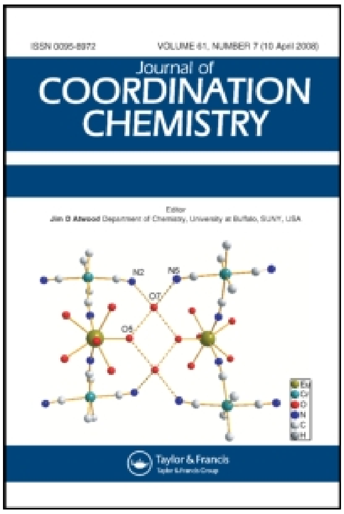

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Synthesis and characterization of two new *β*-octamolybdate complexes $[NH_4][Y(DMF)_5(H_2O)_3][Mo_8O_{26}] \cdot 2CH_3CN$ and $[NH_4][Ce(DMF)_7Mo_8O_{26}]$

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Two new *β*-octamolybdate supported metal complexes $[NH_4][Y(DMF)_5(H_2O)_3][Mo_8O_{26}] \cdot 2CH_3CN$ (**1**) and $[NH_4][Ce(DMF)_7Mo_8O_{26}]$ (**2**) have been synthesized in mixed water and acetonitrile by reaction of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ with MCl_3 ($M^{3+} = Y$ for **1** and Ce for **2**), DMF (DMF = N,*N*-Dimethylformamide) and characterized by elemental analysis, IR spectra, TG analysis, and single-crystal X-ray structural analysis. The single crystal X-ray diffraction analysis reveals that compound **1** consists of discrete $[NH_4][Y(DMF)_5(H_2O)_3][Mo_8O_{26}] \cdot 2CH_3CN$, constructed from *β*-octamolybdate subunits $[Mo_8O_{26}]^{4-}$, ammonium cations, $[Y(DMF)_5(H_2O)_3]^{3+}$ cations and two acetonitrile molecules of crystallization. Y^{3+} is eight-coordinate with five DMF ligands and three water molecules. Compound **2** is built up from DMF coordinated Ce^{III} fragment and *β*-octamolybdate units joined together *via* two terminal oxygen atoms of two molybdenum atoms.

Keywords: Octamolybdate; Polyoxometalates; Crystal structure; Synthesis

1. Introduction

There has been interest in polyoxometalates owing to their fascinating properties and potential applications in fields such as catalysis, medicine, material science, and magnetochemistry [1, 2]. In particular, the chemistry of coordination compounds of polyoxometalates with organic ligands provides knowledge about the interaction of small organic molecules with polyoxometalates surface [3–10].

One important aspect in polyoxometalate chemistry is the modification of polymolybdates with various organic ligands and metal complexes or fragments [11–18]. Polymolybdates, which have oxygen-rich compositions, can act as inorganic ligands to coordinate into the backbone of the above–mentioned complexes. Up to now, eight isomers of $[Mo_8O_{26}]^{4-}$ and the polymolybdates constructed from $[Mo_8O_{26}]^{4-}$ supported inorganic or organic transition metal or rare earth metal complexes have been studied [19–21]. One interesting aspect of octamolybdates is

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seen in varied structural patterns in the solid state and in their structural flexibility in solution [22, 23]. Although a number of organic–inorganic hybrids based on polymolybdates have been synthesized by hydrothermal reaction [24–26], the conventional aqueous solution synthesis for new octamolybdate complexes is still a challenge. We have devoted effort toward preparation of single-crystals of β-octamolybdate supported transition metal or rare earth metal complexes. In this article, we report the synthesis of two new β-octamolybdate complexes $[NH_4][Y(DMF)_5(H_2O)_3][Mo_8O_{26}] \cdot 2CH_3CN$ (**1**) and $[NH_4][Ce(DMF)_7Mo_8O_{26}]$ (**2**). The structure of compounds was characterized by single crystal X-ray diffraction, infrared spectroscopy and thermogravimetric analysis.

2. Experimental

2.1. *Materials and methods*

All the reagents were of analytical or guaranteed purity, and were used without further purification. IR spectra were recorded on a Bruker AXS TENSOR-27 FT-IR spectrometer with KBr pellets in the range 4000–400 cm^{-1}. C, H, and N were determined by using a PE-2400 elemental analyzer. Y, Ce and Mo were determined by using an inductively coupled plasma (ICP) atomic absorption spectrometer (Plasma-Spec-[redacted], USA). TG analyses were performed on a Perkin-Elmer Pyris Diamond thermal analyses system in static air with a heating rate of 10 K min^{-1} from 30 to 700°C.

