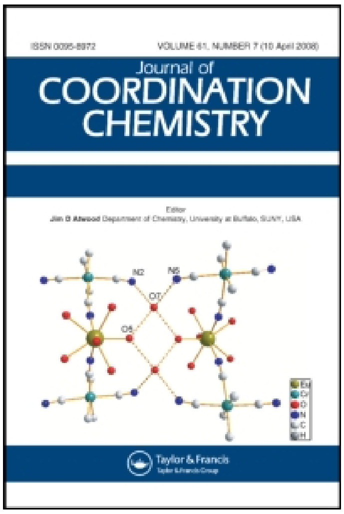

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Synthesis, crystal structures and magnetism of lanthanide(III) binuclear complexes $[Ln_2(\mu_{1,3}\text{-}CH_3CO_2)_2(SCN^-)_4L_2(H_2O)_6]$ (Ln = Gd(III) and Eu(III), L = 4-methylpyridine N-oxide)

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Synthesis, crystal structures and magnetism of lanthanide(III) binuclear complexes $[Ln_2(\mu_{1,3}\text{-}CH_3CO_2)_2(SCN^-)_4L_2(H_2O)_6]$ (Ln = Gd(III) and Eu(III), L = 4-methylpyridine N-oxide)

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Two lanthanide(III) binuclear complexes have been synthesized with acetate as bridging ligand and 4-methylpyridine N-oxide (L), SCN^- and H_2O as terminal ligands and structurally determined by X-ray crystallography. Both crystals $[Gd_2(\mu_{1,3}\text{-}CH_3CO_2)_2(SCN^-)_4(L)_2(H_2O_6)$ (**1**) and $[Eu_2(\mu_{1,3}\text{-}CH_3CO_2)_2(SCN^-)_4(L)_2(H_2O)_6]$ (**2**) belong to monoclinic with space group $P2_1/n$. The relevant cell parameters are as follows: $a = 9.0034(12)$ Å, $b = 15.998(2)$ Å, $c = 12.1277(17)$ Å, $\beta = 100.625(2)^\circ$ for complex **1**; and $a = 9.0168(18)$ Å, $b = 15.990(3)$ Å, $c = 12.142(2)$ Å, $\beta = 100.734(3)^\circ$ for complex **2**; The two lanthanide(III) ions are bridged by two acetate anions forming a binuclear unit, in which L, SCN^- and H_2O as unidentate terminal ligands take part in the coordination. The variable-temperature magnetic susceptibility of **1** was measured in the 4–300 K range; fitting for the susceptibility data reveals that there is no magnetic interaction between the bridged Gd(III) ions.

Keywords: Crystal structure; Lanthanide(III) complex; Magnetism; Aromatic N-oxide; Thiocyanate

1. Introduction

Research has focused on magnetic coupling behavior of multi-nuclear complexes applied to preparation of molecular-based magnets and understanding of biological function of some metallic proteins [1]. Acetate, thiocyanate and pyridine N-oxide and its derivatives are useful bridging ligands and a number of multi-nuclear complexes [2–5] have been synthesized; some exhibit interesting magnetic coupling properties. In order to understand the factors that affect magnetic coupling in complexes with acetate as bridging ligand we prepared the title binuclear complexes and report their synthesis, crystal structures and the magnetic coupling of **1**.

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2. Experimental

2.1. *Reagents*

L was prepared according to the method of literature [6]. Other chemicals were analytical grade and used without further purification.

2.2. *Preparation of [$Gd_2(\mu_{1,3}$-$CH_3CO_2)_2(SCN^-)_4L_2(H_2O)_6$] (1)*

$Gd(ClO_4)_3 \cdot 6H_2O$ (0.3526 g, 0.626 mmol), NaSCN (0.1024 g, 1.26 mmol), 4-methylpyridine N-oxide (0.0702 g, 0.643 mmol) and $Na(CH_3COO)$ (0.0516 g, 0.629 mmol) were dissolved in 5 mL of water, respectively, and then the four solutions were mixed together and stirred for a few minutes. Colorless transparent single crystals were obtained after the mixed solution was allowed to stand for two weeks at room temperature. Yield: 56% (based on L). Anal. Calcd For $C_{20}H_{32}Gd_2N_6O_{12}S_4$: C, 24.23; H, 3.25; N, 8.48; Gd, 31.73%. Found: C, 24.08; H, 3.01; N, 8.82; Gd, 32.29%.

