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Glycerol as Ligand: The Synthesis, Crystal Structure, and Properties of Compounds $[Ln_2(H_2L)_2(H_3L)_4][Re_6Q_8(CN)_6]$, Ln = La, Nd, Gd, Q = S, Se

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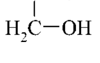
The interaction of aqueous solutions of octahedral cluster anions $[Re_6Q_8(CN)_6]^{4-}$ with rare earth cations in the presence of glycerol resulted in the formation of a new family of compounds $[Ln_2(H_2L)_2(H_3L)_4][Re_6Q_8(CN)_6]$ (where Ln = La, Nd, and Gd; Q = S, Se; H_3L = glycerol; H_2L^- = glycerolate anion). All compounds are isostructural and crystallize in the $P\bar{1}$ space group. Crystal structures are built from octahedral cluster anions $[Re_6Q_8(CN)_6]^{4-}$ and centrosymmetrical dimers $[Ln_2(H_2L)_2(H_3L)_4]^{4+}$ that have three different binding modes of glycerol.

Introduction

The chemistry of octahedral cyanocluster complexes of the type $[Re_6Q_8(CN)_6]^{4-}$ (where Q = S, Se, Te) has been extensively studied over the past decade. The reactions of these anions with transition metal cations lead to the formation of cluster polymers that have Re–CN–M bridges.[1–5] The use of 3d metal complexes with chelating N-donor ligands resulted in formation of low dimensional structures [en,[6,7] trien,[8] 1,2*S*,3*S*,4-butanetetramine (threotab),[9] *N*,*N*′-bis(salicylidene)ethylenediamine (salen)[2]]. Up to now, all the compounds formed by $[Re_6Q_8(CN)_6]^{4-}$ anions and rare earth cations have 3D polymeric structures.[10–12] Attempts to use N-donor ligands were unsuccessful because of their basicity in aqueous solutions and precipitation of rare earth hydroxides.

In search of appropriate chelating ligands that are able to bind the rare earth cations, we have examined polyatomic alcohols. They are good candidates for such complexation because of their high affinity to coordinate rare earth cations, their variable steric requirements and their ability to bridge more then one metal center. The possibility of partial or full deprotonation allows the adjustment of the charge balance of the complexes. In the present work we examined glycerol, a simple, potentially tridentate ligand that may demonstrate variable chelating/bridging modes.



$$\begin{array}{l} H_2C-OH \\ \;\;| \\ HC-OH \\ \;\;| \\ H_2C-OH \end{array}$$

Here we report the synthesis, crystal structure and properties of a series of new compounds of composition $[Ln_2(H_2L)_2(H_3L)_4][Re_6Q_8(CN)_6]$ (Ln = La, Nd, Gd; Q = S, Se; H_3L = glycerol; H_2L^- = glycerolate anion), which contain $[Ln_2(H_2L)_2(H_3L)_4]^{4+}$ dimers. These dimeric structures contain three different modes of chelating glycerol molecules: bidentate, tridentate, and bridging/chelating.

Results and Discussion

X-ray single crystal analysis shows that compounds **1**–**6** are isostructural. Their structures contain $[Re_6Q_8(CN)_6]^{4-}$ (Q = S, Se) anions and binuclear $[Ln_2(\mu\text{-}H_2L)_2(H_3L)_4]^{4+}$ cations. Both anion and cation lie in the centers of symmetry of the unit cell with the space group $P\bar{1}$.

The $[Re_6Q_8(CN)_6]^{4-}$ (Q = S, Se) anions have the typical $M_6Q_8L_6$ structure (Figure 1). The rhenium octahedron is surrounded by eight chalcogen atoms to form the cube Q_8. Additionally, each rhenium atom is coordinated by a terminal CN group. Bond lengths and angles are given in Table 1.

The new centrosymmetric binuclear cation $[Ln_2(H_2L)_2(H_3L)_4]^{4+}$ is shown in Figure 2, Figure 3 and Figure 4. Binding modes of H_2L^- and H_3L are schematically presented in Scheme 1. Two lanthanide atoms are connected by two deprotonated glycerol molecules (C9, C10, C12, O7, O8, O9) (Scheme 1a).