2.2. *Synthesis of $[NH_4][Y(DMF)_5(H_2O)_3][Mo_8O_{26}] \cdot 2CH_3CN$ (1)*

A solution of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (0.32 g, 0.25 mmol) and YCl_3 (0.21 g, 1 mmol) (prepared from Y_2O_3 dissolved in 35% HCl) in 10 mL CH3CN, 6 mL DMF and 3 mL H_2O was adjusted to pH = 0.79 with 6 M HCl under stirring, and then heated at 80°C for 2 h. The resulting colorless solution was allowed to stand at room temperature without further disturbing for about three days to give colorless block crystals, which were filtered, washed with EtOH, Et_2O and dried at room temperature (yield: ac 55.3% based on Mo). Anal. Calcd for **1** (%): C, 12.73; H, 2.86; N, 6.25; Mo, 42.82; Y, 4.96. Found: C, 12.51; H, 2.92; N, 6.48; Mo, 43.08; Y, 4.78.

2.3. *Synthesis of $[NH_4][Ce(DMF)_7Mo_8O_{26}]$ (2)*

Compound **2** was synthesized by the same procedure as **1** except for replacement of YCl_3 with $CeCl_3 \cdot nH_2O$, adjusted to pH = 1.5 with 6 M HCl under stirring. Yellow block crystals were collected (yield: ac 75.6% based on Mo). Anal. Calcd for 2 (%): C, 13.61; H, 2.88; N, 6.04; Mo, 41.41; Ce, 7.56. Found: C, 13.78; H, 2.65; N, 6.28; Mo, 41.26; Ce 7.82.

Table 1. Crystal data and structure refinement for **1** and **2**.

Compounds	**1**	**2**
Empirical formula	$C_{19}H_{51}Mo_8N_8O_{34}Y$	$C_{21}H_{53}Mo_8N_8O_{33}Ce$
Formula weight	1792.11	1853.35
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1/n$
Crystal size (mm^3)	$0.30 \times 0.20 \times 0.15$	$0.38 \times 0.25 \times 0.18$
a(Å)	10.064(3)	10.0665(9)
b(Å)	23.954(7)	21.9800(19)
c(Å)	11.255(3)	23.825(2)
β(°)	105.812(5)	94.3970(10)
V(Å)	2610.5(13)	5256.1(8)
Z	2	4
D_{calc} (g cm^{-3})	2.280	2.342
μ(mm^{-1})	3.050	2.786
F (000)	1736	3572
θ Range for data collection (°)	1.88–25.00	1.95–26.50
Limiting indices	$-11 \le h \le 11$, $-26 \le k \le 28$, $-13 \le l \le 9$	$-12 \le h \le 12$, $-27 \le k \le 27$, $-22 \le l \le 29$
Reflections collected	13,615	29,440
Independent reflections	7716 ($R_{int} = 0.0334$)	10,846 ($R_{int} = 0.0427$)
Absorption correction	Empirical	Empirical
Max. and min. transmission	0.6576 and 0.4614	0.6800 and 0.4887
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0373$, $wR_2 = 0.0718$	$R_1 = 0.0380$, $wR_2 = 0.0766$
R indices (all data)	$R_1 = 0.0547$, $wR_2 = 0.0790$	$R_1 = 0.0657$, $wR_2 = 0.0885$
Goodness-of-fit on F^2	0.994	1.012
Largest diff. peak and hole (e Å^{-3})	0.652 and −0.512	1.897 and −0.684

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

2.4. *Crystal structure determinations of compounds 1 and 2*

The crystal structures of **1** and **2** were determined by single crystal X-ray difffraction. The intensity data were collected on a Bruker SMART APEX ▌X-diffractometer using graphite monochromated Mo-Kα radiation ($\lambda = 0.071073$ Å) at 293 ± 2 K. The structures were solved by direct methods and refined by full-matrix least squares fitting on F^2 by SHELXTL-97 [27]. An empirical absorption correction was applied using the SADABS program. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added theoretically, with fixed isotropic thermal parameters, and included in the structure factor calculations. The Fourier map had a minimum and maximum electron density of −0.512 and 0.652 e Å^{-3} for **1**, and −0.687 and 1.896 e Å^{-3} for **2**. A summary of the X-ray crystal data for the two compounds is shown in table 1. The selected bond lengths and bond angles are listed in table 2.