2.3. *Preparation of [$Eu_2(\mu_{1,3}$-$CH_3CO_2)_2(SCN^-)_4L_2(H_2O)_6$] (2)*

The preparation method of **2** is identical with **1** except $Gd(ClO_4)_2 \cdot 6H_2O$ was replaced by $Eu(ClO_4)_3 \cdot 6H_2O$. The yield of the colorless transparent single crystals is 62% (based on L). Anal. Calcd For $C_{20}H_{32}Eu_2N_6O_{12}S_4$: C, 24.49; H, 3.29; N, 8.57; Eu, 30.99%. Found: C, 24.19; H, 3.18; N, 8.61; Eu, 31.75%.

2.4. *Physical measurements*

Infrared spectra were recorded with a Bruker Tensor 27 infrared spectrometer in the 4000–500 cm^{-1} region using KBr discs. C, H and N elemental analyses were carried out on a Perkin-Elmer 240 instrument, and Gd and Eu were measured through EDTA titration. Variable-temperature magnetic susceptibilities of microcrystalline powder samples of **1** were measured in a magnetic field of 3 KOe in the temperature range 4–300 K on a SQUID magnetometer. The data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from Pascal's constants.

2.5. *Crystal structures determination*

The suitable single crystals of **1** and **2** were selected and subsequently glued to the tip of a glass fiber. Determinations of the crystal structures at 25°C were carried out on an X-ray diffractometer, Model Bruker Smart-1000 CCD using graphite-monochromatic Moka radiation ($\lambda = 0.71073$ Å). Corrections for *Lp* factors were applied and all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms from H_2O were located in difference Fourier map and other hydrogen atoms were placed in calculated positions and all hydrogen atoms were refined using a riding model in their as-found relative positions. The programs for structure solution and refinement were SHELXTL (Bruker, 2001). Crystal structures and data collections and refinement parameters for **1** and **2** are listed in table 1, and selected bond lengths and angles for **1** and **2** are given in tables 2 and 3, respectively.

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

	1	**2**
Empirical formula	$C_{20}H_{32}Gd_2N_6O_{12}S_4$	$C_{20}H_{32}Eu_2N_6O_{12}S_4$
CCDC deposit no.	266,810	261,100
Formula weight	991.26	980.68
Temperature (K)	298	298
Crystal size (mm^3)	0.30 × 0.18 × 0.11	0.21 × 0.10 × 0.08
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a (Å)	9.0034(12)	9.0168(18)
b (Å)	15.998(2)	15.990(3)
c (Å)	12.1277(17)	12.142(2)
β (°)	100.625(2)	100.734(3)
Volume (Å^3)	1716.9(4)	1720.0(6)
Density (calculated) (Mg m^{-3})	1.917	1.894
Absorption coefficient (mm^{-1})	4.134	3.917
$\theta_{\min}$, $\theta_{\max}$ (°)	2.13; 26.00	2.13; 27.09
Measured reflections	9334	9862
Independent reflections	3346	3749
Observed reflections	3055($I > 2\sigma(I)$)	3015($I > 2\sigma(I)$)
Completeness (%)	0.995 ($\theta = 26.00°$)	0.985($\theta = 27.09°$)
Goodness-of-fit on F^2	1.040	1.034
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0285$ $wR_2 = 0.0645$	$R_1 = 0.0415$ $wR_2 = 0.0755$
R indices (all data)	$R_1 = 0.0318$ $wR_2 = 0.0658$	$R_I = 0.0561$ $wR_2 = 0.0807$
Largest diff. peak and hole (e Å^{-3})	0.895 −0.570	0.860 −0.890

