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Two novel types of Ln_2M_2 clusters bridged by cyanide and carboxylate simultaneously

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Abstract

Two novel complexes $[Sm_2(Ac)_2(phen)_4(H_2O)_2\{Fe(CN)_5(NO)\}_2]$ **1** and $[Dy_2(Ac)_2(phen)_4(H_2O)_2\{Fe(CN)_5(NO)\}_2] \cdot 8H_2O$ **2** have been synthesized and structurally and magnetically characterized. Complex **1** crystallizes in the orthorhombic space group of $Aba2$ with $a = 18.6179(3)$, $b = 16.2001(3)$, $c = 20.9875(4)$ Å, and $Z = 4$, while complex **2** crystallizes in the monoclinic space group $P2_1/n$ with $a = 12.0748(3)$, $b = 27.3276(5)$, $c = 22.9096(6)$ Å, $\beta = 93.1001(8)^\circ$, and $Z = 4$. A cyanide and carboxylate anions are bridging tetranuclear clusters, but exhibit different structural features. In **1**, two $[Fe(CN)_5(NO)]^{2-}$ fragments connect the same Sm^{3+} cation in a $[Sm_2(Ac)_2]$ dimer unit to produce a T-shaped motif. In **2**, two $[Fe(CN)_5(NO)]^{2-}$ fragments attach to the two different Dy^{3+} cations in a $[Dy_2(Ac)_2]$ dimer unit, leading to a U-shaped topology. Both examples represent novel structural types among tetranuclear Ln_2M_2 clusters.

Keywords: Lanthanide complexes; Crystal structures; Clusters; Cyanide; Carboxylate; Magnetism

1. Introduction

Polynuclear complexes containing both 4*f* and 3*d* ions have generated great interest in view of their magnetic and electronic properties [1]. Cyanide [2] and carboxylate [3] are suitable candidates for the assembly of 4*f*−3*d* complexes. Many fascinating structures have been synthesized based on the two types of ligands, respectively. $[Fe(CN)_5(NO)]^{2-}$ complexes are known to have metal-to-ligand charge transfer transitions in their optical spectra and extremely long-lived electronic excited states. [4] In the past, the structures and properties of alkali, alkaline earth and transition metals complexes with nitrosylpentacyanoferrates were reported [5]. However, nitroprusside complexes with lanthanide ions were rarely investigated [6]. Here, we present two novel 4*f*−3*d* clusters $[Sm_2(Ac)_2(phen)_4(H_2O)_2\{Fe(CN)_5(NO)\}_2]$ **1** and $[Dy_2(Ac)_2(phen)_4(H_2O)_2\{Fe(CN)_5(NO)\}_2] \cdot 8H_2O$ **2** with simultaneously bridging cyanide and acetate in tetranuclear clusters, which exhibit novel structural types.

2. Experimental

2.1. Synthesis of $[Sm_2(Ac)_2(phen)_4(H_2O)_2\{Fe(CN)_5(NO)\}_2]$ (1)

Compound **1** was prepared by mixing $Na_2[Fe(CN)_5(NO)]$ (1 mmol) and samarium (III) acetate (1 mmol) in 30 mL aqueous solution under stirring and heating, followed by the addition of 10 mL ethanol solution of phenanthroline (2 mmol). The mixture was subsequently heated for 0.5 h. Then the resulting solution was condensed and filtered. The filtrate was allowed to stand at room temperature. After 3 weeks, red needle-like crystals were obtained (yield: 67%). Elemental analysis: Calculated for $C_{62}H_{42}Fe_2N_{20}O_8Sm_2$: C, 46.27; H, 2.61; N, 17.41. Found: C, 46.53; H, 2.82; N, 17.35. IR: 3802w, 3417s, 3219s, 3064m, 3021w, 2164m, 2141s, 1914vs, 1625s, 1573vs, 1520s, 1450 s, 1427 s, 1343w, 1225w, 1142w, 1103w, 1054w, 1024w, 863m, 856s, 785w, 731s, 659m, 639m, 500w, 408m cm^{-1}.

2.2. Synthesis of $[Dy_2(Ac)_2(phen)_4(H_2O)_2\{Fe(CN)_5(NO)\}_2] \cdot 8H_2O$ (2)

Compound **2** was synthesized according to the same procedure as **1** using dysprosium (III) acetate instead

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of samarium (III) acetate (yield 62%). Elemental analysis: Calculated for $C_{62}H_{58}Dy_2Fe_2N_{20}O_{16}$: C, 30.5; H, 3.70; N, 3.23. Found: C, 29.8; H, 3.88; N, 3.12. IR: 3801w, 3418s, 3230s, 3066m, 3021w, 2166s, 2150s, 2141s, 1914vs, 1627s, 1577vs, 1521s, 1451s, 1427s, 1350 m, 1226w, 1143m, 1104m, 1054w, 1024m, 857s, 777w, 731s, 659m, 639m, 504w, 438w, 409m cm^{-1}.