3. Results and discussion

3.1. *X-ray structure*

Compound **1** is a charge-compensating compound, which consists of one β-$[Mo_8O_{26}]^{4-}$ anion, one $[Y(DMF)_5(H_2O)_3]^{3+}$, ammonium, and two acetonitrile molecules of crystallization. The polyoxoanion of compound **1** exhibits a classical

Table 2. Selected bond lengths (Å) and bond angles (°) for compound **1** and **2**.

Compound **1**			
Y(1)–O(27)	2.348(7)	Y(1)–O(28)	2.282(8)
Y(1)–O(29)	2.349(7)	Y(1)–O(30)	2.380(7)
Y(1)–O(31)	2.290(8)	Y(1)–O(32)	2.311(8)
Y(1)–O(33)	2.361(7)	Y(1)–O(34)	2.373(8)
Mo(1)–O(1)	1.942(6)	Mo(2)–O(3)	2.337(6)
Mo(1)–O(2)	1.683(6)	Mo(2)–O(6)	2.008(6)
Mo(1)–O(3)	1.940(6)	Mo(2)–O(7)	1.698(6)
Mo(1)–O(4)	1.748(6)	Mo(2)–O(8)	1.862(6)
Mo(1)–O(5)	2.146(6)	Mo(2)–O(17)	2.313(6)
Mo(1)–O(17)	2.337(6)	Mo(2)–O(18)	1.702(6)
Mo(3)–O(3)	1.993(6)	Mo(4)–O(5)	2.355(6)
Mo(3)–O(5)	2.315(6)	Mo(4)–O(6)	1.953(6)
Mo(3)–O(6)	2.330(6)	Mo(4)–O(12)	1.708(6)
Mo(3)–O(9)	1.878(6)	Mo(4)–O(13)	1.749(7)
Mo(3)–O(10)	1.711(7)	Mo(4)–O(17)	2.144(6)
Mo(3)–O(11)	1.686(7)	Mo(4)–O(19)	1.950(6)
O(27)–Y(1)–O(33)	72.7(3)	O(27)–Y(1)–O(30)	72.3(3)
O(28)–Y(1)–O(27)	73.0(3)	O(28)–Y(1)–O(29)	76.2(3)
O(28)–Y(1)–O(31)	82.7(3)	O(28)–Y(1)–O(34)	81.1(3)
O(29)–Y(1)–O(34)	73.4(3)	O(31)–Y(1)–O(27)	77.6(3)
O(31)–Y(1)–O(30)	75.7(3)	O(31)–Y(1)–O(34)	72.1(3)
O(32)–Y(1)–O(29)	77.2(3)	O(32)–Y(1)–O(30)	68.9(3)
O(32)–Y(1)–O(33)	83.2(3)	O(32)–Y(1)–O(34)	75.5(3)
O(33)–Y(1)–O(30)	80.2(3)		
Compound **2**			
Ce(1)–O(1)	2.619(4)	Ce(1)–O(2)	2.581(4)
Ce(1)–O(27)	2.514(5)	Ce(1)–O(28)	2.539(4)
Ce(1)–O(29)	2.467(5)	Ce(1)–O(30)	2.485(5)
Ce(1)–O(31)	2.547(6)	Ce(1)–O(32)	2.482(5)
Ce(1)–O(33)	2.496(5)		
Mo(1)–O(2)	1.710(4)	Mo(2)–O(1)	1.717(4)
Mo(1)–O(3)	2.000(4)	Mo(2)–O(3)	2.337(4)
Mo(1)–O(4)	2.355(4)	Mo(2)–O(4)	1.989(4)
Mo(1)–O(6)	1.883(4)	Mo(2)–O(5)	1.885(4)
Mo(1)–O(7)	1.693(4)	Mo(2)–O(8)	1.699(4)
Mo(1)–O(12)	2.269(4)	Mo(2)–O(17)	2.287(4)
Mo(7)–O(17)	2.366(4)	Mo(8)–O(12)	2.367(4)
Mo(7)–O(19)	1.889(4)	Mo(8)–O(20)	2.006(4)
Mo(7)–O(20)	2.325(4)	Mo(8)–O(21)	1.703(4)
Mo(7)–O(24)	2.007(4)	Mo(8)–O(22)	1.894(4)
Mo(7)–O(25)	1.707(4)	Mo(8)–O(23)	1.695(4)
Mo(7)–O(26)	1.685(4)	Mo(8)–O(24)	2.317(4)
O(2)–Mo(1)–O(3)	97.29(17)	O(1)–Mo(2)–O(3)	87.92(17)
O(2)–Mo(1)–O(4)	86.14(17)	O(1)–Mo(2)–O(4)	97.67(17)
O(2)–Mo(1)–O(6)	102.21(18)	O(1)–Mo(2)–O(5)	102.88(18)
O(7)–Mo(1)–O(2)	105.2(2)	O(8)–Mo(2)–O(1)	105.5(2)
O(26)–Mo(7)–O(19)	102.7(2)	O(23)–Mo(8)–O(20)	102.49(19)
O(26)–Mo(7)–O(24)	101.06(18)	O(23)–Mo(8)–O(21)	104.3(2)
O(26)–Mo(7)–O(20)	90.48(18)	O(23)–Mo(8)–O(22)	101.2(2)
O(26)–Mo(7)–O(25)	104.5(2)	O(23)–Mo(8)–O(24)	91.01(19)
O(2)–Ce(1)–O(1)	64.18(12)	O(29)–Ce(1)–O(27)	72.54(17)
O(27)–Ce(1)–O(28)	72.20(15)	O(29)–Ce(1)–O(28)	70.35(16)
O(27)–Ce(1)–O(2)	67.88(14)	O(32)–Ce(1)–O(1)	83.83(17)
O(27)–Ce(1)–O(1)	81.46(15)	O(32)–Ce(1)–O(2)	68.13(15)
O(28)–Ce(1)–O(1)	67.93(14)	O(33)–Ce(1)–O(2)	66.46(13)