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

Gd1–O2	2.349(3)	Gd1–O1	2.376(3)	Gd1–O5	2.438(2)
Gd1–N1	2.457(4)	Gd1–N2	2.471(4)	Gd1–O6	2.496(3)
Gd1–O4	2.390(3)	GD1–O3A	2.421(3)		
O2–Gd1–O1	78.52(10)	O2–Gd1–O4	139.42(10)		
O1–Gd1–O4	140.14(10)	O2–Gd1–O3A	109.86(9)		
O1–Gd1–O3A	75.55(10)	O4–Gd1–O3A	78.40(9)		
O2–Gd1–O5	72.65(9)	O1–Gd1–O5	130.08(9)		
O4–Gd1–O5	70.77(9)	O3A–Gd1–O5	77.17(9)		
O2–Gd1–N1	81.97(11)	O1–Gd1–N1	78.25(12)		
O4–Gd1–N1	112.38(12)	O3A–Gd1–N1	148.14(12)		
O5–Gd1–N1	134.42(12)	O2–Gd1–N2	149.30(11)		
O1–Gd1–N2	76.12(11)	O4–Gd1–N2	70.07(11)		
O3A–Gd1–N2	80.18(11)	O5–Gd1–N2	137.79(10)		
N1–Gd1–N2	76.19(13)	O2–Gd1–O6	81.99(10)		
O1–Gd 1–O6	144.54(10)	O4–Gd1–O6	69.32(10)		
O3a–Gd1–O6	139.45(10)	O5–Gd1–O6	69.58(9)		
N1–Gd1–O6	69.87(12)	N2–Gd1–O6	109.69(12)		

Symmetry transformation: O3A: $-x+2$, $-y+2$, $-z$.

Table 3. Selected bond distance (Å) and angles (°) for **2**.

Eu1–O2	2.367(4)	Eu1–O1	2.387(4)	Eu1–O4	2.394(4)
Eu1–O6	2.425(4)	Eu1–O5	2.448(3)	Eu1–N3	2.471(5)
Eu1–N2	2.485(5)	Eu1–O3	2.510(4)	Eu1–O2A	2.952(4)
O2–Eu1–O1	78.79(13)		O2–Eu1–O4		139.41(13)
O1–Eu1–O4	139.94(13)		O2–Eu1–O6		110.33(12)
O1–Eu1–O6	75.49(13)		O4–Eu1–O6		78.26(12)
O2–Eu1–O5	72.66(12)		O1–Eu1–O5		130.52(12)
O4–Eu1–O5	70.71(12)		O6–Eu1–O5		77.73(12)
O2–Eu1–N3	81.94(15)		O1–Eu1–N3		78.33(16)
O4–Eu1–N3	112.22(16)		O6–Eu1–N3		147.97(15)
O5–Eu1–N3	134.08(14)		O2–Eu1–N2		149.29(14)
O1–Eu1–N2	75.98(14)		O4–Eu1–N2		70.01(14)
O6–Eu1–N2	79.91(15)		O5–Eu1–N2		137.84(14)
N3–Eu1–N2	76.09(17)		O2–Eu1–O3		81.99(13)
O1–Eu1–O3	144.66(14)		O4–Eu1–O3		69.22(13)
O6–Eu1–O3	139.48(13)		O5–Eu1–O3		69.28(12)
N3–Eu1–O3	69.78(15)		N2–Eu1–O3		109.49(15)
O2–Eu1–O2A	63.91(13)		O1–Eu1–O2A		64.55(11)
O4–Eu1–O2A	114.81(12)		O6–Eu1–O2A		46.49(11)
O5–Eu1–O2A	66.75(11)		N3–Eu1–O2A		132.91(15)
N2–Eu1–O2A	118.35(14)		O3–Eu1–O2A		130.32(12)

Symmetry transformation: O2A: $-x+1$, $-y$, $-z$.