2.3. *Physical measurements*

Elemental analyses of C, H, N were performed by a Carlo Erba 1106 elemental analyzer. IR spectra were recorded as KBr pellets on a Nicolet 750 FTIR in the 400–4000 cm^{-1} region. Magnetic susceptibility of crystal samples restrained in parafilm was measured on an Oxford Maglab 2000 system. Diamagnetic corrections were applied for magnetic susceptibility data using Pascal's constants.

2.4. *Crystallography*

A red crystal of each **1** (0.40 × 0.30 × 0.30 mm) and **2** (0.36 × 0.32 × 0.24 mm) was selected for the X-ray diffraction structural analysis. The data collections were performed on a Nonius Kappa CCD diffractometer with graphite monochromatized Mo-$K\alpha$ radiation (0.71073 Å) at 293 K. The structures were solved by direct methods and refined by full matrix least-squares techniques based on F^2 using the SHELX-97 program. [7] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of water molecules were located from a difference Fourier map and refined with a rigid model for **1**, but were not found for **2**. All organic hydrogen atoms were placed on calculated positions. The details of crystal data for compounds **1** and **2** are listed in Table 1. Atomic coordinates and U_{eq} values are given in Tables 2 and 3, and selected bond lengths and angles are given in Tables 4 and 5, respectively.

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

Compound	**1**	**2**
Formula	$C_{62}H_{42}Fe_2N_{20}O_8Sm_2$	$C_{62}H_{58}Dy_2Fe_2N_{20}O_{16}$
Formula weight	1607.56	1776.00
Crystal system	Orthorhombic	Monoclinic
Space group	$Aba2$ (No. 41)	$P2_1/n$ (No. 14)
a(Å)	18.6179(3)	12.0748(3)
b(Å)	16.2001(3)	27.3276(5)
c(Å)	20.9875(4)	22.9096(6)
β(°)	90	93.1001(8)
V(Å^3)	6330.1(2)	7548.5(3)
Z	4	4
D_{calc}(Mg/m^3)	1.687	1.579
μ(mm^{-1})	2.349	2.410
F(000)	3176	3528
Unique/observed ref.	7543/6024	17896/11305
R_{int}	0.0577	0.0825
Flack parameter	0.00	
GoF	1.013	1.030
$R1$ and w$R2[I > 2\sigma(I)]$	0.0232,0.0486	0.0518,0.1153

3. Results and discussions

3.1. *Description of the structure*

X-ray structural analyses revealed that compounds **1** and **2** (Figs. 1 and 2) consist of tetranuclear Ln_2Fe_2

Table 2
Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for **1**. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U_{eq}
Sm(1)	0	0	2676(1)	22(1)
Sm(2)	0	0	83(1)	23(1)
Fe(1)	2853(1)	448(1)	730(1)	28(1)
O(1)	3474(2)	−1073(2)	1017(2)	80(1)
O(2)	460(1)	844(2)	1889(1)	39(1)
O(3)	119(1)	950(2)	884(1)	46(1)
O(4)	1145(1)	578(1)	3068(1)	33(1)
N(1)	1319(2)	−71(2)	356(1)	36(1)
N(2)	2320(2)	2226(2)	481(2)	50(1)
N(3)	4258(2)	1358(3)	1058(2)	65(1)
N(4)	2229(1)	699(2)	2082(1)	43(1)
N(5)	3261(2)	408(2)	−697(2)	52(1)
N(6)	3201(2)	−469(2)	888(1)	43(1)
N(7)	−378(2)	1352(2)	−435(1)	32(1)
N(8)	715(1)	455(2)	−943(1)	33(1)
N(9)	408(1)	−1000(2)	3586(1)	30(1)
N(10)	998(1)	−1036(2)	2395(1)	28(1)
C(1)	1896(2)	98(2)	490(2)	30(1)
C(2)	2508(2)	1562(2)	572(1)	34(1)
C(3)	3739(2)	1017(2)	933(2)	39(1)
C(4)	2476(2)	615(2)	1591(2)	32(1)
C(5)	3119(2)	429(2)	−167(2)	35(1)
C(6)	−875(2)	1831(2)	−182(2)	42(1)
C(7)	−1240(2)	2444(2)	−517(2)	50(1)
C(8)	−1078(2)	2554(3)	−1134(2)	52(1)
C(9)	−546(2)	2085(2)	−1433(2)	39(1)
C(10)	−342(2)	2189(3)	−2079(2)	54(1)
C(11)	178(2)	1717(3)	−2336(2)	57(1)
C(12)	553(2)	1112(2)	−1971(2)	42(1)
C(13)	1124(2)	644(3)	−2213(2)	56(1)
C(14)	1493(2)	125(3)	−1815(2)	57(1)
C(15)	1272(2)	46(2)	−1186(2)	41(1)
C(16)	369(2)	998(2)	−1325(2)	33(1)
C(17)	−197(2)	1485(2)	−1058(2)	32(1)
C(18)	122(2)	−1012(2)	4163(2)	35(1)
C(19)	382(2)	−1479(3)	4671(2)	44(1)
C(20)	956(2)	−1979(3)	4565(2)	51(1)
C(21)	1274(2)	−2015(2)	3961(2)	42(1)
C(22)	1847(2)	−2564(3)	3808(2)	58(1)
C(23)	2105(2)	−2616(3)	3213(2)	54(1)
C(24)	1836(2)	−2104(2)	2713(2)	40(1)
C(25)	2087(2)	−2144(2)	2079(2)	46(1)
C(26)	1798(2)	−1642(2)	1633(2)	42(1)
C(27)	1260(2)	−1086(2)	1805(2)	35(1)
C(28)	1279(2)	−1540(2)	2847(2)	31(1)
C(29)	980(2)	−1502(2)	3483(2)	31(1)
C(30)	427(1)	1225(2)	1375(2)	28(1)
C(31)	755(2)	2062(2)	1325(2)	54(1)