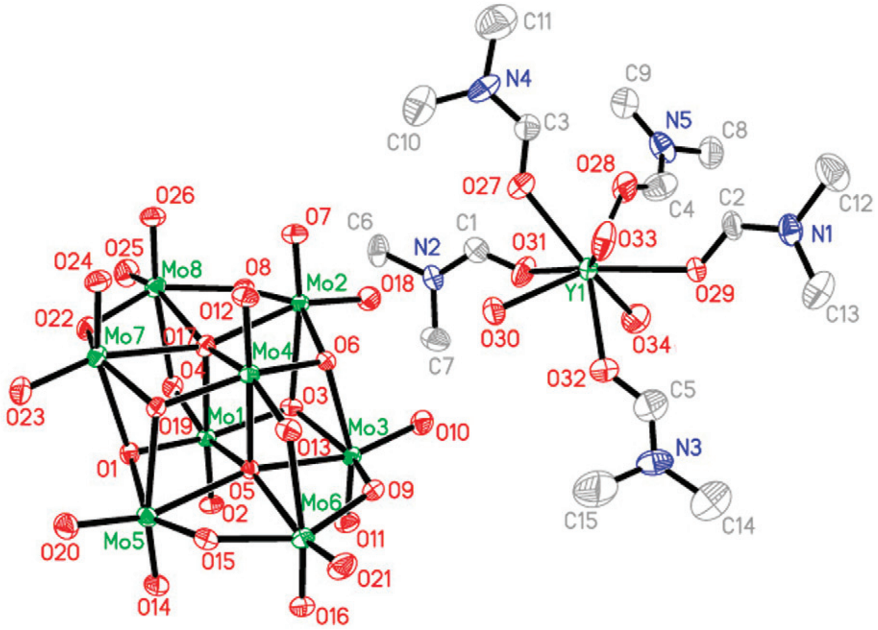

Figure 1. Molecular structure with atomic labeling for compound **1**. Thermal ellipsoids are plotted at 30% probability level. Hydrogen atoms, ammonium cations, and two non-coordinated CH_3CN molecules are omitted for clarity.

β-octamolybdate supported structure. As shown in figure 1, the $[Mo_8O_{26}]^{4-}$ moiety consists of eight edge-sharing $\{MoO_6\}$ octahedra and displays the characteristic β-octamolybdate arrangement, a classical isomer of octamolybdate clusters, in which two centrosymmetrically related cyclic $\{Mo_4O_{13}\}$ units are cross-linked by bridging oxygen atoms. All molybdenum sites exhibit +6 oxidation state, possessing octahedral coordination geometry with different distortion. Mo–O bonds can be divided into four categories: (i) Mo–$O_{(t)}$ bonds, 1.678(7) ~ 1.712(6) Å; (ii) Mo–O(μ_2) bonds, 1.749(7) ~ 2.275(6) Å; (iii) Mo–O(μ_3) bonds, 1.940(6) ~ 2.358(6) Å; (iv) Mo–O(μ_5) bonds, 2.144(6) ~ 2.489(6) Å, and the mean values are 1.697, 1.940, 2.095 and 2.327 Å, respectively. The results show that MoO_6 octahedra of the anion are severely distorted, indicating strong interaction between the polyanions and $[Y(DMF)_5(H_2O)_3]^{3+}$. The coordination environments of Y^{3+} are shown in figure 2. The coordination number of Y^{3+} is 8 (five O atoms from the DMF ligands, and the remaining three O atoms from three water molecules). The average Y–O (water) distance is 2.371 Å, longer than the average Y–O (DMF) 2.316 Å.

