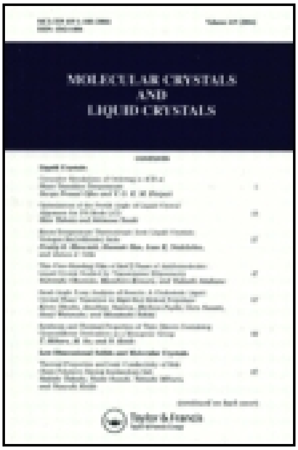

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Structure and Magnetism of Cyano-Bridged Hetero-Binuclear Complexes $RE(dpdo)_2(H_2O)_3Fe(CN)_6 \cdot 4H_2O$ (RE=Gd, Y)

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Structure and Magnetism of Cyano-Bridged Hetero-Binuclear Complexes $RE(dpdo)_2(H_2O)_3Fe(CN)_6{\bullet}4H_2O$ (RE=Gd, Y)

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Two heterobinuclear cyano-bridged RE-Fe complexes $RE(dpdo)_2(H_2O)_3Fe(CN)_6{\bullet}4H_2O$ (RE=Gd,Y; dpdo=2,2'-Dipyridyl N,N'-Dioxide) were synthesized with identical structure. Gd-Fe complex crystallizes in triclinic crystal system, space group P-1 with a = 10.305(2), b = 12.475(1), c = 13.903(1)Å, α = 85.34(1), β = 88.08(1), γ = 70.54(1)°, V = 1679.6(4) $Å^3$, Z = 2. In Gd-Fe binuclear unit, $Gd^{3+}$is eight coordinated by one N atom from one CN^- group, four O atoms from two bidentate dpdo molecules and three O atoms from water molecules, forming a square anti-prism. Gd and Fe are bridged via one CN^- group from $Fe(CN)_6^{3-}$ ion with Gd-Fe separation 5.507(1)Å. The nearest inter-molecular distances of Gd-Fe, Gd-Gd, Fe-Fe are 7.457(1), 7.984(1), and 8.409(1)Å respectively. There are hydrogen bond intra- and inter-molecular connections. The intra-molecular coupling of Gd-Fe is weakly ferromagnetic, meanwhile the interactions between the binuclear units are weakly antiferromagnetic in character.

Keywords: cyano-bridged; hetero-binuclear complexes; structure; magnetism

INTRODUCTION

Many works were made on structure and magnetism of heterobimetallic molecular systems in last two decades[1,2]. Since the ferromagnetic Gd^{3+}-Cu^{2+}

coupling was observed by Gatteschi in 1985 [3], the investigation on 4f-3d molecular magnetism was emerged, but mainly focused on Ln-Cu complexes up to date[4-5], except for a few reports on Ln-Cr, Ln-Fe, Gd-Ni and Gd-Co systems[6-9]. For Gd-Fe molecules, only a 3D compound GdFe(CN).$4H_2O$ was structurally and magnetically characterized[6]. Due to the complication of 3D connection in the compound, the nature of magnetic coupling between Gd and Fe is still open for further research. In order to determine the magnetic coupling nature of Gd-Fe, binuclear Gd-Fe, and Y-Fe complexes were synthesized, and their structures and magnetic properties were investigated in this paper.

EXPERIMENTAL SECTION

Synthesis of $RE(dpdo)_2(H_2O)_3Fe(CN)_6{\cdot}4H_2O$

dpdo was purchased from Aldrich and used without further purification. Other chemicals were all reagent grade. The title complex was prepared by mixing an aqueous solution of $K_3Fe(CN)_6$ (0.5mmol, 10mL) and an aqueous or alcohol solution of dpdo (1mmol, 10mL), followed by the slow addition of an aqueous solution of $RE(NO_3)_3$(1mmol, 10 mL, RE=Gd or Y) without any stirring. The resulting solution was allowed to slowly diffuse and evaporate at room temperature in a dark bottle. After two days, bright yellow single crystals were obtained and noted as [GdFe] and [YFe] respectively, which were collected by filtration, washed with small amounts of water and ethanol, and dried in air. Anal. Calcd for $C_{26}H_{30}FeGdN_{10}O_{11}$: C, 35.82; H, 3.44; N, 16.07. Found: C, 35.58; H, 3.30; N, 16.47. Anal. Calcd for $C_{26}H_{30}FeYN_{10}O_{11}$: C, 38.85; H,3.24; N, 17.43. Found: C, 38.33; H,3.53; N,17.54 .