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å $\times 10^3$) for **2**. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U_{eq}
Dy(1)	3771(1)	4241(1)	7604(1)	36(1)
Dy(2)	4212(1)	2426(1)	7129(1)	35(1)
Fe(1)	7092(1)	5357(1)	6733(1)	39(1)
Fe(2)	7667(1)	1619(1)	5954(1)	47(1)
O(1)	8632(2)	5006(1)	7573(1)	87(1)
O(2)	9301(2)	1862(1)	6806(1)	76(1)
O(3)	4921(1)	3672(1)	7240(1)	57(1)
O(4)	5713(1)	2946(1)	7284(1)	48(1)
O(5)	3310(1)	3582(1)	8139(1)	55(1)
O(6)	3628(1)	2814(1)	7925(1)	52(1)
O(7)	5162(2)	4245(1)	8354(1)	79(1)
O(8)	5246(1)	1950(1)	7830(1)	55(1)
O(9)	7832(3)	2442(1)	7622(2)	173(2)
O(10)	476(5)	223(3)	4624(4)	471(6)
O(11)	8048(2)	−856(1)	312(1)	79(1)
O(12)	−703(7)	3864(3)	8941(2)	205(3)
O(12′)	−178(8)	3335(5)	8780(4)	374(6)
O(13)	10719(3)	1497(1)	4128(1)	178(2)
O(14)	4938(2)	1684(1)	8912(1)	66(1)
O(15)	3131(2)	1695(1)	9523(1)	96(1)
O(16)	2983(9)	586(3)	3994(4)	250(5)
O(16′)	2321(3)	437(1)	3441(2)	95(2)
N(1)	2784(2)	4620(1)	8447(1)	47(1)
N(2)	2684(1)	5045(1)	7370(1)	38(1)
N(3)	1774(2)	4057(1)	7258(1)	41(1)
N(4)	3399(2)	4225(1)	6513(1)	38(1)
N(5)	5143(2)	4854(1)	7317(1)	46(1)
N(6)	5240(2)	5757(1)	5885(1)	66(1)
N(7)	7038(2)	4462(1)	5909(1)	64(1)
N(8)	8851(2)	5801(1)	5965(1)	69(1)
N(9)	7139(3)	6392(1)	7286(1)	90(1)
N(10)	8015(2)	5144(1)	7220(1)	49(1)
N(11)	2755(1)	1839(1)	7502(1)	40(1)
N(12)	3358(2)	1813(1)	6380(1)	42(1)
N(13)	4273(2)	2882(1)	6174(1)	45(1)
N(14)	2367(2)	2788(1)	6747(1)	44(1)
N(15)	5745(2)	2000(1)	6659(1)	45(1)
N(16)	7428(2)	548(1)	6335(1)	102(1)
N(17)	5841(2)	1388(1)	5000(1)	120(1)
N(18)	7798(2)	2638(1)	5412(1)	100(1)
N(19)	9334(2)	1253(1)	5081(1)	87(1)
N(20)	8644(2)	1752(1)	6463(1)	48(1)
C(1)	2875(2)	4441(1)	8979(1)	58(1)
C(2)	2252(3)	4606(1)	9439(1)	78(1)
C(3)	1475(2)	4958(1)	9332(1)	72(1)
C(4)	1325(2)	5154(1)	8768(1)	53(1)
C(5)	522(2)	5521(1)	8616(1)	62(1)
C(6)	421(2)	5709(1)	8082(1)	67(1)
C(7)	1131(2)	5556(1)	7624(1)	49(1)
C(8)	1063(2)	5743(1)	7071(1)	59(1)
