mo–$O_{bridging}$ vibration, indicating the existence of Mo–O_b–Mo bridges in Mo_8O_{26} cluster compared to complex **4**. For complexes **5** and **6**, antisymmetric stretching vibrations $\nu_{as}(COO^-)$ appear between 1686 and 1610 cm^{-1}. The corresponding symmetric stretches $\nu_s(COO^-)$ appear between 1472 and 1312 cm^{-1}. All of the carboxy absorptions are shifted to lower wavenumbers with respect to those of free propanediaminetetraacetic acid. These observations are also in accord with the formation of a chelate ring and the bridging mode of the propanediaminetetraacetate. Loss of the proton and the absence of a carboxylic acidic group in compound **5** and **6** reduce the numbers of bands and displace them to lower frequencies. In the region between 982 and 857 cm^{-1}, these complexes show several bands that result from the presence of *cis*-dioxo cores in two different environments. The low wavenumbers of symmetric MoO_2 stretching may be explained by intramolecular hydrogen bonding and the coordination of potassium or ammonium cations. For compound **7**, the strong bands from 942 to 883 cm^{-1} are attributed to the Mo=O stretching. UV-vis reflective spectra of **1** and **2** show two bands at 296 and 299 nm respectively [Figure S2], which may be assigned to charge-transfer transitions for ligands to molybdenum ions.

NMR Analyses

The solution ^{13}C-NMR spectra of iminodiacetate complexes **1**, **2** and **4** were measured in D_2O respectively [Figure 6]. Owing to the dissociations, the ^{13}C-NMR of three complexes show two sets of resonances, which are attributed to the iminodiacetate ligands in the molybdenum complexes and the decomposed free iminodiacetates. The ^{13}C-NMR signals of the three complexes at 182.66, 182.48 and 182.47 ppm, and 59.45, 59.10 and 59.18 ppm can be assigned to the β-carboxylate and methylene carbons in **1**, **2** and **4** respectively. In comparison with the free iminodiacetate [H_2ida, ^{13}C NMR δ_c (D_2O; ppm), 172.83 $(CO_2)_{\beta\text{-carboxy}}$, 50.73 $(C\text{-}O)_{\alpha\text{-methylene}}$], large downshifts of the β-carboxyate (Δδ 9.83, 9.65 and 9.64 ppm) and methylene (Δδ 8.72, 8.37 and 8.45 ppm) imply the involvement of carboxy coordination. The similarities of the NMR spectra of the three molybdenum complexes suggest that the similar coordination modes of iminodiacetate exist not only in the solid state but also in solution. In addition, the close Δδ value of three complexes indicate that Mo_8O_{26} cluster in **1** and **2** may have a little effect to shift ^{13}C-NMR signals in solution. This may be ascribed to the interval of Mo–O–Mo bonds between the Mo_8O_{26} and MoO_3ida unit

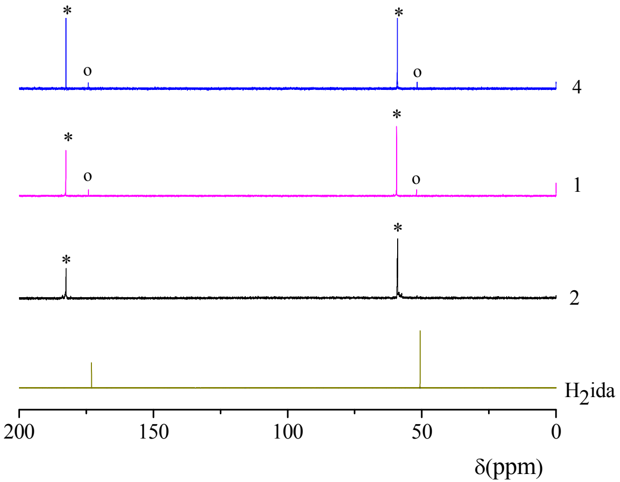


Figure 6. ^{13}C NMR spectra of the complexes: $(NH_4)_8\{\gamma\text{-}Mo_8O_{26}[MoO_3(ida)]_2\}\cdot 6H_2O$ (**1**), $K_8\{\gamma\text{-}Mo_8O_{26}[MoO_2(ida)]_2\}\cdot 12H_2O$ (**2**), $(NH_4)_4[MoO_3(ida)]_2\cdot 3H_2O$ (**4**), and H_2ida. The symbol * indicates resonance signals for the coordinated ligand, o for the free ligand.