In structures **1**, **3**, **4**, and **6**, all ligands are ordered, while in **2** and **5** one of the carbon atoms of a bridging glycerolate ligand is disordered over two positions with equal weights. Each of the Ln atoms are additionally coordinated by two glycerol molecules as tridentate (C1, C2, C3, O1, O2, O3) and bidentate (C4, C5, C6, O4, O5, O6) ligands (Scheme 1b and c). The Ln–O bond lengths (for OH groups) lie within

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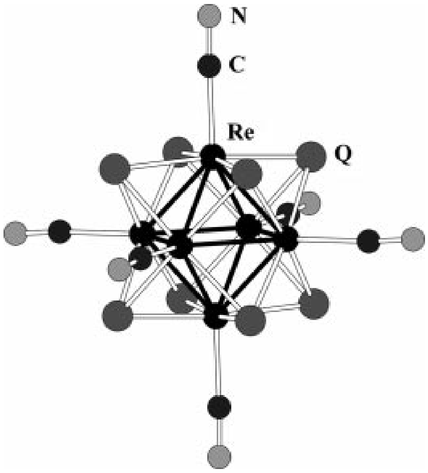


Figure 1. Structure of $[Re_6Q_8(CN)_6]^{4-}$ anions.

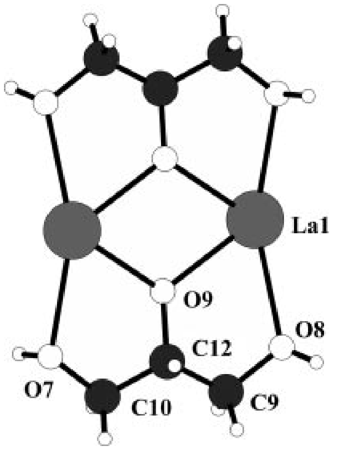


Figure 3. Centrosymmetric $[La_2(\mu\text{-}H_2L)_2]^{4+}$ fragment.

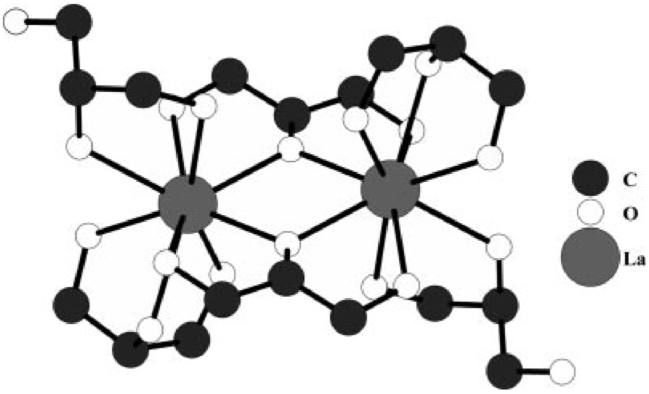


Figure 2. Structure of $[La_2(\mu\text{-}H_2L)_2(H_3L)_4]^{4+}$ cation. Hydrogen atoms are omitted for clarity.

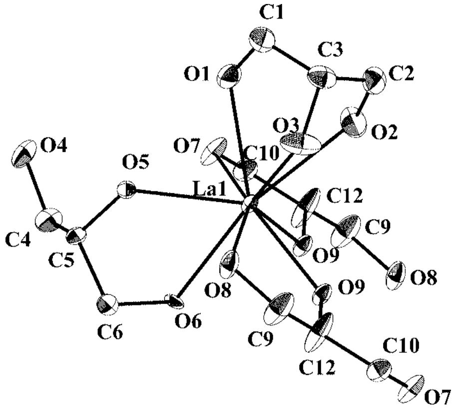
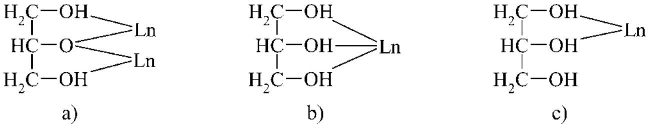


Figure 4. Environment of La in the structure of **1**. Hydrogen atoms are omitted for clarity.



