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Lanthanide (III) addition of $[Mo_2O_3S(HNTA)_2]^{2-}$ ($Ln = $ Eu, Dy)

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ABSTRACT

The reactions of $LnCl_3 \cdot 6H_2O$ ($Ln = $ Eu or Dy) and $Na_2[Mo_2O_3S(HNTA)_2] \cdot 6H_2O$ afford $Na[Mo_2O_3S(HNTA)_2]_2 \cdot Eu(H_2O)_9 \cdot 3H_2O$ (**1**) (NTA = nitrilotriacetate) and $Na\{(H_2O)_6Dy[Mo_2O_3S(HNTA)_2]_2\} \cdot 7.5H_2O$ (**2**), respectively. The $[Mo_2O_3S(HNTA)_2]^{2-}$ cluster units of **1** are interconnected by Na^+ into a 3-D open framework with rutile topology templated by $Eu(H_2O)_9^{3+}$. The coordination of $[Mo_2O_3S(HNTA)_2]^{2-}$ to the slightly smaller Dy^{3+} ion of greater ionic potential as a consequence of lanthanide contraction has been observed to form the pentanuclear heterometallic $\{Dy(H_2O)_6[Mo_2O_3S(HNTA)_2]_2\}^-$, which is linked by Na^+ and hydrogen bonds between the protonated carboxylate groups into a 3-D supramolecular framework. The weak antiferromagnetic interactions between the Dy^{3+} ions of **2** have been observed.

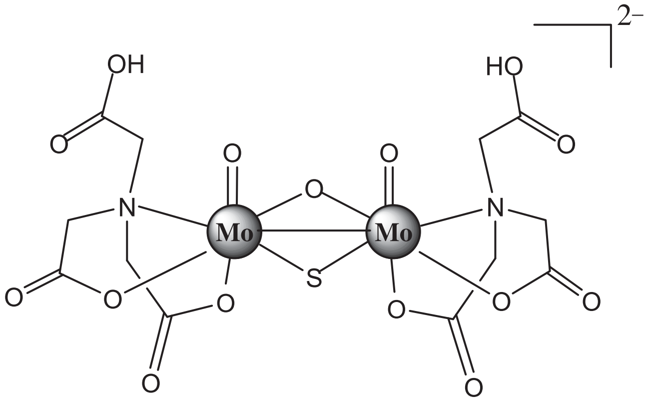
1. Introduction

Although dinuclear oxomolybdenum (V) compounds of the chelating ligand ethylenediaminetetraacetate (EDTA) and propylenediaminetetraacetate (PDTA) have been widely studied, the first crystal structure of such a potassium salt did not appear until 1967 [1,2]. The structures of the sodium salts were also reported [3–5]. As compared with the EDTA and PDTA species, the NTA complexes of molybdenum (VI) are much less reported [3]. To our best knowledge, the NTA–Mo(V) complexes have not been documented in the literature. Recently, we obtained the two Mo(V)–NTA cluster anions $[Mo_2O_4(HNTA)_2]^{2-}$ and $[Mo_2O_3S(HNTA)_2]^{2-}$ [4] (Scheme 1), respectively, which can be used as cluster building blocks to construct multidimensional architectures through the additional coordination of the polycarboxylic arms. Herein, we wish to report the reactions of $[Mo_2O_3S(HNTA)_2]^{2-}$ and lanthanide ions ($Ln = $ Eu, Dy), which produced $Na[Mo_2O_3S(HNTA)_2]_2 \cdot Eu(H_2O)_9 \cdot 3H_2O$ (**1**) and $Na\{(H_2O)_6Dy[Mo_2O_3S(HNTA)_2]_2\} \cdot 7.5H_2O$ (**2**), respectively. Compound **1** has a three-dimensional (3-D) porous framework structure with the rutile $(4.6^2)_2(4^26^{10}8^3)$ topology [5,6] with $Eu(H_2O)_9^{3+}$ as a template. In compound **2**, $Dy(H_2O)_6^{3+}$ is coordinated to the two $[Mo_2O_3S(HNTA)_2]^{2-}$ through carboxylic oxygen atoms to form the pentanuclear $\{(H_2O)_6Dy[Mo_2O_3S(HNTA)_2]_2\}^-$ which is linked together by Na^+ and extensive hydrogen bonds into 3-D supramlecular network.