C(9)	1795(2)	5602(1)	6682(1)	59(1)
C(10)	2629(2)	5264(1)	6856(1)	50(1)
C(11)	1945(2)	5194(1)	7758(1)	41(1)
C(12)	2016(2)	4984(1)	8336(1)	42(1)
C(13)	990(2)	3960(1)	7618(1)	50(1)
C(14)	−148(2)	3978(1)	7434(1)	61(1)
C(15)	−456(2)	4097(1)	6888(1)	59(1)
C(16)	341(2)	4205(1)	6487(1)	50(1)
C(17)	89(2)	4334(1)	5898(1)	65(1)
C(18)	893(2)	4411(1)	5525(1)	71(1)
C(19)	2044(2)	4386(1)	5712(1)	53(1)
C(20)	2897(2)	4474(1)	5345(1)	65(1)
C(21)	3976(2)	4426(1)	5557(1)	59(1)
C(22)	4193(2)	4302(1)	6141(1)	48(1)
C(23)	2323(2)	4254(1)	6292(1)	40(1)
C(24)	1466(2)	4172(1)	6695(1)	41(1)
C(25)	5861(2)	5067(1)	7118(1)	41(1)
C(26)	5966(2)	5615(1)	6195(1)	45(1)
C(27)	7069(2)	4789(1)	6218(1)	47(1)
C(28)	8189(2)	5637(1)	6239(1)	50(1)
C(29)	7054(2)	6006(1)	7105(1)	55(1)
C(30)	2454(2)	1848(1)	8057(1)	46(1)
C(31)	1563(2)	1577(1)	8243(1)	56(1)
C(32)	971(2)	1291(1)	7861(1)	55(1)
C(33)	1272(2)	1253(1)	7289(1)	48(1)
C(34)	711(2)	940(1)	6860(1)	57(1)
C(35)	1012(2)	920(1)	6327(1)	60(1)
C(36)	1920(2)	1215(1)	6130(1)	52(1)
C(37)	2277(2)	1203(1)	5546(1)	66(1)
C(38)	3146(2)	1483(1)	5404(1)	65(1)
C(39)	3670(2)	1784(1)	5836(1)	50(1)
C(40)	2481(2)	1526(1)	6524(1)	40(1)
C(41)	2174(2)	1543(1)	7119(1)	37(1)
C(42)	5202(2)	2968(1)	5901(1)	55(1)
C(43)	5210(2)	3148(1)	5336(1)	76(1)
C(44)	4237(3)	3241(1)	5035(1)	84(1)
C(45)	3234(2)	3157(1)	5299(1)	63(1)
C(46)	2196(3)	3240(1)	5008(1)	86(1)
C(47)	1257(3)	3176(1)	5285(1)	85(1)
C(48)	1258(2)	3026(1)	5884(1)	60(1)
C(49)	318(2)	2988(1)	6212(1)	72(1)
C(50)	408(2)	2868(1)	6781(1)	65(1)
C(51)	1452(2)	2771(1)	7036(1)	55(1)
C(52)	2292(2)	2925(1)	6177(1)	43(1)
C(53)	3292(2)	2982(1)	5870(1)	45(1)
C(54)	6451(2)	1845(1)	6403(1)	42(1)
C(55)	7489(2)	951(1)	6194(1)	62(1)
C(56)	6523(2)	1478(1)	5347(1)	74(1)
C(57)	7720(2)	2259(1)	5605(1)	66(1)
C(58)	8720(2)	1394(1)	5405(1)	60(1)
C(59)	5749(2)	3405(1)	7284(1)	43(1)
C(60)	6864(2)	3637(1)	7323(2)	92(1)
C(61)	3391(2)	3140(1)	8261(1)	54(1)
C(62)	3012(5)	2998(1)	8866(1)	163(2)