Scheme 1. Coordination modes of the glycerol molecule to lanthanide(III) cations in compounds **1**–**6**.

2.540–2.706, 2.485–2.664, and 2.440–2.631 Å for Ln = La, Nd, and Gd, respectively. The Ln–(μ-O) bonds are distinctly shorter. The mean distances are equal to 2.397, 2.346, and 2.312 Å for Ln = La, Nd, and Gd, respectively (see Table 2). The coordination number of the Ln^{III} ion in the complexes is nine, and the coordination polyhedron of lanthanide(III) may be described as a distorted tricapped trigonal prism.

In the crystal packing, there is an extensive system of hydrogen bonds between the nitrogen atoms of the CN groups and the OH groups of glycerol and glycerolate ligands (Figure 5). The shortest contacts lie within the range 2.70–3.00 Å.

According to the Cambridge Structural Database (CSD V.5.25), there are no known examples of lanthanide(III) complexes bearing glycerol or glycerolate anions. Scheme 2 presents the coordination modes of glycerol and glycerolate anions (H_2L^-, HL^{2-}, and L^{3-}) in structurally characterized complexes of transition metals.

Table 1. Selected bond lengths [Å] in $[Re_6Q_8(CN)_6]^{4-}$ cluster anions in **1**–**6**.

	1	**2**	**3**	**4**	**5**	**6**
Re–Re	2.5988(5)–2.6055(5) mean 2.602(3)	2.5971(5)–2.6055(5) mean 2.601(4)	2.6012(4)–2.6089(4) mean 2.606(3)	2.6319(7)–2.6368(6) mean 2.634(2)	2.6310(4)–2.6364(4) mean 2.635(2)	2.6312(6)–2.6356(6) mean 2.634(2)
Re-Q	2.404(2)–2.414(2) mean 2.407(3)	2.408(2)–2.4166(19) mean 2.414(5)	2.4095(15)–2.4217(14) mean 2.415(4)	2.5184(12)–2.5372(11) mean 2.525(6)	2.5174(8)–2.5319(8) mean 2.523(5)	2.5169(13)–2.5292(13) mean 2.523(4)
Re–C	2.113(9)–2.126(9) mean 2.118(7)	2.108(8)–2.132(8) mean 2.116(14)	2.114(7)–2.118(6) mean 2.115(2)	2.099(12)–2.119(13) mean 2.108(10)	2.105(8)–2.127(9) mean 2.112(13)	2.114(15)–2.128(15) mean 2.120(7)
C–N	1.132(12)–1.149(12) mean 1.143(9)	1.113(11)–1.136(10) mean 1.123(12)	1.122(9)–1.139(8) mean 1.133(10)	1.110(16)–1.143(15) mean 1.129(17)	1.122(10)–1.153(10) mean 1.136(16)	1.104(17)–1.125(17) mean 1.114(11)

Table 2. Ligand environment of Ln atoms for **1**–**6**.

	1	**2**	**3**	**4**	**5**	**6**
Ln–O(OH) [Å]	2.540(6)–2.690(8) mean 2.595(49)	2.485(5)–2.637(6) mean 2.540(51)	2.440(4)–2.602(5) mean 2.509(58)	2.546(8)–2.706(10) mean 2.605(52)	2.474(5)–2.664(7) mean 2.558(67)	2.425(8)–2.6310(7) mean 2.510(79)
Ln–(μ_2-O) [Å]	2.383(6), 2.405(6) mean 2.394	2.330(5), 2.349(5) mean 2.340	2.300(4), 2.315(4) mean 2.308	2.388(7), 2.410(8) mean 2.349	2.342(5), 2.362(5) mean 2.352	2.301(8), 2.333(8) mean 2.317
Ln–(μ_2-O)–Ln [°]	111.8(2)	112.2(2)	112.2(2)	111.8(3)	112.2(2)	112.5(3)