2. Experimental

2.1. General procedure

All chemicals were obtained from commercial sources and used without further purification. The compound $Na_2[Mo_2O_3S(HNTA)_2] \cdot 6H_2O$ was prepared according to the published procedure [4]. Elemental analyses were performed on a Vario EL III elemental analyzer. IR spectra were recorded on a Magna 750 FT-IR spectrometer photometer as KBr pellets in the range



Scheme 1. The $[Mo_2O_3S(HNTA)_2]^{2-}$ cluster anion.

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Table 1
Crystallographic data for **1** and **2**.

Compound	**1**	**2**
Chemical formula	$C_{24}H_{52}EuMo_4NaN_4O_{42}S_2$	$C_{24}H_{56}DyMo_4NaN_4O_{44}S_2$
Formula weight	1691.51	1738.08
Crystal system	Orthorhombic	Monoclinic
Space group	*Pna*2(1)	*P*21/*c*
a (Å)	18.450(15)	11.369(5)
b (Å)	20.710(12)	34.634(16)
c (Å)	14.174(2)	17.193(6)
β (deg)		129.749(19)
V (Å^3)	5416(5)	5205(4)
Dc (g cm^{-3})	2.045	2.172
μ (mm^{-1})	2.239	2.564
Z	4	4
Wavelength (Å)	0.71073	0.71073
F(000)	3240	3300
Crystal size (mm)	0.54 × 0.10 × 0.10	0.20 × 0.05 × 0.04
θ range (deg)	2.87–27.48	2.33–27.50
Reflections collected	39963	39641
Goodness-of-fit on F^2	1.057	1.088
$R1[I>2\sigma(I)]$	0.0413	0.0705
$wR2[I>2\sigma(I)]$	0.0953	0.1502
$R1$ (all data)	0.0475	0.0929
$wR2$ (all data)	0.0998	0.1648

Table 2
Selected bond lengths (Å) of **1** and **2**.

Complex **1**			
Eu(1)–O(39)	2.424(6)	Eu(1)–O(31)	2.466(5)
Eu(1)–O(32)	2.445(7)	Eu(1)–O(35)	2.472(6)
Eu(1)–O(34)	2.445(7)	Eu(1)–O(36)	2.506(9)
Eu(1)–O(37)	2.448(5)	Eu(1)–O(33)	2.517(7)
Eu(1)–O(38)	2.455(6)		
Complex **2**			
Dy(1)–O(3)	2.278(7)	Dy(1)–O(33)	2.394(7)
Dy(1)–O(16)	2.280(7)	Dy(1)–O(36)	2.426(7)
Dy(1)–O(31)	2.342(10)	Dy(1)–O(32A)	2.394(2)
Dy(1)–O(35)	2.380(8)	Dy(1)–O(32B)	2.53(2)
Dy(1)–O(34)	2.414(9)		

4000–400 cm^{-1}. Variable-temperature susceptibility measurements were carried out in the temperature range of 2–300 K at a magnetic field of 0.5 T on polycrystalline samples with a Quantum Design MPMS-5 magnetometer.

2.2. *Preparation of Na[Mo$_2$O$_3$S(HNTA)$_2$]$_2$ · Eu(H$_2$O)$_9$ · 3H$_2$O (**1**)*

A mixture of $EuCl_3 \cdot 6H_2O$ (0.037 g, 0.1 mmol) and $Na_2[Mo_2O_3S(HNTA)_2] \cdot 6H_2O$ (0.16 g, 0.2 mmol) in H_2O (12 ml) was stirred for 10 min and filtered off. The filtrate was left in air to evaporate the solvent and red crystals were obtained after a few days. Calc. for $C_{24}H_{52}EuMo_4NaN_4O_{42}S_2$: C, 17.04; H, 3.10; N, 3.31. Found: C, 17.11; H, 3.18; N, 3.30. IR (KBr; cm^{-1}): 3420m, 3002w, 2948w, 1729w, 1697s, 1384s, 1316w, 1226m, 1108m, 989w, 923m, 879w, 692w, 603w, 515w.