clusters bridged by cyanide and acetate anions simultaneously. The cluster core of compound **1** is illustrated in Fig. 1. Two Sm^{3+} ions are located in a mirror plane and linked by two acetate anions in classical $\eta^1 : \eta^1 : \mu_2$ fashion with a Sm–Sm separation of 5.4419(2) Å, much longer than that in the dimer compound $[Ce_2(CH_3CO_2)_6(phen)_2]$ (4.035 Å) [8]. This, for example, results from the different bridging modes of the acetate units. The carboxyl groups adopt an *anti–anti* manner in **1**, whereas a $\eta^1 : \eta^1 : \mu_2$ fashion is used in $[Ce_2(CH_3CO_2)_6(phen)_2]$ [8] which makes the metal–metal separation much shorter. Sm1 is eight-fold coordinated by four N atoms from two chelating phen molecules (mean Sm–N distance: 2.595(2) Å), two water molecules

Table 4
Selected bond lengths (Å) and angles (deg) for **1**

Sm(1)–O(2)	2.309(2)	Sm(1)–O(4)	2.470(2)
Sm(1)–N(10)	2.572(2)	Sm(1)–N(9)	2.617(3)
Sm(2)–O(3)	2.290(2)	Sm(2)–N(1)	2.525(3)
Sm(2)–N(7)	2.544(3)	Sm(2)–N(8)	2.636(3)
Fe(1)–N(6)	1.654(3)	Fe(1)–C(1)	1.936(3)
Fe(1)–C(3)	1.937(3)	Fe(1)–C(2)	1.944(4)
Fe(1)–C(5)	1.947(3)	Fe(1)–C(4)	1.957(3)
O(1)–N(6)	1.135(4)	N(1)–C(1)	1.144(4)
N(2)–C(2)	1.148(4)	N(3)–C(3)	1.143(4)
N(4)–C(4)	1.137(4)	N(5)–C(5)	1.144(4)
C(1)–N(1)–Sm(2)	163.5(3)	N(5)–C(5)–Fe(1)	178.4(3)
O(1)–N(6)–Fe(1)	175.6(3)	N(1)–C(1)–Fe(1)	176.6(3)
N(2)–C(2)–Fe(1)	178.4(3)	N(3)–C(3)–Fe(1)	179.2(4)
N(4)–C(4)–Fe(1)	177.0(3)		

Table 5
Selected bond lengths (Å) and angles (deg) for **2**

Dy(1)–O(5)	2.2638(15)	Dy(1)–O(3)	2.2733(16)
Dy(1)–O(7)	2.3374(19)	Dy(1)–N(5)	2.4718(18)
Dy(1)–N(4)	2.5156(18)	Dy(1)–N(1)	2.544(2)
Dy(1)–N(3)	2.5476(18)	Dy(1)–N(2)	2.6014(16)
Dy(2)–O(6)	2.2543(16)	Dy(2)–O(4)	2.3154(15)
Dy(2)–O(8)	2.3699(16)	Dy(2)–N(15)	2.4809(19)
Dy(2)–N(13)	2.5230(19)	Dy(2)–N(14)	2.5490(18)
Dy(2)–N(11)	2.5605(17)	Dy(2)–N(12)	2.5746(18)
Fe(1)–N(10)	1.641(2)	Fe(1)–C(26)	1.919(2)
Fe(1)–C(25)	1.939(2)	Fe(1)–C(28)	1.945(3)
Fe(1)–C(27)	1.951(2)	Fe(1)–C(29)	1.967(3)
Fe(2)–N(20)	1.654(2)	Fe(2)–C(55)	1.921(3)
Fe(2)–C(57)	1.926(3)	Fe(2)–C(58)	1.936(3)
Fe(2)–C(54)	1.940(2)	Fe(2)–C(56)	1.944(3)
O(1)–N(10)	1.133(3)	O(2)–N(20)	1.128(3)
C(25)–N(5)–Dy(1)	166.56(17)	O(1)–N(10)–Fe(1)	177.4(2)
C(54)–N(15)–Dy(2)	172.72(17)	O(2)–N(20)–Fe(2)	177.16(18)
N(5)–C(25)–Fe(1)	173.5(2)	N(6)–C(26)–Fe(1)	176.2(2)
N(7)–C(27)–Fe(1)	178.5(2)	N(8)–C(28)–Fe(1)	178.0(2)
N(9)–C(29)–Fe(1)	172.1(3)	N(15)–C(54)–Fe(2)	176.8(2)
N(16)–C(55)–Fe(2)	177.2(3)	N(17)–C(56)–Fe(2)	178.5(3)
N(18)–C(57)–Fe(2)	176.9(3)	N(19)–C(58)–Fe(2)	178.9(3)

(Sm–O = 2.470(2) Å) and two carboxyl oxygen atoms (Sm–O = 2.309(2) Å), forming a square antiprism, in which the top and bottom planes are occupied by O2, O4, N9a, N10a and O2a, O4a, N9, N10 (symmetry code a: $-x$, $-y$, z), respectively. Sm2 has the same coordination number as Sm1 and completes its coordination sphere with four N atoms from two chelating phen ligands (mean Sm–N distance: 2.590(3) Å), two carboxyl oxygen atoms (Sm–O = 2.290(2) Å) and two bridging cyanide anions (Sm–N = 2.525(3) Å), also generating a square antiprism, in which the top and bottom planes are occupied by O3, N1, N7, N8 and O3a, N1a, N7a, N8a, respectively.

Two $[Fe(CN)_5(NO)]^{2-}$ units monodentately connect Sm2 in opposite direction with Sm···Fe distance of 5.5303(2) Å. The bridging cyanide ligands coordinate to Sm^{3+} ions in a bent fashion with the Sm–N≡C bond angles being 163.5(3) Å. The coordination figure about the Fe^{2+} ion is a distorted octahedron, and the Fe–N–O and Fe–C–N groups are nearly linear. The Fe–C distances range from 1.936(5) to 1.957(3) Å, whereas the Fe–N distance of 1.654(3) Å is comparable with that observed in $PrFe(CN)_5(NO)(phen)_2(NO_3)(H_2O)\cdot H_2O$ [6].