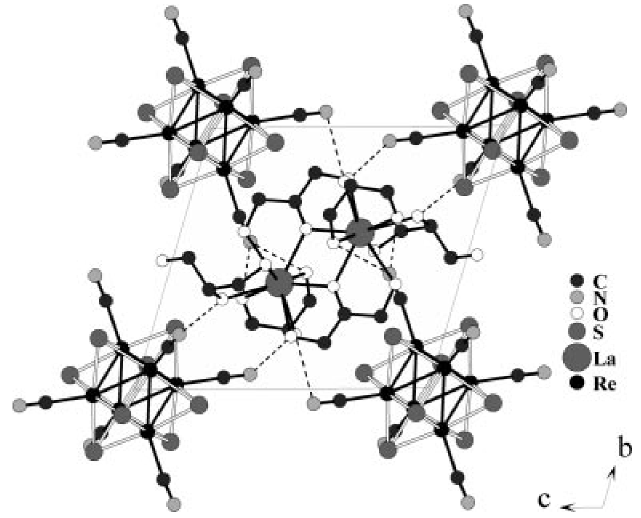
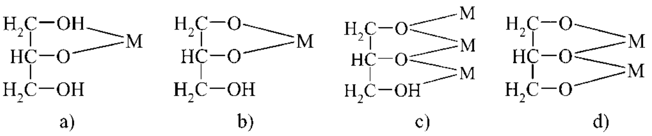


Figure 5. Crystal packing in the structure of **1**. Hydrogen atoms are omitted for clarity. Shortest N···O(OH) contacts are shown.



Scheme 2. Coordination modes of the glycerolate anions (H_2L^-, HL^{2-}, and L^{3-}) to transition metals in structurally characterized complexes; a) chelating coordination of H_2L^-;[13] b) chelating coordination of HL^{2-};[14–17] c) chelating/bridging coordination of HL^{2-};[18,19] d) chelating/bridging coordination of L^{3-}.[17,20]

There is only one crystal structure in which glycerol exists in the form of $[H_2L]^-$. Coordination of this ligand to a vanadium atom by one oxo- and one hydroxo group was found in oxo(propane-1,3-diol-2-olato)(salicylaldehyde hydroxyphenylmethylenehydrazonato-*N*,O,O′)vanadium(V)[13] (Scheme 2a). As in the cases of **1**–**6**, deprotonation of glycerol also occurred during crystallization in the presence of excess glycerol. The chelating coordination of HL^{2-} (Scheme 2b) has been reported for several molecular complexes of platinum,[14,15] vanadium,[16] and copper.[17] The glycerolate anions HL^{2-} and L^{3-} often served as both chelating and bridging ligands (Scheme 2c and d). These coordination modes were encountered in numerous complexes of transition metals, e.g. $CoHL$,[18] $ZnHL$,[19] $Li_3[Cu_3L_3]\cdot19H_2O$,[20] $Na_3[Cu_3L_3]\cdot7H_2O$, and $Na_{10}[Cu_3L_3]_3(NO_3)\cdot30H_2O$.[17]

Mass Spectra

In the ESI (positive mode) mass spectra of complex **1** in glycerol/water solution several peaks appear that clearly support the proposed structure. Specifically, an intense signal at $m/z = 207.2$ (75%) is assigned to $[La_2(\mu\text{-}H_2L)_2(H_3L)_4]^{4+}$. In addition, several mass peaks consistent with the association of this cation with glycerol molecules $\{[La_2(\mu\text{-}H_2L)_2(H_3L)_4]^{4+}\cdot(H_3L)_n\}$, $n = 2, 4, 6, 8$ [$m/z = 253.3$ (96%), 299.1 (100%), 345.1 (47%), 391.3 (10%)] are observed. The spectrum also contains minor peaks belonging to unidentified species. These data unequivocally confirm the presence of the $[La_2(\mu\text{-}H_2L)_2(H_3L)_4]^{4+}$ cations in solution that were observed in the solid state.