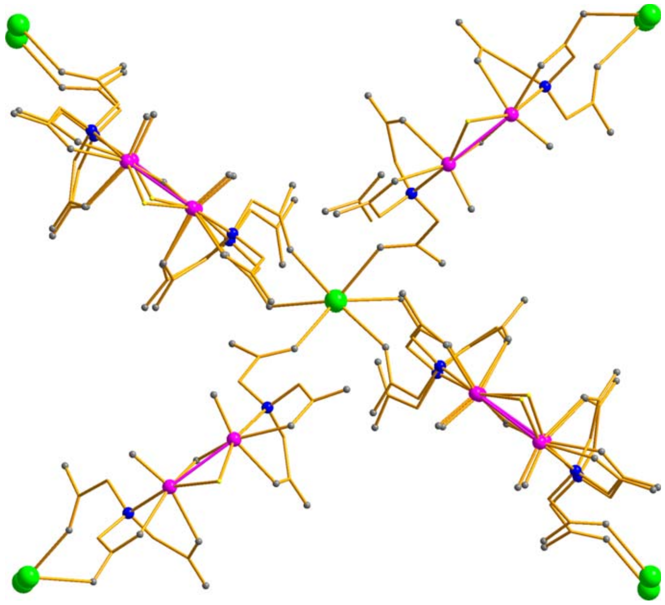

Fig. 2. The connecting mode of Na$^+$ ions and $[Mo_2O_3S(HNTA)_2]^{2-}$ cluster anions.

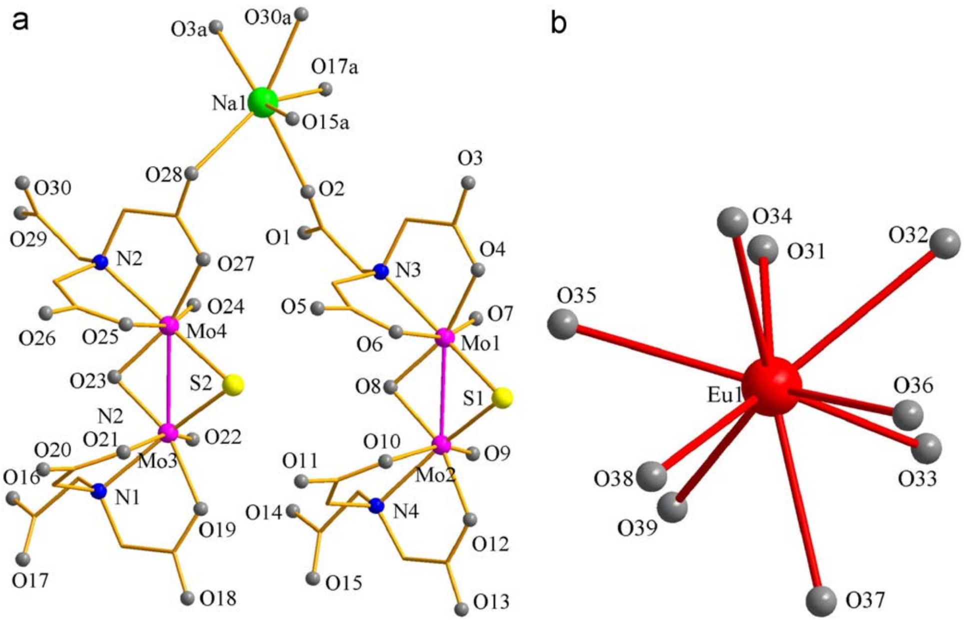

Fig. 1. (a) Structure of $Na[Mo_2O_3S(HNTA)_2]^{2-}$ of **1**. (b) The tri-capped trigonal prism structure of $[Eu(H_2O)_9]^{3+}$ of **1**. Hydrogen atoms are omitted for clarity.