The cluster core of compound **2** has the same composition as **1**, but exhibits different structural features. Two Dy^{3+} ions have similar coordination environments and all coordinate to two phen molecules (average Dy–N distance: 2.5520 Å), two carboxyl oxygen atoms (average Dy–$O_{carboxyl}$ distance: 2.2767 Å), one water molecule (Dy–O_{aqu} = 2.3537 Å) and one bridging cyanide group (Dy–N = 2.4764 Å), forming distorted square antiprisms. The top and bottom planes are occupied by O3, O5, N3, N4 and N1, N2, N5, O7 for Dy1, and O4, O6, N13, N14 and O8, N11, N12, N15 for Dy2, respectively.

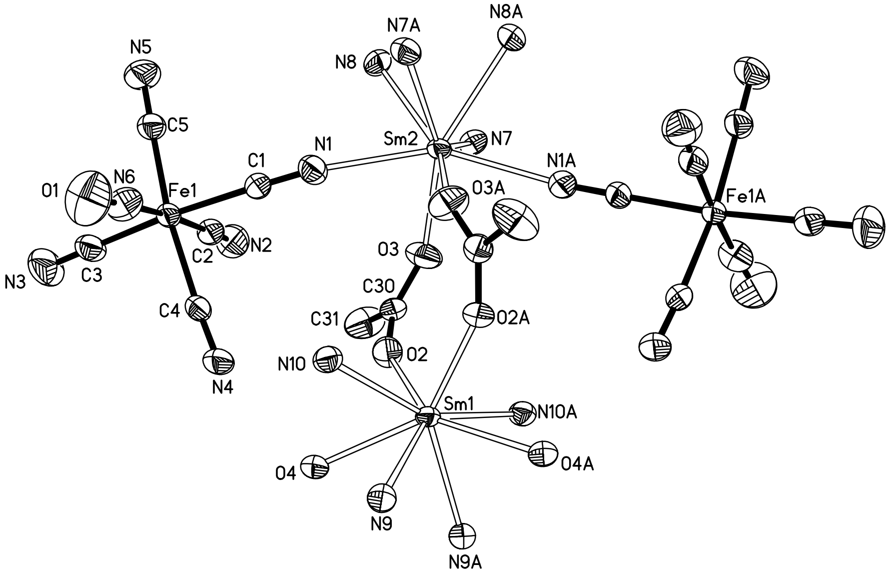


Fig. 1. The molecular structure of compound **1** (the carbon atoms of phen were omitted for clarity).

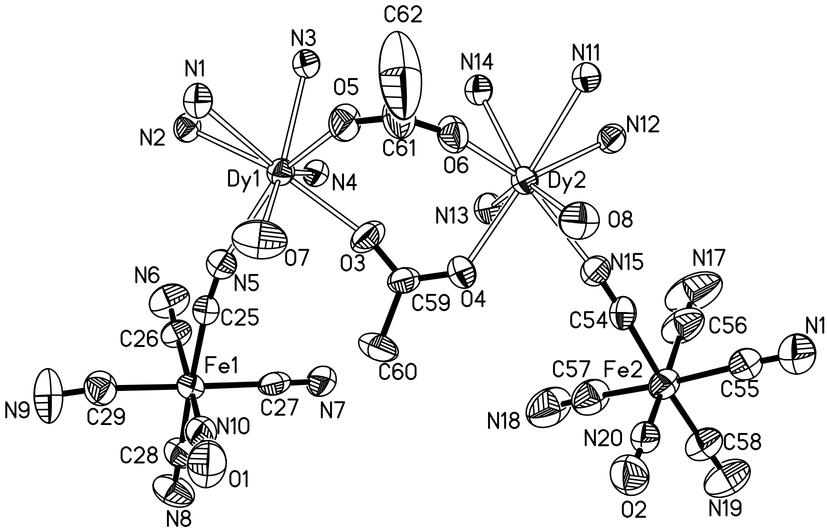
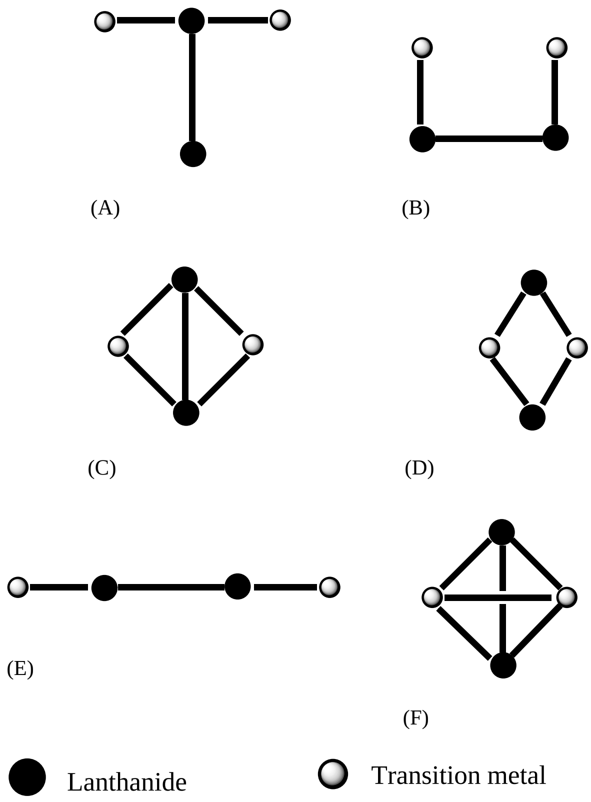


Fig. 2. The molecular structure of compound **2** (the carbon atoms of phen were omitted for clarity).