Determination of Crystal Structure

A single crystal of dimensions 0.40 × 0.37 × 0.23 mm for [GdFe] was employed. X-ray data were collected on an Enraf-Nonius CAD4 Mach3 diffractometer, using graphite-monochromated Mo Kα radiation in a range of $0° \le 2\theta \le 54°$ at room temperature. The unit cell parameters were determined from 25 reflections in the range of $11.66° \le \theta \le 14.09°$, yielding triclinic crystal system, space group P-1 with a = 10.305(2), b = 12.475(1), c = 13.903(1)Å, α = 85.34(1), β = 88.08(1), γ = 70.54(1)°, V = 1679.6(4) $Å^3$, Z = 2. The data reduction and a ψ-scan absorption correction were applied by XRAYACS[10], and the structure was solved by direct methods and refined by full-matrix least-squares technique using SHELXL-97[11]. All non-H atoms were refined anisotropically, and all H atoms were located by difference Fourier synthesis and refined isotropic with distance restrains for C-H, O-H and H...H (0.93, 0.96 and 1.52Å respectively). The final refinement converged to R_1 = 0.038 and wR_2 = 0.097 for all 7291 unique reflections. The largest residual peak and hole in the last difference fourier map were 3.088 and -2.082 $eÅ^{-3}$ (0.92 and 0.86Å from Gd respectively). [YFe] is isomorphous with [GdFe], checked by powder X-ray diffraction data.

Magnetic Measurements

Magnetic susceptibility and magnetization of powdered crystal samples restrained in parafilm (27mg for [GdFe], 44mg for [YFe]) were measured on an Oxford Maglab2000 magnetic measurement system. Diamagnetic corrections were applied for magnetic susceptibility data using Pascal's constants.

RESULTS AND DISCUSSION

Synthesis and Structure

It is well known that mixing Gd^{3+} and $Fe(CN)_6^{3-}$ will yield a three dimensional network connection[6]. To obtain title 0D binuclear molecules, the second ligand dpdo was introduced into the system, which is very important to break the 3D connection and afford the title 0D binuclear complexes. Similar approach has been used to get lower dimensional cyano-bridged heterobimetallic molecules[12-13].

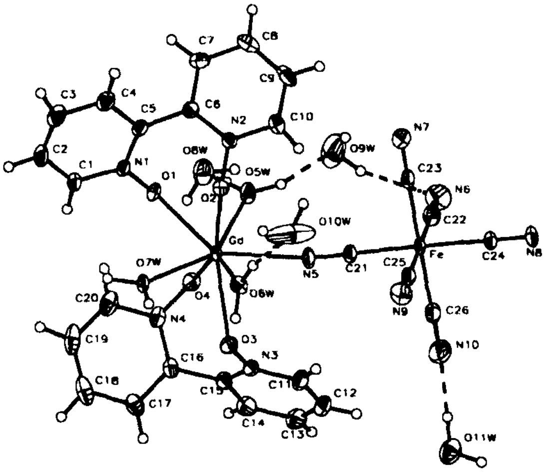

FIGURE 1 ORTEP view of $Gd(dpdo)_2(H_2O)_3Fe(CN)_6 \cdot 4H_2O$ (30% probability ellipsoids)