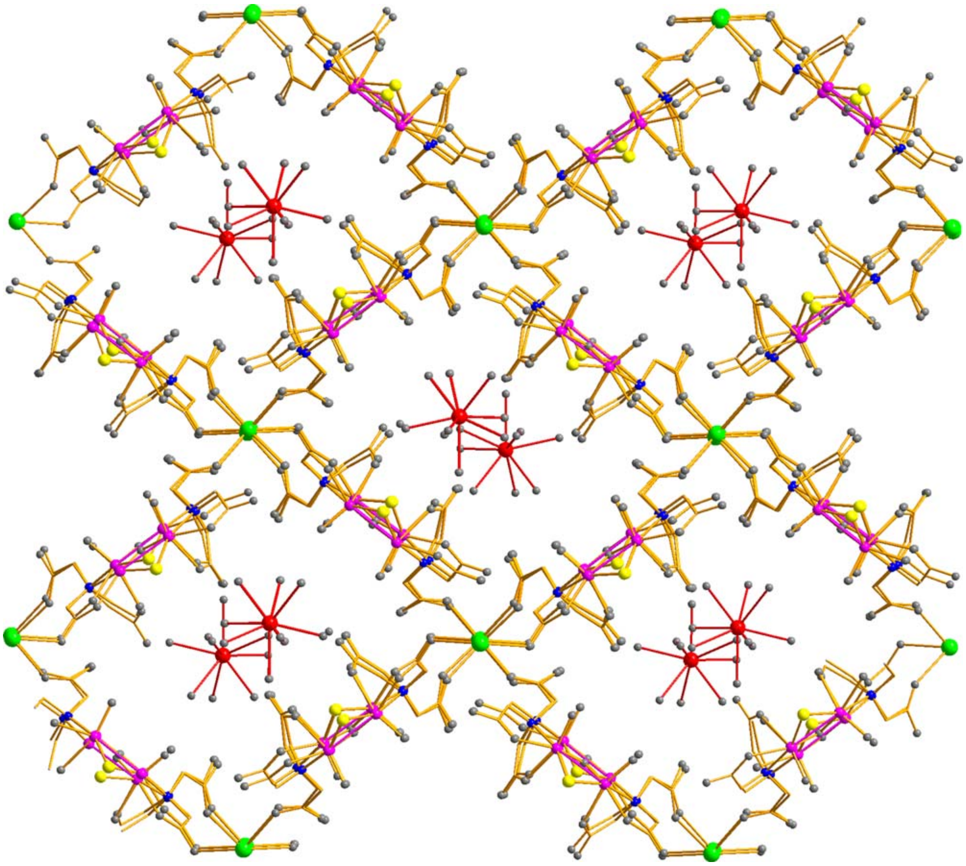

Fig. 3. 3-D open framework $Na[Mo_2O_3S(HNTA)_2]^{3-}$ templated by $Eu(H_2O)_9^{3+}$.

2.3. *Preparation of $Na\{(H_2O)_6Dy[Mo_2O_3S(HNTA)_2]_2\}_2 \cdot 7.5H_2O$ (**2**)*

Compound **2** was prepared by the identical procedure of 1 except $EuCl_3 \cdot 6H2O$ was replaced by $DyCl_3 \cdot 6H2O$. Calc. for $C_{24}H_{55}DyMo_4NaN_4O_{43.50}S_2$: C, 16.67; H, 3.21; N, 3.24. Found: C, 16.59; H, 3.28; N, 3.31. IR (KBr; cm^{-1}): 3434m, 2936m, 1636s, 1397s, 1389s, 990w, 946m, 929m, 884w, 781w, 626w, 529w.