IR Spectra

The different coordination modes of glycerol molecules and the presence of the deprotonated H_2L^- species lead to changes in the vibrational frequencies of the ligand in complexes **1-6** relative to those of pure glycerol. In complexes **1**–**6** ν_{CO} vibrations are shifted to lower frequencies relative to those of the free ligand. For example, in complex **1** the ν_{CO} vibrations are shifted to 1095 and 1029 cm^{-1}, while in pure glycerol these vibrations are located at 1109 and 1034 cm^{-1}. The δ_{COH} vibrations centered at 1331 cm^{-1} in glycerol are shifted to higher frequencies and are split into several well-defined peaks. Although the vibrational frequencies of the glycerol ligand change upon coordination in compounds **1**–**6**, these frequencies are almost insensitive to nature of lanthanide(III) ions.

The ν_{CN} vibrations of $[Re_6Q_8(CN)_6]^{4-}$ are split into three peaks and are shifted to higher frequencies relative to those of $K_4[Re_6S_8(CN)_6]$ (2117 cm^{-1})[21] and $K_4[Re_6Se_8(CN)_6]\cdot3.5H_2O$ (2107 cm^{-1}).[22] The ν_{OH} vibrations in **1**–**6** gave broad bands in the range 3500–3250 cm^{-1} with no resolved lines in the spectra.

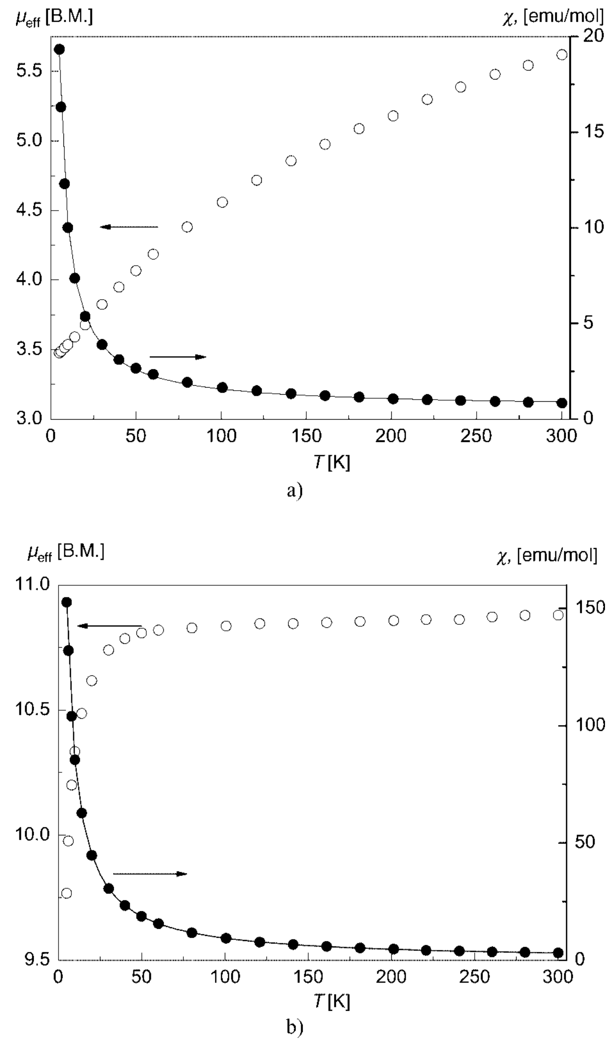
Magnetic Data

Magnetic measurements carried out in the range 5–300 K show that La compounds **1** and **4** are diamagnetic, while Nd and Gd compounds **2**, **3**, **5**, and **6** are paramagnetic.

Neodymium-containing compounds **2** and **5** demonstrate complex temperature dependence of the magnetic susceptibility and effective magnetic moments. The effective magnetic moments for these complexes at 300 K are 4.61 and

3.91 B.M. per Nd^{3+} cation (6.53 and 5.61 B.M. per $[Nd_2(H_2L)_2(H_3L)_4]^{4+}$ dimer), and 4.40 and 3.48 at 5 K – the moments gradually increase with an increase in temperature. The room-temperature values per ion appreciably exceed the usual value of 3.62 B.M. known for Nd^{III}.[23] Moreover, as illustrated in Figure 6a, even at 300 K the magnetic moment does not reach a plateau but continues to grow. Further studies are needed to interpret this behavior.