3. Results and discussion

3.1. *Crystal structure of 1*

Figure 1 shows the coordination diagram with atom numbering scheme of **1**. The Gd1 atom is coordinated by O1, O2, O3A, O4, O5, O6, N1 and N2 atoms, in which O4, O5 and O6 are from three H_2O molecules, O1 from L ligand, N1 and N2 from two thiocyanate anions, O2 and O3A atoms from two acetate bridging ligands. The data from table 2 indicate that Gd1 lies in a square antiprism coordination environment. In this crystal the two Gd(III) ions with separation of 4.546 Å were connected by two acetate bridging anions forming a binuclear complex. Table 4 shows the hydrogen bonds in the crystal; in addition to intra-complex hydrogen bonds there are hydrogen bonds between neighbour complexes. In addition to hydrogen bonds there is significant π–π stacking between neighbouring pyridine rings with distances $\mathrm{Cg} \cdots \mathrm{Cg}^{\mathrm{i}} = 4.093(3)$ Å and $\mathrm{Cg} \cdots \mathrm{Cg}^{\mathrm{i}}_{\mathrm{perp}} = 3.520$ A (symmetry code (i): $2-x$, $2-y$, $1-z$; Cg is the centroid of pyridine ring N3/C1–C5; $\mathrm{Cg} \cdots \mathrm{Cg}^{\mathrm{i}}_{\mathrm{perp}}$ is the perpendicular distance from Cg to ring Cg^{i}). Hydrogen bonds and the π–π stacking interactions stabilize the binuclear complex.

3.2. *Crystal structure of 2*

Figure 2 displays the coordination structure of **2**, and table 3 gives the relevant coordinated bond lengths and the associated angles. From figure 2 and table 3, **2** is almost identical with **1** in coordination structure except minor differences between the bond lengths and the angles, attributable to lanthanide contraction. In **2** there also exist

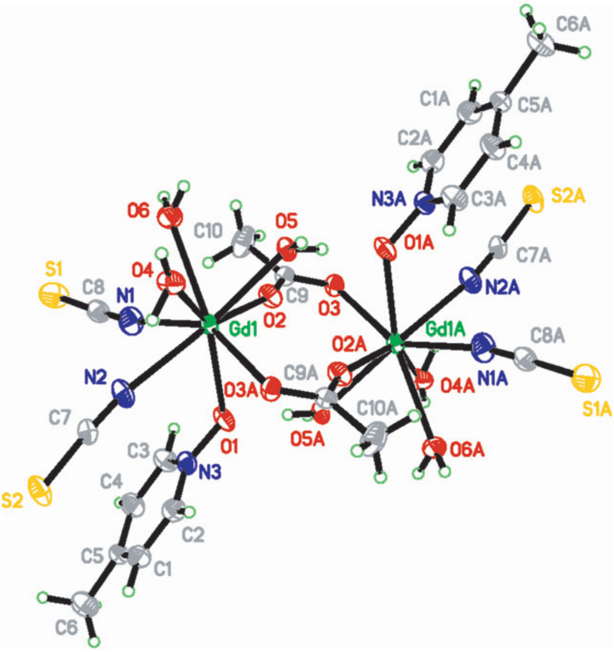

Figure 1. Coordination diagram of **1** with the atom numbering scheme.

Table 4. Hydrogen bond distances (Å) and bond angles (°) for **1** and **2**.

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠D–H···A
1				
O4–H16···N2	0.888	2.207	2.791	122.95
O5–H7···O1^{i}	0.89	1.79	2.680(4)	175.4
O4–H16···O3^{ii}	0.89	2.09	2.693(4)	124.1
O5–H5···S1^{iii}	0.89	2.63	3.229(3)	125.2
O5–H7···N3^{iv}	0.89	2.60	3.420(4)	154.1
O5–H6···S2^{v}	0.89	2.40	3.279(3)	168.2
O6–H9···S2^{vi}	0.90	2.49	3.336(3)	158.1
O6–H8···S1^{vii}	0.89	2.79	3.608(3)	151.7
2				
O5–H1···O1^{i}	0.90	1.78	2.673(5)	176.1
O4–H6···O6^{ii}	0.90	1.79	2.688(5)	173.4
O4–H5···S2^{iii}	0.89	2.35	3.237(4)	169.4
O5–H2···S1^{iv}	0.90	2.38	3.281(4)	177.3
O5–H1···N1^{v}	0.90	2.62	3.417(6)	148.6
O3–H3···S2^{vi}	0.89	2.76	3.626(5)	162.7
O3–H4···S1^{vii}	0.89	2.46	3.328(4)	164.8