2.4. *Crystal structure determination and refinement*

Suitable single crystals of compounds **1** and **2** were mounted on a Rigaku Mercury CCD diffractometer equipped with a graphite-monochromated Mo*K*α radiation ($\lambda = 0.71073$ Å). The *CrystalClear* software was used for data reduction and empirical absorption correction [7]. The structures were solved by the direct methods and successive Fourier difference syntheses, and refined by the full-matrix least-squares method on F^2 (SHELXTL version 5.1) [8]. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms attached to C atoms and carboxyl O atoms were located at geometrically calculated positions and treated by constrained refinement (see Tables 1 and 2).

3. Results and discussion

3.1. *$Na[Mo_2O_3S(HNTA)_2]_2 \cdot Eu(H_2O)_9 \cdot 3H_2O$ (**1**)*

Compound **1** consists of $Na[Mo_2O_3S(HNTA)_2]_2^{3-}$ (Fig. 1a) charge balanced by $Eu(H_2O)_9^{3+}$ (Fig. 1b) as depicted in Fig. 1. $[Mo_2O_3S(HNTA)_2]^{2-}$ has a basic $[Mo_2O_2(\mu\text{–}O)(\mu\text{–}S)]^{2-}$ core similar to that of $[Mo_2O_3S(EDTA)]^{2-}$ [9,10]. Each Mo (V) atom has distorted octahedral coordination geometry without counting the Mo–Mo single bonds (2.5730(13), 2.5629(13) Å). Unlike the case in

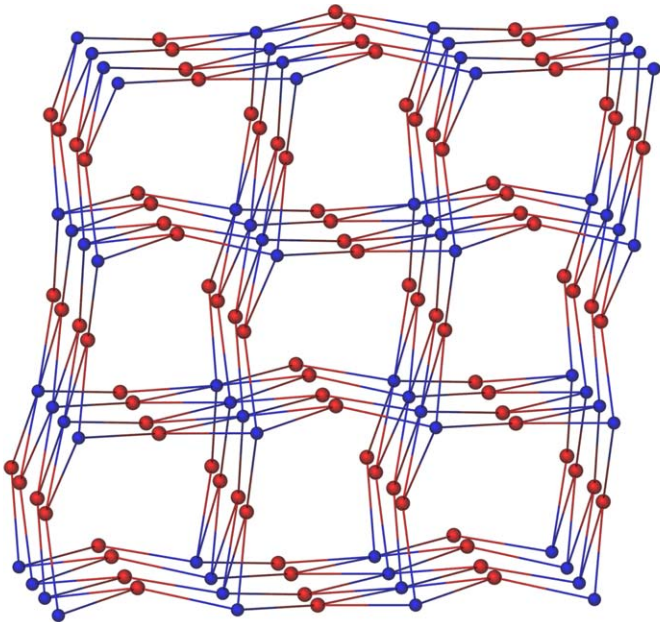

Fig. 4. The distorted rutile topological net observed in **1**. Six-connected nodes (Na): blue; three-connected nodes (cluster anions): red. (For interpretation of the references to the color in this figure legend, the reader is referred to the web version of this article).