The effective magnetic moments for **3** and **6** at 300 K are 8.05 and 7.71 B.M. per Gd^{III} cation (11.38 and 10.9 B.M. per $[Gd_2(H_2L)_2(H_3L)_4]^{4+}$ dimer), which are close to the usual value of 7.9 B.M. for isolated Gd^{III} ions.[23] The behavior of the susceptibility upon a decrease in temperature of these complexes for gadolinium-containing compounds **3** and **6** is very similar. Magnetic susceptibility for these complexes can be satisfactorily described with Curie–Weiss law $\chi_M = C/(T - \theta)$. Fitting of the experimental data gave equations $\chi_M = 18.0/(T + 1.20)$ and $\chi_M = 14.83/(T + 1.10)$ for **3** and **6**, respectively. Such dependence is typical for Gd^{III} ions having a half-filled shell, $4f^7$. The values of θ are comparable to those found in other O-bridged Gd^{III} dimers.[24,25] The temperature-dependent magnetic data for **6** are shown in Figure 6b.



a)

b)

Figure 6. Magnetic susceptibility (solid circles) and effective magnetic moments (open circles) for **5** (a) and **6** (b).

Using equation

$$\theta = \frac{2S(S+1)}{3k_B}\sum_i^n z_i J_{ex,i}$$

for the case of two magnetic centers, we may estimate the exchange interactions in these dimers.[26] The values of J are –0.079 and –0.073 cm^{-1} for **3** and **6**, respectively, which correspond to very weak antiferromagnetic interactions between the two gadolinium cations in the $[Gd_2(H_2L)_2(H_3L)_4]^{4+}$ dimers.

Conclusions

Glycerol molecules effectively coordinate with rare earth cations resulting in the formation of a new dimeric moiety $[Ln_2(\mu\text{-}H_2L)_2(H_3L)_4]^{4+}$. The observation of three different binding modes of glycerol in these structures demonstrates that this ligand is very attractive and potentially may form numerous complexes with rare earth cations.

Experimental Section

The Materials and Methods

General: Elemental analyses for C, H, N, and S (Carlo Erba 1106) were performed in the Laboratory of Microanalysis of the Institute of Organic Chemistry, Novosibirsk. IR spectra were recorded on KBr disks with a Scimitar FTS 2000c spectrometer in the range 4000–375 cm^{-1}. Magnetic susceptibility measurements for powder samples were carried out in the temperature range from 5 to 300 K in an applied magnetic field of 100 G using a Quantum Design MPMS-5 SQUID magnetometer. The starting cluster compounds $K_4[Re_6S_8(CN)_6]$[21] and $K_4[Re_6Se_8(CN)_6]\cdot 3.5H_2O$[22] were synthesized as described previously. Other reagents were used as purchased.

Synthesis of $[La_2(H_2L)_2(H_3L)_4][Re_6S_8(CN)_6]$ (1): To a solution of $LaCl_3\cdot 7H_2O$ (150 mg, 0.404 mmol) in H_2O (20 mL) were added KOH (0.3 mL of a 0.1 M solution) and glycerol (3 mL), and the mixture was boiled for 15 min. The obtained clear solution was mixed with a solution of $K_4[Re_6S_8(CN)_6]$ (80 mg, 0.0474 mmol) in H_2O (10 mL) and boiled (evaporated under heating) until the precipitation of yellow-orange compound **1**. The crystals were filtered, washed with ethanol (4 × 10 mL), and dried in air. Yield: 75.5 mg (67.5%). $C_{24}H_{46}La_2N_6O_{18}Re_6S_8$: calcd. C 12.22, H 1.97, N 3.56; found C 12.42, H 2.00, N 3.66%. IR: ν_{CN} = 2118, 2129, 2141 cm^{-1}; ν_{CO} = 1095, 1029 cm^{-1}; δ_{COH} = 1361, 1348, 1334 cm^{-1}.