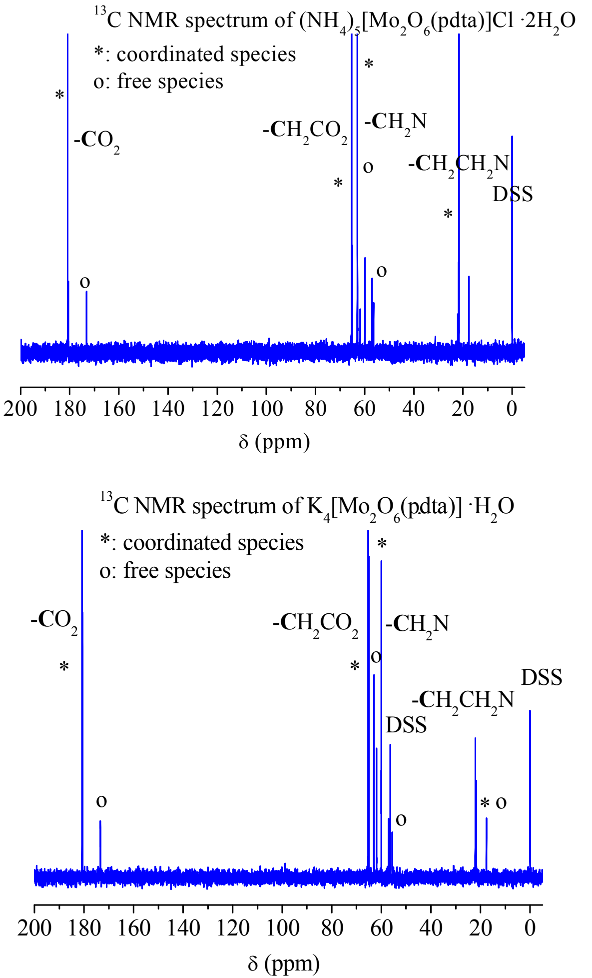


Figure 7. ^{13}C NMR spectra of $(NH_4)_5[Mo_2O_6(1,3\text{-}pdta)]Cl\cdot 2H_2O$ (**5**) and $K_4[Mo_2O_6(1,3\text{-}pdta)]\cdot 3H_2O$ (**6**); x indicates resonance signals of the coordinated ligand, o for the free ligand.

The ^{13}C-NMR spectra of **5** and **6** in Figure 7 show two sets of resonances, which can be attributed to the propanediaminetetraacetates in the molybdenum complexes and the decomposed free propanediaminetetraacetate [K_2H_2pdta: ^{13}C NMR δ_C (D_2O) 171.9 $(CO_2)_\beta$, 58.8 (CH_2CO_2) 55.8 (CH_2N) 22.2 (CH_2)]. Complex **5** shows two resonances in the downfield region (180.7 and 173.1 ppm) for carboxy groups of the pdta ligand. The spectrum also shows six lines at δ = 65.3, 65.1, 63.0, 61.9, 59.9 and 56.4 ppm and two lines at 21.8 and 21.7 ppm, which can be assigned to the CH_2 groups of the pdta ligand. Complex **6** shows the similar result. The ^{1}H-NMR spectra of complexes **5** and **6** also show that they decompose in the solution. From the ^{1}H NMR spectra we can estimate the amount of free ligands. At first, it's quite confusing that the amount (~ 5% for **5** and ~ 27% for **6**) are different for **5** and **6**. After meticulous check, we got a conclusion that this can be attributed to the solutions of **5** and **6** with different pH values

Bond Valence Calculation

According to the valence sum role, the molybdenum oxidation state can be calculated with the linear correlation.[18] The sum of the Mo valences in the synthesized complexes except for **2** are in the range of 5.605-6.512 as shown in Table S2, in agreement with the expected value of 6.00. Bond valence sum calculations show that the oxidation states of the Mo atoms are 5.21, 5.27, 6.00, 6.03 and 6.06 for **2** respectively. The oxidation states of complex **2** are assigned both +5 and +6. To aid in the rationalization of the result, EPR technique was also carried out for **2** and the spectrum of a crystalline sample of **2** is shown in Figure 8. **2** gives a strong EPR signal (g = 1.93) at room temperature to be ascribed to Mo(V) (d^1) coupled with the other atoms. The results are in good agreement with the bond valence sum calculation and the molecular structure described above.

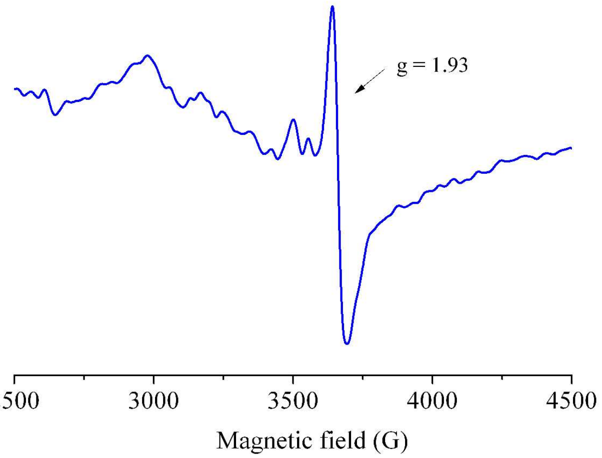


Figure 8. EPR spectrum of complex $K_8\{\gamma\text{-}Mo_8O_{26}[MoO_2(ida)]_2\}\cdot 12H_2O$ (**2**).

Conclusions

In summary, γ-octamolybdate based units were investigated for Mo-ida and Mo-1,3-pdta systems in solid and solution. Selection of organic ligands, reductant and synthetic condition influence the nature of γ-octamolybdate isolated species, while it preserves its basic structure in the different reactions. Moreover, an interesting decanuclear mixed-valent molybdate

2 with Mo_8O_{26}(VI/V) core is obtained. The partially reduced product **2** enriches the chemistry of Mo_8O_{26} with its decamer $(NH_4)_8\{\gamma\text{-}Mo_8O_{26}[MoO_3(ida)]_2\}\cdot 6H_2O$ (**1**). Studies of the other types of isolated mixed-valent Mo_8O_{26}(VI/V) complexes (~ 1.0 nm) are underway.

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Notes and references

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† Electronic Supplementary Information (ESI) is available: IR spectra of **1** ~ **7**, UV spectra of **1** and **2**, 3D perspective view of **4**, 2D perspective view of **1**, ^{1}H NMR spectra of **5** and **6**, bond valence caculations of molybdate complexes and the comparisons of the Mo–O and Mo–N distances (Å) in the minodiacetato and propanediaminetetraacetato molybdates. For ESI and crystallographic data in CIF or other electronic formats see DOI: 10.1039/b000000x/

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