An ORTEP drawing of binuclear molecule [GdFe] is given in Figure 1. The selected bond distances and angles are listed in Table 1. In the binuclear molecule, Gd^{3+} is eight coordinated by one N atom from one CN^- group, four O atoms from two bidentate dpdo molecules and three O atoms from water molecules, forming a square anti-prism. The two parallel square faces of the prism are defined by two sets of atoms (O1, O2, O6W, O7W) and (O3, O4, O5W, N5) respectively with 1.1(1)° dihedral angle between them. The dihedral angles between the two pyridine rings are 58.3(1) and 61.9(2)° for two dpdo's respectively, which are smaller than that in free ligand (67.5°)[14]. Gd and Fe are bridged via one CN^- group of $Fe(CN)_6^{3-}$ moiety with Gd-Fe separation 5.507(1)Å. The torsion angle of Gd-N(5)-C(21)-Fe is 54(7)°. Intramolecular hydrogen bonds are also shown in Figure 1, the H-bond distances are 2.69, 2.71, 2.63, 3.08, and 2.88Å for O5W...O9W, O5W...O8W, O6W...O10W, O9W...N6 and O11W...N10 respectively. Figure 2 shows a molecular packing diagram of binuclear units of [GdFe] projected onto the *ab* plane. The nearest inter-molecular distances of Gd-Fe, Gd-Gd, Fe-Fe are 7.457(1), 7.984(1), and 8.409(1)Å respectively. Inter-molecular hydrogen bond distances range from 2.74 to 3.14Å(O6W...O10W [-x, -y, -z+1] 3.006, O6W...N9 [-x, -y, -z+1] 3.027, O7W...N9 [-x, -y, -z+1] 2.780, O7W...N8 [x-1, y+1, z] 2.736, O8W...O11W [-x, -y, -z] 2.792, O8W...N6 [-x+1, -y, -z] 2.957, O10W...N7 [-x+1, -y, -z+1]2.865, O11W...O1 [x, y-1, z] 3.027, O11W...O8W [x, y-1, z] 3.143Å).

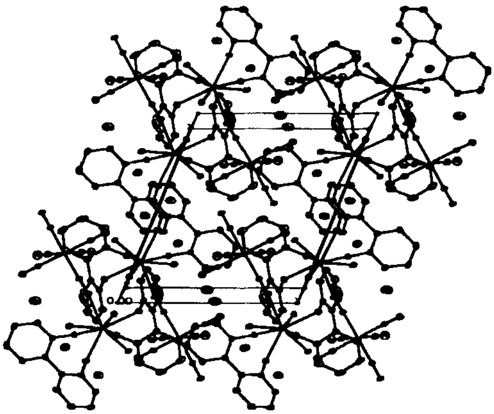

FIGURE 2 Projection along the *c*-axis of [GdFe], showing a molecular packing of binuclear units.

TABLE 1 Selected bond lengths [Å] and angles [°] for [GdFe].

Bond lengths			
Gd-O(2)	2.325(2)	Gd-O(4)	2.356(2)
Gd-O(7W)	2.383(2)	Gd-O(5W)	2.399(3)
Gd-O(6W)	2.400(2)	Gd-O(1)	2.415(2)
Gd-O(3)	2.433(2)	Gd-N(5)	2.478(3)
Fe-C(24)	1.930(3)	Fe-C(21)	1.935(3)

Fe-C(25)	1.936(4)	Fe-C(22)	1.936(4)
Fe-C(23)	1.948(4)	Fe-C(26)	1.949(4)
O(1)-N(1)	1.324(4)	O(2)-N(2)	1.328(4)
O(3)-N(3)	1.327(4)	O(4)-N(4)	1.329(4)
N(5)-C(21)	1.141(5)	N(6)-C(22)	1.144(6)
N(7)-C(23)	1.141(6)	N(8)-C(24)	1.148(5)
N(9)-C(25)	1.137(5)	N(10)-C(26)	1.142(6)
Bond angles			
O(2)-Gd-O(4)	148.91(9)	O(2)-Gd-O(7W)	90.22(9)
O(4)-Gd-O(7W)	93.17(9)	O(2)-Gd-O(5W)	85.63(10)
O(4)-Gd-O(5W)	73.65(10)	O(7W)-Gd-O(5W)	144.00(9)
O(2)-Gd-O(6W)	69.43(9)	O(4)-Gd-O(6W)	140.63(9)
O(7W)-Gd-O(6W)	72.38(9)	O(5W)-Gd-O(6W)	137.36(9)
O(2)-Gd-O(1)	72.73(8)	O(4)-Gd-O(1)	78.22(9)
O(7W)-Gd-O(1)	75.66(8)	O(5W)-Gd-O(1)	68.96(9)
O(6W)-Gd-O(1)	129.51(9)	O(2)-Gd-O(3)	140.11(8)
O(4)-Gd-O(3)	70.58(9)	O(7W)-Gd-O(3)	78.47(9)
O(5W)-Gd-O(3)	125.00(10)	O(6W)-Gd-O(3)	70.69(9)
O(1)-Gd-O(3)	137.85(9)	O(2)-Gd-N(5)	90.97(11)
O(4)-Gd-N(5)	102.52(11)	O(7W)-Gd-N(5)	146.84(10)
O(5W)-Gd-N(5)	69.09(10)	O(6W)-Gd-N(5)	77.09(10)
O(1)-Gd-N(5)	135.84(10)	O(3)-Gd-N(5)	79.53(10)
C(24)-Fe-C(21)	177.70(15)	C(24)-Fe-C(25)	90.21(15)
C(24)-Fe-C(22)	89.63(17)	C(21)-Fe-C(25)	87.51(15)
C(21)-Fe-C(22)	92.65(17)	C(25)-Fe-C(22)	179.31(19)
C(24)-Fe-C(23)	90.25(15)	C(21)-Fe-C(23)	89.52(15)
C(25)-Fe-C(23)	91.00(16)	C(22)-Fe-C(23)	88.32(18)
C(24)-Fe-C(26)	90.38(16)	C(21)-Fe-C(26)	89.96(15)
C(25)-Fe-C(26)	91.76(17)	C(22)-Fe-C(26)	88.92(19)
C(23)-Fe-C(26)	177.17(17)	N(1)-O(1)-Gd	126.94(19)
N(2)-O(2)-Gd	120.50(19)	N(3)-O(3)-Gd	122.9(2)
N(4)-O(4)-Gd	118.1(2)	C(21)-N(5)-Gd	166.3(3)
N(5)-C(21)-Fe	177.1(3)	N(8)-C(24)-Fe	179.4(4)
N(6)-C(22)-Fe	179.0(5)	N(7)-C(23)-Fe	177.4(4)
N(9)-C(25)-Fe	179.0(4)	N(10)-C(26)-Fe	178.3(5)