Symmetry codes for 1: (i) $-x+2, -y+2, -z$; (ii) $x-1, y, z$; (iii) $x-1/2, -y+3/2, z-1/2$; (iv) $-x+2, -y+2, -z$; (v) $-x+1, -y+2, -z$; (vi) $x+1/2, -y+3/2, z-1/2$; (vii) $x-1/2, -y+3/2, z-1/2$; for **2**: (i) $-x+1, -y, -z$; (ii) $-x, -y, -z$; (iii) $x-1/2, -y+1/2, z-1/2$; (iv) $-x, -y, -z$; (v) $-x+1, -y, -z$; (vi) $x-1/2, -y+1/2, z-1/2$; (vii) $x+1/2, -y+1/2, z-1/2$.

hydrogen bonds between neighbouring complexes as shown in table 4, and almost identical π–π stacking interactions between the neighbouring pyridine rings (Cg represents pyridine ring and Cg···Cg^{i} = 4.061(4) Å and Cg···Cg$^{i}_{perp}$ = 3.522 A; symmetry code (i): $1-x, -y, 1-z$).

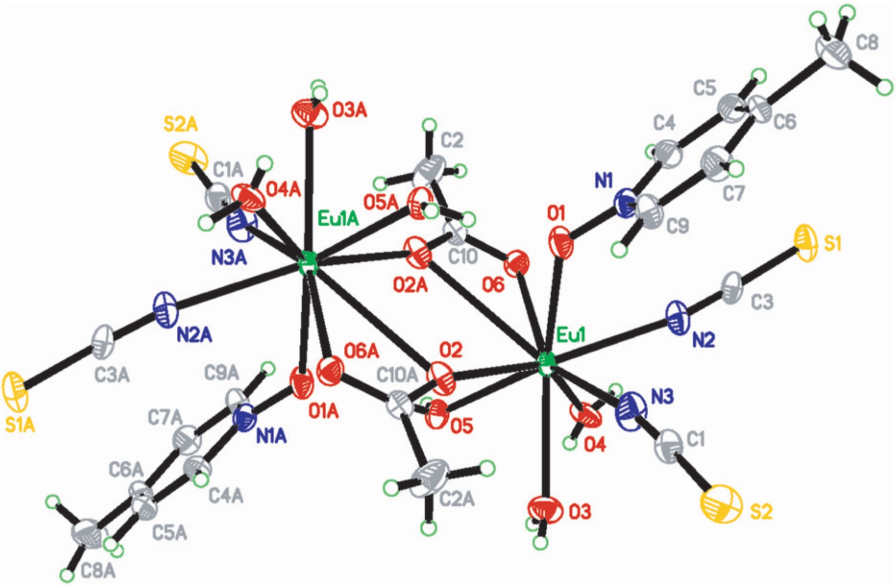

Figure 2. Coordination diagram of **2** with the atom numbering scheme.