Two $[Fe(CN)_5(NO)]^{2-}$ units monodentately connect two different Dy^{3+} ions in the same directions with Dy1⋯Fe1 and Dy2⋯Fe2 distances being 5.4999(3) and 5.5447(4) Å, respectively. The bridging cyanide ligands coordinate to Dy^{3+} cations in a slightly bent fashion with C25–N5–Dy1 and C54–N15–Dy2 angles being 166.56(17) and 172.72(17)°. The coordination symmetry about the Fe^{2+} is again distorted octahedral, and the Fe–N–O and Fe–C–N groups are nearly linear. The Fe–C distances vary between 1.919(2) and 1.967(3) Å, whereas the Fe–N distances are in the range from 1.641 to 1.654 Å, in perfect agreement with that ones found in compound **1**.

The cluster cores of compounds **1** and **2** have the same chemical composition, but different structural features. In compound **1**, two $[Fe(CN)_5(NO)]^{2-}$ units are bonded to the same lanthanide cation in *trans* fashion, leading to an approximately T-shaped structural motif (Scheme 1A). The Fe1–Sm2–Fe1a and Fe1–Sm2–Sm1 angles are 151.58° and 75.79°, respectively. On the contrary, in **2**, two $[Fe(CN)_5(NO)]^{2-}$ anions link two different Dy^{3+} ions of the Dy_2 subunit in *cis* fashion, giving rise to an approximately U-shaped feature (Scheme 1B). The Fe1–Dy1–Dy2 and Fe2–Dy2–Dy1 angles are 112.00° and 125.40°, respectively. The lanthanide contraction should be responsible for the structural differences. There are two large $[Fe(CN)_5(NO)]^{2-}$ groups attached to the larger Sm^{3+} ion, giving the T-shaped structure, while for the smaller Dy^{3+} ion only one nitroprusside anion can be attached to a single lanthanide center, hence the U-shaped pattern emerges.



Scheme 1. The structural types of Ln_2M_2 clusters: (A) T-shaped, (B) U-shaped, (C) Butterfly, (D) Rhombus, (E) Linear, (F) Tetrahedron.

The hitherto reported Ln_2M_2 cluster cores have four kinds of structural types (Scheme 1C–F). In $[Dy(hfac)_3CuSatn(OH)]_2$ (hfac = hexafluoroacetylacetone; CuSatnOH = [N-(3-aminopropyl)salicylaldiminato]hydroxocopper(II)), [9a] $[Mn_2Ln_2O_2(O_2CCMe_3)_8(HO_2CCMe_3)_2(MeOH)_2]$, [9b] $Cu_2Gd_2(mhp)_4(OMe)_2(NO_3)_4(Hmhp)_2(MeOH)_2$ (mhp = 6-methyl-2-pyridonate), [9c] $[Co_2Dy_2(OH)(chp)_6(NO_3)_5]^{2+}$ (chp = 6-chloro-2-pyridonate), [9d] and $Cu_2La_2(chp)_8(Hchp)_2(NO_3)_2] \cdot 2(Hchp) \cdot 2MeCN$, [9e] the four metal cations are arranged in a butterfly fashion. In $[Fe_2(CN)_4(phen)_4Yb_2Cl_6(H_2O)_2] \cdot 2H_2O \cdot 2CH_3OH$, [10] cyanide connects the Fe and Yb cations to produce a rhombus motif, whereas a linear structural motif was found in the compounds $[Ln_2Zn_2$

$(O_2CEt)_8(C_9H_7N)_2(NO_3)_2(H_2O)]$, $[Yb_2Zn_2(O_2CEt)_8(C_9H_7N)_2(NO_3)_2]$, [11a] and $[Cu_2Ln_2(\text{betaine})_{10}(H_2O)_8](ClO_4)_{10} \cdot 2H_2O$ [11b]. Very recently, a μ_4-O bridged tetrahedral cluster $[Gd_2Co_2(\mu_4\text{-}O)(\mu_2\text{-}H_2O)(CDTA)_2(H_2O)_6] \cdot 10H_2O$ (H_4CDTA = *trans*-1,2-cyclohexanedinitrilotetraacetic acid) has been reported [12].