Synthesis of $[Nd_2(H_2L)_2(H_3L)_4][Re_6S_8(CN)_6]$ (2): Compound **2** was prepared using the same procedure, though $NdCl_3\cdot 6H_2O$ (150 mg, 0.418 mmol) was used instead of $LaCl_3\cdot 7H_2O$. Yield: 63.0 mg (56.1%). $C_{24}H_{46}Nd_2N_6O_{18}Re_6S_8$: calcd. C 12.17, H 1.96, N 3.55; found C 12.22, H 2.06, N 3.45%. IR: ν_{CN} = 2118, 2129, 2141 cm^{-1}; ν_{CO} = 1095, 1028 cm^{-1}; δ_{COH} = 1359, 1346, 1332 cm^{-1}.

Synthesis of $[Gd_2(H_2L)_2(H_3L)_4][Re_6S_8(CN)_6]$ (3): Compound **3** was prepared using the same procedure as for **1**, though $GdCl_3\cdot 6H_2O$ (150 mg, 0.404 mmol) was used instead of $LaCl_3\cdot 7H_2O$. Yield: 66.1 mg (58.2%). $C_{24}H_{46}Gd_2N_6O_{18}Re_6S_8$: calcd. C 12.04, H 1.94,

Table 3. Crystal data and structure refinement for **1**–**6**.

	1	**2**	**3**	**4**	**5**	**6**
Empirical formula	$C_{24}H_{46}La_2N_6O_{18}Re_6S_8$	$C_{24}H_{46}N_6Nd_2O_{18}Re_6S_8$	$C_{24}H_{46}Gd_2N_6O_{18}Re_6S_8$	$C_{24}H_{46}La_2N_6O_{18}Re_6Se_8$	$C_{24}H_{46}N_6Nd_2O_{18}Re_6Se_8$	$C_{24}H_{46}Gd_2N_6O_{18}Re_6Se_8$
Formula mass	2358.17	2368.83	2394.85	2733.37	2744.03	2770.05
Crystal system	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic
Space group, *Z*	$P\bar{1}$, 1	$P\bar{1}$, 1	$P\bar{1}$, 1	$P\bar{1}$, 1	$P\bar{1}$, 1	$P\bar{1}$, 1
a [Å]	10.0978(9)	10.0906(14)	10.1319(10)	10.2163(10)	10.2295(6)	10.2521(4)
b [Å]	10.8864(10)	10.8001(15)	10.7506(12)	10.9502(11)	10.8649(6)	10.7892(4)
c [Å]	11.8475(11)	11.6978(16)	11.7590(14)	11.8852(12)	11.8240(6)	11.8388(5)
α [°]	105.868(2)	105.917(5)	105.889(4)	105.343(5)	105.234(2)	104.975(1)
β [°]	97.791(1)	97.405(4)	97.354(4)	97.756(5)	97.445(2)	97.315(2)
γ [°]	94.010(1)	93.980(4)	93.793(4)	93.614(5)	93.566(2)	93.411(1)
V [Å^3]	1233.3(2)	1208.4(3)	1214.9(2)	1263.7(2)	1250.9(1)	1248.90(9)
D_x [g/cm^3]	3.175	3.255	3.273	3.592	3.643	3.683
μ [mm^{-1}]	16.756	17.483	17.982	21.785	22.375	22.987
Crystal size [mm]	0.15 × 0.10 × 0.10	0.20 × 0.15 × 0.14	0.33 × 0.20 × 0.15	0.28 × 0.16 × 0.15	0.05 × 0.06 × 0.10	0.10 × 0.10 × 0.15
2θ range [°]	1.81–25.00	3.39–25.00	1.82–25.00	2.91–25.00	1.81–25.00	1.80 to 25.00
Reflections collected/ unique	6373/4254	10141/4154	16883/4217	19948/4229	21168/4317	10800/4257
R_{int}	0.0178	0.0296	0.0228	0.0408	0.0265	0.0334
Refined parameters	280	298	281	280	290	281
$T_{min.}/T_{max.}$	0.345	0.349	0.500	0.455	0.536	0.470
R_1/wR_2 [$I > 2\sigma(I)$]	0.0321/0.0761	0.0333/0.0854	0.0211/0.0532	0.0353/0.0834	0.0294/0.0793	0.0407/0.1058
R_1/wR_2 (all data)	0.0372/0.0793	0.0370/0.0873	0.0233/0.0539	0.0529/0.0925	0.0364/0.0894	0.0533/0.1137
GoF	1.030	1.037	1.074	1.015	1.117	1.057