Magnetic Properties

Temperature dependence of $\chi_m T$ curve, where χ_m is magnetic susceptibility and T is temperature, measured at different applied DC magnetic fields 2kOe, 10kOe for [GdFe], 10kOe for [YFe] is depicted in Figure 3.

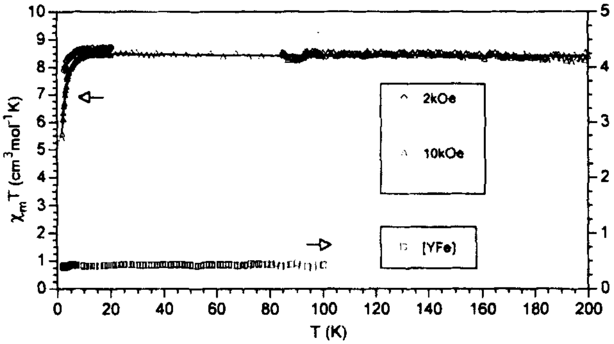

FIGURE 3 Temperature dependence $\chi_m T$ measured at different applied magnetic fields 2kOe, 10kOe for [GdFe], 10kOe for [YFe].

For [GdFe] compound, when temperature is above 10K, $\chi_m T$ keeps almost a constant value, slightly larger than the expected spin-only value of 8.25 cm^{3}mol^{-1}K for free Gd^{3+} and Fe^{3+} ions. The decrease of $\chi_m T$ at low temperature in both fields (2kOe and 10kOe) is due to an intermolecular antiferromagnetic interaction and/or field saturation effect. The magnetic susceptibility data can be fit by the spin-Hamiltonian $\mathbf{H} = -2J_{Gd-Fe}S_{Gd}\bullet S_{Fe} + g\beta S_Z H - zJ'\langle S_Z\rangle S_Z$, based on the binuclear structure with the spin $S_{Gd}=7/2$, $S_{Fe}=1/2$ including an intermolecular interaction term within the molecular field approach. Using equation 1 deduced from above Hamiltonian, the best fit parameters for two sets data measured at different fields are listed in Table 2.

$$\chi_m T = ((4N\beta^2 g^2/k)(15+7\exp(-8J/kT))/(9+7\exp(-8J/kT))/ (1-(zJ'/kT)(15+7\exp(-8J/kT))/(9+7\exp(-8J/kT)) \qquad (1)$$

TABLE 2 The best fit parameters for [GdFe] at two different magnetic fields

Magnetic field	g	$J_{Gd\text{-}Fe}$ (cm^{-1})	zJ' (cm^{-1})	R*
DC 10kOe	2.017(1)	1.15(5)	-0.144(1)	8.8×10^{-5}
DC 2kOe	2.057(3)	0.41(4)	-0.083(2)	1.1×10^{-5}