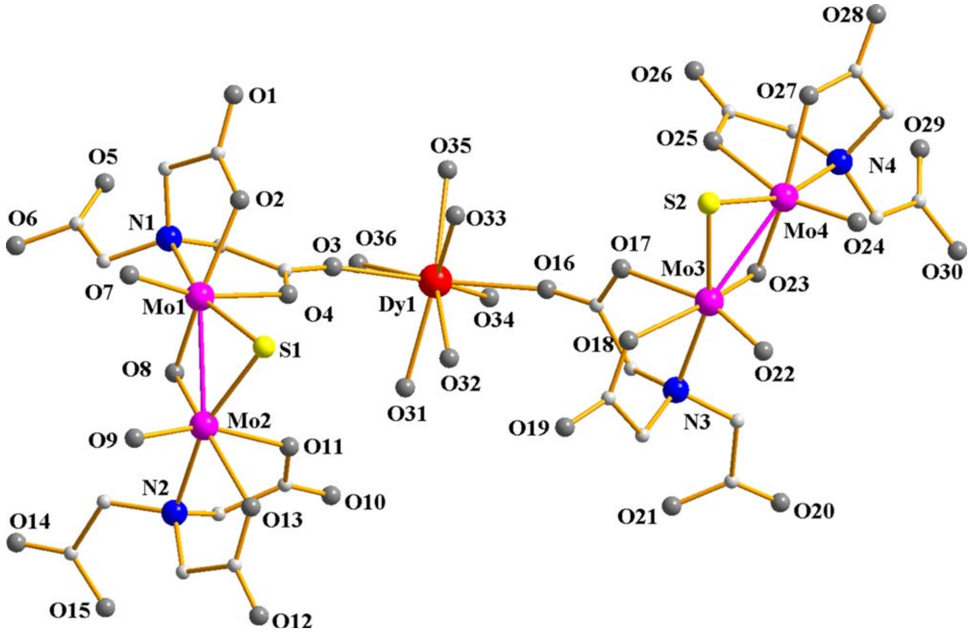

Fig. 5. Structure of $\{Dy(H_2O)_6[Mo_2O_3S(HNTA)_2]_2\}^-$ of **2**. Hydrogen atoms are omitted for clarity.

$[Mo_2O_3S(EDTA)]^{2-}$, the N atom is *trans* to the bridging oxygen atom rather than the terminal oxide atom, presumably caused by the repulsion between the free mono-protonated carboxylate arms. As a consequence, the equatorial positions of the octahedral coordination geometry of the Mo^V center are occupied by the N, carboxylic O, bridging O atoms and apical ones by the terminal and carboxylic O, respectively. One carboxylate group of each NTA ligand is protonated for charge balance, as suggested by the strong absorption at 1697 cm^{-1} in the IR spectrum. The counter anion Eu^{3+} is coordinated by nine water molecules to complete the tricapped trigonal prism geometry (Fig. 1b). As shown in Figs. 2 and 3, the $[Mo_2O_3S(HNTA)_2]^{2-}$ cluster units are connected by Na^+ to yield a 3-D open framework with large rectangular channels with 29.6% (1601 Å^3 per unit cell) free space of the total volume (5416 Å^3) based on platon calculation. The channeled framework is templated by the counter cation $Eu(H_2O)_9^{3+}$ as displayed in Fig. 3 with three of the coordination water molecules being hydrogen bonded to the carboxylate groups from the host network (O–H–O, 2.774, 2.809, 2.988 Å).

Better insight into the nature of this intricate 3-D open framework can be achieved by the topological approach, that is, by reducing the multidimensional structures to simple node and connection nets. As depicted in Fig. 2, each Na atom is coordinated to six carboxyl oxygen atoms from the six cluster anions and each cluster anion bridges three neighboring Na^+ ions. Therefore, the Na^+ ion and cluster anion act as 6- and 3- connected nodes, respectively, in 1:2 ratio. Thus the 3-D network of **1** is a binodal (3, 6) net with the topology of $(4.6^2)_2(4^2 6^{10} 8^3)$. As shown in Fig. 4, the adjacent chains are mutually inclined at an angle of 76.7° rather than perpendicular in the rutile topology, indicative of a distorted rutile structure of the open framework of **1**. This is caused by the deformed trigonal prismatic coordination environments of the Na^+ ions.

3.2. $Na\{(H_2O)_6Dy[Mo_2O_3S(HNTA)_2]_2\} \cdot 7.5H_2O$ (**2**)

The $[Mo_2O_3S(HNTA)_2]^{2-}$ cluster unit of **2** has a similar structure to that of **1**. However, it is of special interest that the Dy aqua ion is coordinated to the two $[Mo_2O_3S(HNTA)_2]^{2-}$ cluster units through the carboxylate oxygen atoms O_3 and O_{16} at the *trans* positions because of the repulsion between the cluster anions to form $\{(H_2O)_6Dy[Mo_2O_3S(HNTA)_2]_2\}^-$, which is believed to result from the two H_2O displacement of $Dy(H_2O)_8^{3+}$ with the cluster ligand. The preference of Dy^{3+} for the harder (more negative) carboxylate oxygen instead of water molecule is presumably assigned to the smaller ionic radius (0.908 Å; Eu^{3+}, 0.950 Å) as a consequence of lanthanide contraction and thus greater ionic potential ($\Phi = Z/r$, Z, oxidation state, r, ionic radius). The six coordinating water molecules complete the anti-square coordination geometry of Dy^{3+} (Fig. 5).