Compounds **1** and **2** are remarkably different from those patterns mentioned above. They exhibit novel T- and U-shaped structural features, respectively. Moreover, they also serve as the first $4f-3d$ coordination clusters assembled by cyanide and carboxylate simultaneously. Moreover, it may be expected that the two $[Fe(CN)_5(NO)]^{2-}$ units are able to link two different lanthanide ions of Ln_2 subunit in *trans* fashion to yield even a Z-shaped structure. Further exploration is in progress in our laboratory.

4. Magnetic properties

Since the Fe^{2+} cation in $[Fe(CN)_5(NO)]^{2-}$ unit without any unpaired electrons is diamagnetic, the magnetic behavior of the tetranuclear Ln_2Fe_2 complexes is just contributed by lanthanide ions. The temperature dependence of the magnetic susceptibility at the temperature ranges 2–300 K under 10 kOe applied field was measured for both compounds (see Figs. 3 and 4). The χ_M T value for **1** at room temperature is $0.61\,cm^3\,mol^{-1}\,K$, very close to $0.63\,cm^3\,mol^{-1}\,K$ for two free Sm^{3+} cations. It decreases continuously as the temperature is lowered, and reaches $0.07\,cm^3\,mol^{-1}\,K$ at 2 K. $\chi_M T$ value for **2** at room temperature is $28.02\,cm^3\,mol^{-1}\,K$, very close to $28.25\,cm^3\,mol^{-1}\,K$ for the two free Dy^{3+} cations. $\chi_M T$ remains almost a

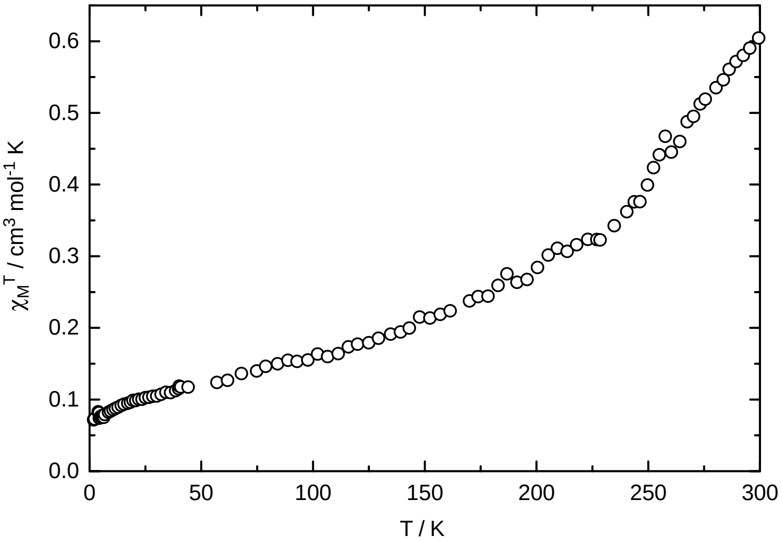


Fig. 3. Temperature dependence of $\chi_M T$ for **1** in an applied field of 10 kOe.

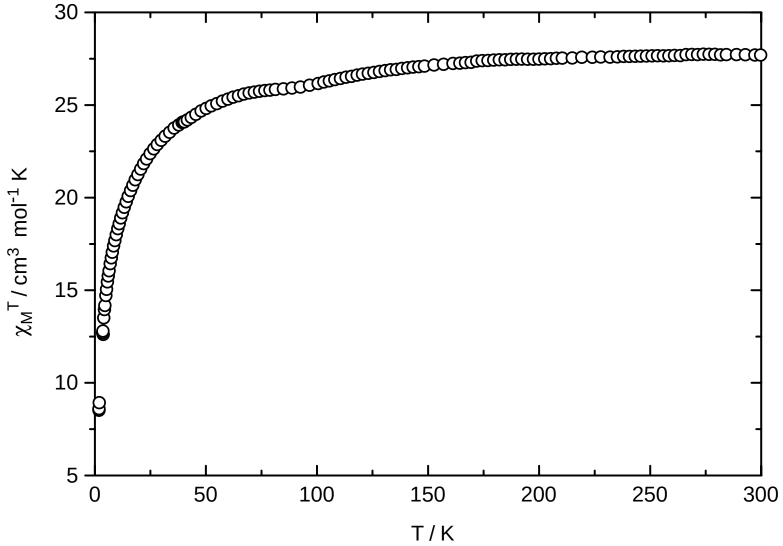


Fig. 4. Temperature dependence of χ_M T for **2** in an applied field of 10 kOe.

constant from 300 to 50 K, and then decreases dramatically as the temperature is lowered below 50 K, reaching a minimum value of 8.93 $\mathrm{cm}^3\,\mathrm{mol}^{-1}\,\mathrm{K}$ at 2 K. The reduction of $\chi_M T$ for both compounds may mostly arise from the splitting of crystal field of lanthanide ions, considering the larger $Ln\cdots Ln$ separation, but the possibility of antiferromagnetic interactions in a pair of Sm^{3+} and Dy^{3+} cations cannot be ruled out either.

Acknowledgments

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