The structure of compound **2**, as shown in figure 3, is isomorphic with a La analogue reported by Lu *et al*. [14]. In contrast to **1**, the centrosymmetric anion β-$[Mo_8O_{26}]^{4-}$ is linked to one DMF coordinated Ce^{III} atom through two terminal oxygen atoms (Ce(1)–O(2), 2.581(4) Å; Ce(1)–O(1), 2.619(4) Å) on one side, producing a noncentrosymmetric anionic cluster. Finally, seven oxygen atoms from DMF complete the nine-coordinate environment for cerium with Ce–O distances ranging from 2.467(5) to 2.619(4) Å and angles involving the neighbor oxygen atoms in the range of 66.46(13)° ~ 83.83(17)°. The bond length of Mo(1)–O(2) and Mo(2)–O(1) are 1.710(4) and 1.717(4) Å, respectively, while the length of Mo(7)–O(26) and Mo(8)–O(23) are

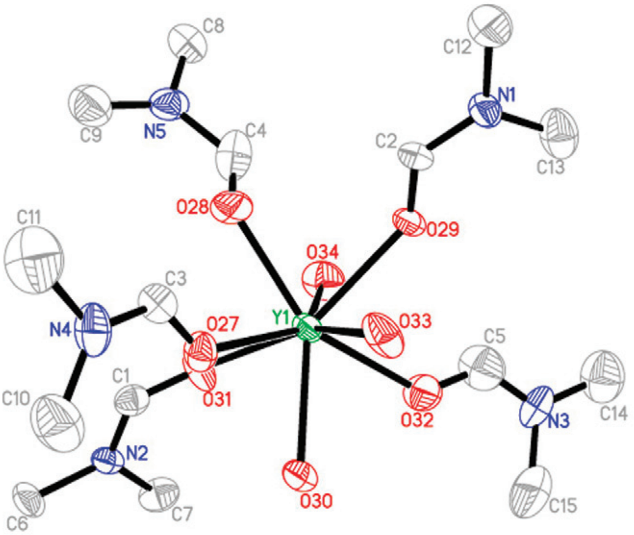

Figure 2. Coordination environment diagram of Y^{3+} in compound **1**. Thermal ellipsoids are plotted at 30% probability level. Hydrogen atoms are omitted for clarity.

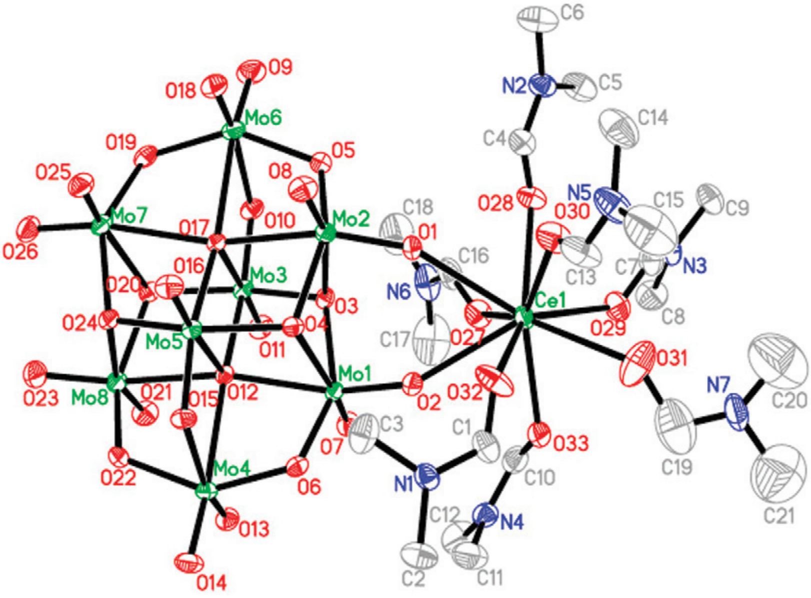

Figure 3. Molecular structure with atomic labeling for **2**. Thermal ellipsoids are plotted at 30% probability level. All H atoms are omitted for clarity.

relatively short, 1.685(4) and 1.695(4) Å, respectively. The bond angles between molybdenum and terminal oxygen atoms are in the range 86.14(17) ~ 105.5(2)°, whereas the angles of opposite side are smaller (84.43(15) ~ 104.5(2)°), as expected. The results show that β-$[Mo_8O_{26}]^{4-}$ is severely distorted, indicating the strong interaction between the polyanion and one DMF coordinated Ce^{3+} cation.