The heterometallic cluster anions $\{(H_2O)_6Dy[Mo_2O_3S(HNTA)_2]_2\}^-$ are linked by Na^+ ions to form a 1-D zigzag chain (Fig. 6a). The adjacent chains are linked together through hydrogen bonds (O1a–O30 2.879 Å, a: $-x+2$, $y+1/2$, $-z+1/2$) between the carboxyl groups to form a 2-D supramolecular layer which is further stabilized by the formation of 3-D supramolecular frameworks (Fig. 6b) through the extensive interlayer hydrogen bonds between carboxylate groups (O21–O1b 2.587 Å; O15–O28c 2.550 Å) and between the coordination water and carboxylate oxygen atom (O19–O35d 2.758 Å) (b: x, $-y+1/2$, $z+1/2$; c: $x-1$, $-y+1/2$, $z+1/2$; d: $x-1$, $-y+1/2$, $z-1/2$). The unusually short O21–O1b and O15–O28c hydrogen bonds reveal that the two protons are mainly located within these two pair of oxygen atoms.

The temperature-dependent magnetic susceptibility of **2** has been measured over the temperature range 2–300 K. The plots of effective magnetic moment (μ_{eff}) and molar magnetic susceptibility (χ_m) versus temperature (T) are shown in Fig. 7. μ_{eff} decreases from 10.95 μ_B at 300 K, which is larger than the spin-only value (5.92 μ_B) but similar to the calculated value (10.65 μ_B), based on the spin–orbital coupling at room temperature [11]. The value remains almost constant over the temperature range 300–80 K and then decreases to 6.76 μ_B at 2 K. The magnetic susceptibility data (2–300 K) has been fitted by the Curie–Weiss law, $\chi_m = C/(T-\theta)$ to give $C = 15.3\ cm^3\ K\ mol^{-1}$ and $\theta = -0.65$ K. The small negative Weiss value (−0.65 K) reveals the weak antiferromagnetic interactions between the lanthanide ions.

4. Conclusion

In conclusion, the dimolybdenum (V) $[Mo_2O_3S(HNTA)_2]^{2-}$ has been used as a cluster building block to constitute the 3-D