N 3.51; found C 12.00, H 1.90, N 3.43%. IR: ν_{CN} = 2118, 2131, 2143 cm^{-1}; ν_{CO} = 1093, 1022 cm^{-1}; δ_{COH} = 1359, 1344 cm^{-1}.

Synthesis of $[La_2(H_2L)_2(H_3L)_4][Re_6Se_8(CN)_6]$ (4): Compound **4** was prepared using the same procedure as for **1**, though $K_4[Re_6Se_8(CN)_6]\cdot 3.5H_2O$ (100 mg, 0.0471 mmol) instead of $K_4[Re_6S_8(CN)_6]$ was used. Yield: 78.8 mg (61.2%). $C_{24}H_{46}La_2N_6O_{18}Re_6Se_8$: calcd. C 10.55, H 1.70, N 3.07; found C 10.70, H 1.90, N 3.00%. IR: ν_{CN} = 2102, 2118, 2127 cm^{-1}; ν_{CO} = 1095, 1031 cm^{-1}; δ_{COH} = 1359, 1346, 1332 cm^{-1}.

Synthesis of $[Nd_2(H_2L)_2(H_3L)_4][Re_6Se_8(CN)_6]$ (5): Compound **5** was prepared using the same procedure as for **2**, though $K_4[Re_6Se_8(CN)_6]\cdot 3.5H_2O$ (100 mg, 0.0471 mmol) instead of $K_4[Re_6S_8(CN)_6]$ was used. Yield: 89.4 mg (69.2%). $C_{24}H_{46}Nd_2N_6O_{18}Re_6Se_8$: calcd. C 12.17, H 1.96, N 3.55; found C 10.50, H 1.69, N 3.06%. IR: ν_{CN} = 2102, 2118, 2127 cm^{-1}; ν_{CO} = 1095, 1029 cm^{-1}; δ_{COH} = 1359, 1346, 1332 cm^{-1}.

Synthesis of $[Gd_2(H_2L)_2(H_3L)_4][Re_6Se_8(CN)_6]$ (6): Compound **6** was prepared using the same procedure as for **3**, though $K_4[Re_6Se_8(CN)_6]\cdot 3.5H_2O$ (100 mg, 0.0471 mmol) instead of $K_4[Re_6S_8(CN)_6]$ was used. Yield: 92.0 mg (70.5%). For $C_{24}H_{46}Gd_2N_6O_{18}Re_6Se_8$: calcd. C 10.41, H 1.67, N 3.03; found C 10.10, H 1.80, N 2.90%. IR: ν_{CN} = 2104, 2120, 2129 cm^{-1}; ν_{CO} = 1095, 1028 cm^{-1}; δ_{COH} = 1357 cm^{-1}.

X-ray Structural Studies: Diffraction measurements were carried out by standard technique on a Bruker SMART AXS diffractometer equipped with a CCD area detector (**1**) and a Buker-Nonius X8Apex CCD (**2**–**6**) using graphite-monochromated Mo-K_α radiation. Details of diffraction experiments, structure solution and refinement parameters are given in Table 3. Absorption corrections were applied using the SADABS program.[27,28] The crystal structures were solved independently by direct methods and then refined using the SHELX package.[29] Hydrogen atoms of CH and CH_2 groups were refined geometrically. Hydrogen atoms of OH groups were located from last different electron density maps and fixed. Our attempts to refine them were unsuccessful. Final refinement was done by full-matrix least-squares method. All non-hydrogen atoms were refined anisotropically. CCDC-269462 to -269467 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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