$*R = \Sigma(\chi_mT^{obsd}-\chi_mT^{calcd})^2/\Sigma(\chi_mT^{obsd})^2$

Based on the fit results, intra-molecular Gd-Fe coupling $J_{Gd\text{-}Fe}$ is around 0.4-1.1cm^{-1}, suggesting a weak ferromagnetic interaction. This seems in contradiction with the observation in 3D GdFe(CN)$_6$.4H$_2$O, where a ferrimagnetic phase was found based on field dependence of magnetization, suggesting an antiparallel orientation of Gd and Fe sublattices[6]. The change in the sign of the magnetic coupling is sensitive to the small change in the geometry of the coupling metal ions for cyano-bridged Mn-Fe complexes[13], however for almost reported Gd-Cu complexes, the coupling $J_{Gd\text{-}Cu}$ is always positive regardless of coordination environments of Gd and Cu ions[3-5]. This implies that dipole-dipole interactions may have main contribution to the Gd-Cu coupling, while superexchange interactions through covalent bonds are more important for the coupling between transition metal ions. In fact, as pointed in [6], the transition element is decisive for the magnetic interactions in 3D LnFe(CN)$_6$.nH$_2$O. It is the next-nearest neighbors (NNN) antiferromagnetic interactions between Fe ions via Gd that result in the final ferrimagnetic behavior even if the coupling between Gd-Fe might be ferromagnetic. In another word, in 3D compound GdFe(CN)$_6$.4H$_2$O, stronger NNN Fe-Fe antiferromagnetic interaction has main contribution to the magnetic behavior of the compound regardless of the sign of very weak Gd-Fe coupling. Therefore it is very difficult to conclude the nature of the Gd-Fe coupling in GdFe(CN)$_6$.4H$_2$O. But for the title binuclear complex, when the inter-molecular interactions are taken into consideration, the intra-molecular coupling of Gd-Fe is ferromagnetic in spite of very weak exchange constant J_{GdFe}.

From the Table 2, inter-molecular interactions seem to be weak antiferromagnetic in character, which is smaller one order than intramolecular interaction in magnitude. Based on the molecular packing, the binuclear units are connected just through weak H-bonds with rather long separations (>7.5Å) between metal ions, the intermolecular interactions should be also very weak, which is convinced by the magnetic behavior of isomer [YFe]. The magnetic susceptibility data for [YFe] in temperature range 2-100K can be reasonably well fitted with Curie-Weiss law (χ_m=C/(T-θ)) with C=0.406(4) $cm^3mol^{-1}K$, and Weiss constant θ=-0.21(3), suggesting a very weak antiferromagnetic intermolecular Fe-Fe interaction.

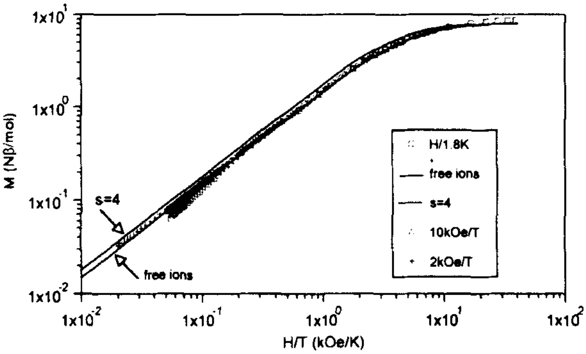

FIGURE 4. Magnetization M *vis* H/T diagram.

Furthermore, besides the inter-molecular interactions field saturation effects also has contribution to the reduction of χ_mT at lower temperature for [GdFe]. It can be seen from Figure 3, where a larger reduction of χ_mT was observed when a larger magnetic field was applied. This can be also confirmed by magnetization M *vis* H/T diagram shown in Figure 4, where above *ca.* 2-3kOe/K, M deviated from paramagnetic linear range. Meanwhile, all data measured at different fields and temperatures follow the Brillouin function calculated for non-interacting spin-only ions Gd and Fe with small deviation, indicating very weak intra- and inter- molecular magnetic interactions.

In summary, the first binuclear [GdFe] complex was obtained and structurally characterized , the intra-molecular coupling of Gd-Fe is weakly ferromagnetic, meanwhile the interactions between the binuclear units are weakly antiferromagnetic in character.

Acknowledgments

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