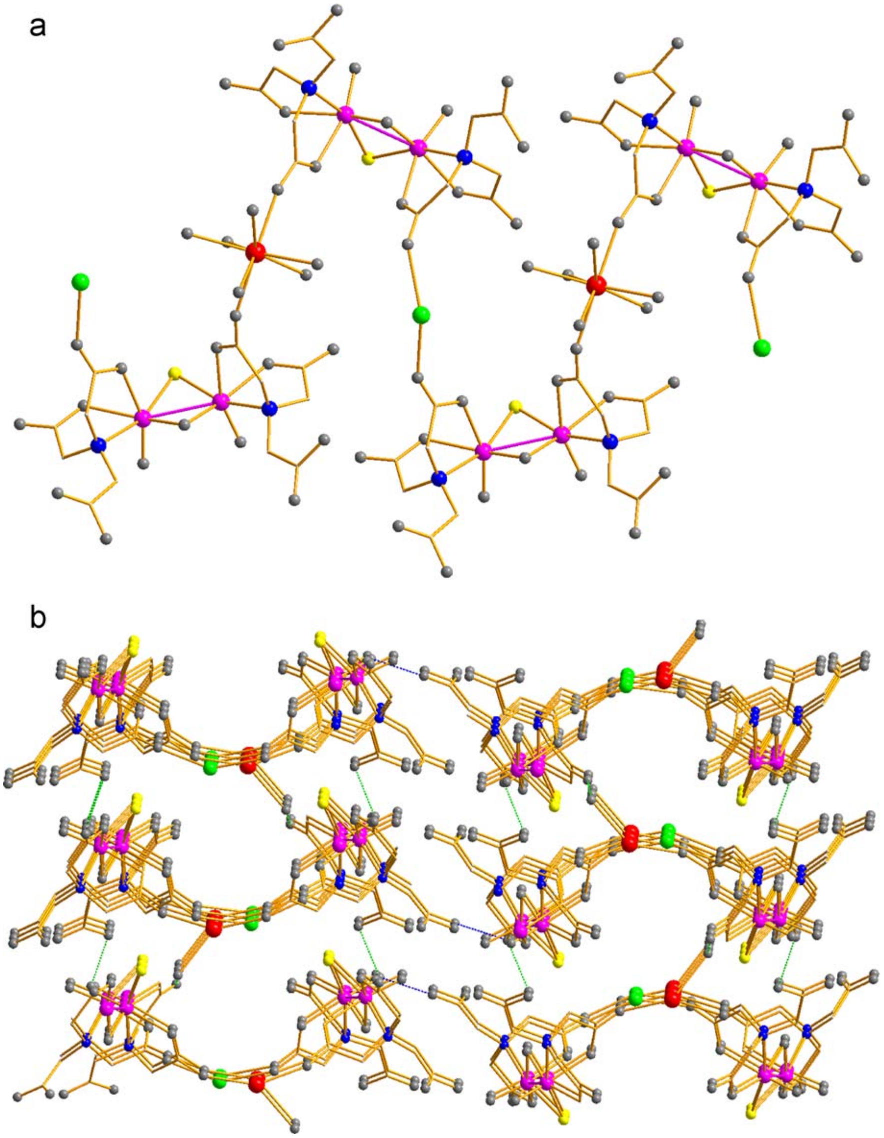

Fig. 6. (a) 1D zigzag chain of Na{Dy(H_2O)$_6$[Mo_2O_3S(HNTA)$_2$]$_2$}; (b) 3-D network formed by the hydrogen bonds between chain (blue) and layers (green). (Mo, purple; Dy, red; Na, green; S, yellow; N, blue; O, grey). (For interpretation of the references to the color in this figure legend, the reader is referred to the web version of this article.)

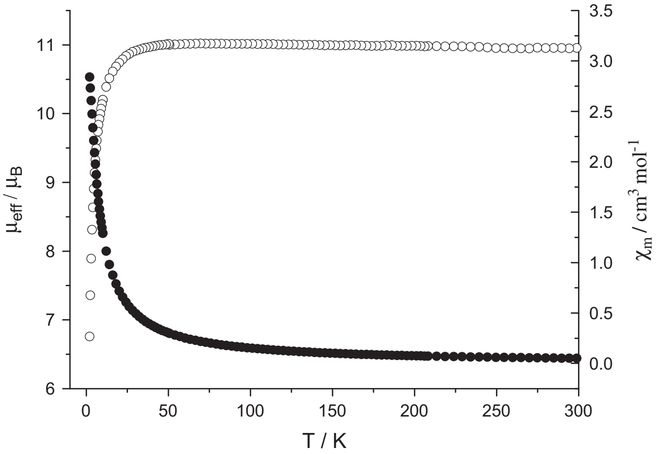

Fig. 7. Plots of μ_{eff} (hollow) and χ_m (hatched) vs. temperature for **2**.

channeled framework templated by lanthanide (Eu^{3+}) aqua ions as observed in compound **1**. Use of Dy^{3+} of smaller radius and thus greater ionic potential instead of Eu^{3+} leads to the coordination of the cluster ligand to the Dy^{3+} ions through the carboxylic oxygen atoms to form the pentanuclear heterometallic {(H_2O)$_6$Dy[Mo_2O_3S(HNTA)$_2$]$_2$}$^-$ in **2**. These results reveal the significant role of lanthanide contraction in the substitution reactions of lanthanide aqua ions and also the potential of [Mo_2O_3S(HNTA)$_2$]$^{2-}$ in the construction of cluster-based coordination polymers.

Acknowledgments

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