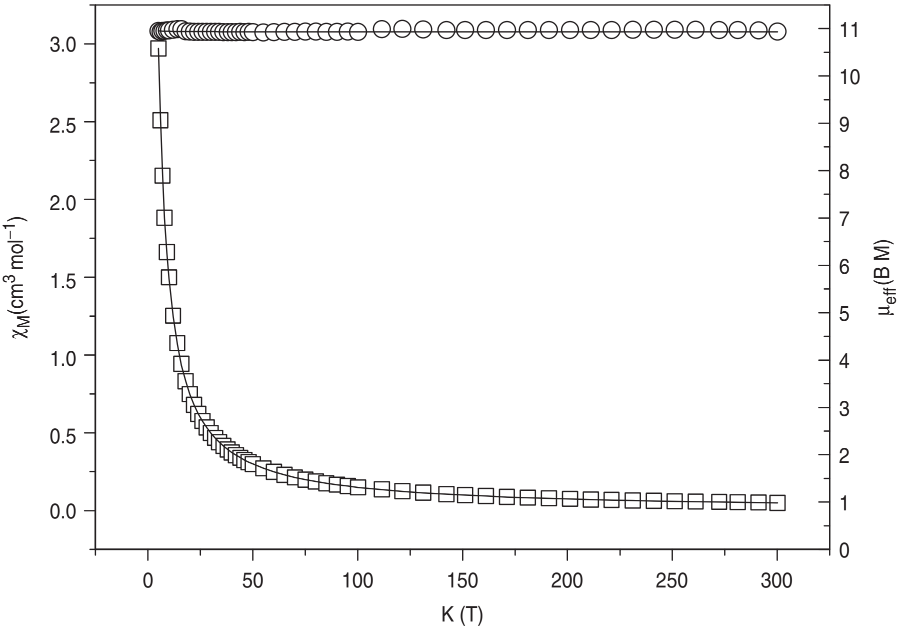

Figure 3. Plots of χ_M (open squares for experimental data, curve for theoretical value) and μ_{eff} (open circles for experimental data, curve for theoretical values) *vs.* *T* for the complex.

3.3. *Infrared spectra*

The characteristic absorption of NCS^- appears at 2080(s) cm^{-1} for 1 and 2093(s) cm^{-1} for **2**. The peaks at 1605(s) and 1460(s) for **1**, 1602(s) and 1460(s) for **2** may be attributed to the asymmetric (ν_{as}) and symmetric (ν_s) vibrations of the carboxyl groups, and the small separation between asymmetric and symmetric vibrations suggests that carboxyl groups are bidentate in agreement with the X-ray result. The peaks at 1549(s) and 1492(s) for **1** and 1548(s) for **2** may arise from the vibrations of the pyridine N-oxide.

3.4. *Magnetic properties*

The variable temperature (5–300 K) magnetic susceptibility was measured and the experimental results are shown in figure 3, where χ_M is the molar magnetic susceptibility per binuclear Gd(III) unit, and μ_{eff} is the magnetic moment for binuclear Gd(III) ions. Figure 3 displays that the χ_M values increase with decreasing temperature. The μ_{eff} value at 300 K is 10.94 BM which is close to the expected value for an isolated binuclear Gd(III) (11.22 for $g_{av} = 2$) at room temperature, and the μ_{eff} values show little change with temperature drop and the value at 5.05 K is 10.95 BM, which implies a very weak anti-ferromagnetic coupling between the bridged binuclear Gd(III) ions. The fitting of the magnetic susceptibilities was made with the binuclear Gd(III) formula [7] as shown in following equation, deduced from the isotropic spin Hamiltonian $\boldsymbol{H} = J\mathbf{S}_{Gd1}\mathbf{S}_{Gd2}(\mathbf{S}_{Gd1} = \mathbf{S}_{Gd2} = 7/2)$.

$$
\begin{aligned}
\chi_M &= \left[\frac{(2N\beta^2 g^2)}{kT}\right]\left[\frac{A}{B}\right]\\
A &= \exp(x) + 5\ \exp(3x) + 14\ \exp(6x) + 30\ \exp(10x)\\
&\quad + 55\ \exp(15x) + 91\ \exp(21x) + 140\ \exp(28x)\\
B &= 1 + 3\ \exp(x) + 5\ \exp(3x) + 7\ \exp(6x) + 9\ \exp(10x)\\
&\quad + 11\ \exp(15x) + 13\ \exp(21x) + 15\ \exp(28x)\\
x &= \frac{J}{(kT)}
\end{aligned}
$$

The theoretical model gave a good fitting with the experimental data and the agreement factor $R = 9.95 \times 10^{-6}$ [R is defined as $R = \Sigma(\chi_{Obsd} - \chi_{Calcd})^2/(\chi_{Obsd})^2$], $g = 1.95$ and $J = -0.002\ cm^{-1}$. $J = -0.002\ cm^{-1}$ means that there is no magnetic interaction between the acetate bridged binuclear Gd(III) ions, whereas the magnetic interaction of the similar binuclear Gd(III) complex, $[Gd_2(\mu\text{-}CH_3CO_2)_4(CH_3COO)_2(phen)_2]$ [7], exhibits $J = 0.053\ cm^{-1}$.

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