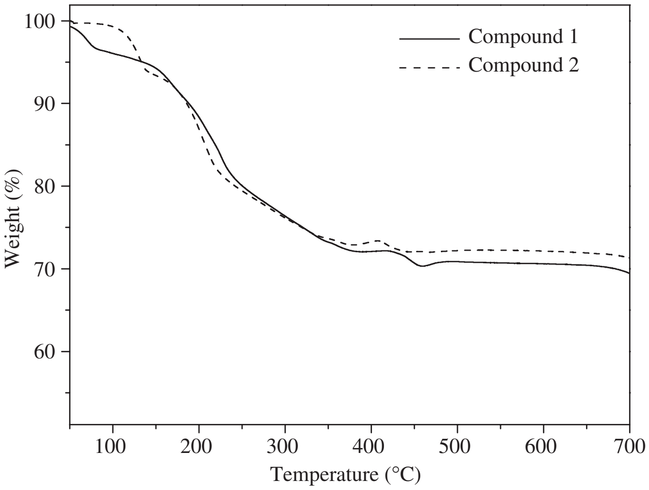

Figure 4. TG curves for **1** and **2**.

3.2. *IR spectroscopy*

In the IR spectrum of compound **1**, strong peaks at 945, 912 and 845 cm^{-1} are attributed to Mo–O$_t$ stretching vibrations, while the peaks at 721 and 669 cm^{-1} are vibrations of Mo–O$_b$–Mo. Comparing the IR spectrum of compound **1** with that of β-[Mo$_8$O$_{26}$]$^{4-}$, it can be observed that the shape of the peaks in the range 600–1000 cm^{-1} is nearly identical to that of β-[Mo$_8$O$_{26}$]$^{4-}$ except for slight shifts of some peaks due to the effect of coordination, which indicating that the polyanion still retains the basic β-[Mo$_8$O$_{26}$]$^{4-}$ structure [28]. This is in agreement with the result of single-crystal X-ray diffraction analysis. In addition, the resonances at 1653 and 1116 cm^{-1} in compound **1** are assigned to the ν_{as}(C=O) and ν_{as}(C–N) asymmetric stretching vibrations of DMF. The IR spectra indicates that there is strong interaction between the polyanions and organic groups in solid state. Similar IR characteristics have been observed for compound **2**.

3.3. *Thermogravimetric analysis*

The TG curves for **1**, and **2** are shown in figure 4. The thermogravimetric analysis of compound **1** shows four continuous weight loss steps. The first step weight loss is 4.60% in the ca 50–135°C temperature range, corresponding to the loss of two isolated CH3CN molecules (Calcd 4.58%). The second weight loss step is 12.26% in the temperature range of ca 135–228°C, corresponding to the loss of three coordinated DMF molecules (Calcd 12.23%). The third step (Calcd 10.20%) occurs in the temperature range of 228–365°C, corresponding to the removal of the other two coordinated DMF molecules and two coordinated water molecules (Calcd 10.16%). The fourth weight loss step started at ca 365°C up to 540°C to give a weight loss of ca 1.90% (Calcd 1.95%), corresponding to the loss of one water and ammonia molecules. The remaining weight of 70.69% (Calcd 70.78%) indicates that the final products are the mixture of MoO$_3$ and Y$_2$O$_3$. The thermogravimetric curve of compound **2** exhibits three continuous weight loss steps in the temperature range of 100–495°C with a total weight loss of 27.83%. These are assigned to the removal of DMF molecules (Calcd 28.52%). The remaining weight of 72.16% indicates that the final products are the mixture of MoO_3 and Ce_2O_3 (Calcd 71.48%). The TG analysis is in agreement with that of the structure determination.

Supplementary material

Crystallographic data for the structure of **1** and **2** reported in this article have been deposited with the Cambridge Crystallographic Data center, CCDC Number 606788 for **1** and 606789 for **2**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (Email: deposit@ccdc.cam.ac.uk).

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