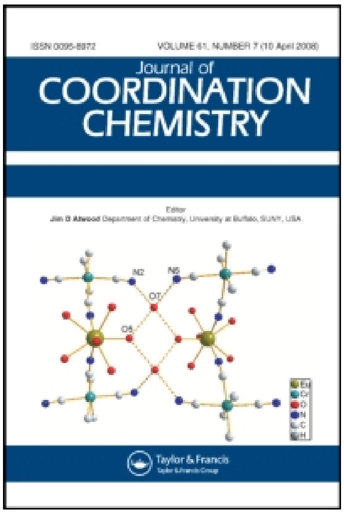

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The syntheses and magnetic properties of a series of heterospin [$Ln^{III}Cu^{II}_4$] pentanuclear complexes

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The syntheses and magnetic properties of a series of heterospin $[Ln^{III}Cu^{II}_4]$ pentanuclear complexes

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Twelve oxamide-bridged Ln(III)–Cu(II) heteropentanuclear complexes $Ln[Cu(PMoxd)]_4(ClO_4)_3 \cdot 5H_2O$ (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, and PMoxd = the *N*,*N*′-Bi(α-pyridylmethyl)-oxamide dianion) and 12 oxamide-bridged Ln(III)–Cu(II) heteropentanuclear complexes with the formula of $Ln[Cu(PEoxd)]_4(ClO_4)_3 \cdot 5H_2O$ (PEoxd = the *N*,*N*′-Bi(α-pyridylethyl)-oxamide dianion) were synthesized and characterized. The magnetic properties of $Gd[Cu(PMoxd)]_4(ClO_4)_3 \cdot 5H_2O$ (**7**) and $Gd[Cu(PEoxd)]_4(ClO_4)_3 \cdot 2H_2O$ (**19**) show that there are ferromagnetic interactions between Gd(III) and Cu(II) in the complexes with $J_{Cu-Gd} = 1.38\,cm^{-1}$ and $J_{Cu-Gd} = 1.00\,cm^{-1}$, respectively. Fluorescent quenching phenomena for $Eu[Cu(PMoxd)]_4(ClO_4)_3 \cdot 5H_2O$ (**6**) and $Tb[Cu(PMoxd)]_4(ClO_4)_3 \cdot 5H_2O$ (**8**) were also observed.

Keywords: Lanthanide; Copper; Pentanuclear complex; Magnetism

1. Introduction

Heteropolynuclear complexes containing d-transition metals have been studied intensively, while heteropolynuclear complexes containing both d- and f-metal ions are less studied with weaker interactions and their large orbital contribution making magnetic behavior difficult to be treated [1]. In 1985, Gatteschi and his partners synthesized a series of Cu(II)–Gd(III)–Cu(II) trinuclear complexes with weak ferromagnetic interaction between Cu(II) and Gd(III) [2]. After that, heteropolynuclear complexes containing 3d- and 4f-metals attracted interest, for example, dinuclear GdCu [1, 3, 4], tetranuclear Gd_2Cu_2 [5] and $GdCu_3$ [6], pentanuclear $GdCu_4$ [7], and hexanuclear Gd_2Cu_4 [8] complexes have been reported. However, oxamide-bridged $[Ln^{III}Cu^{II}_4]$ pentanuclear complexes have rarely been reported [7, 9–12].

In this article, using two oxamide–Cu(II) fragments, we synthesized and characterized 12 $[Ln^{III}Cu^{II}_4]$ heteropentanuclear complexes with [Cu(PMoxd)] [scheme 1(a)] and another 12 $[Ln^{III}Cu^{II}_4]$ heteropentanuclear complexes with [Cu(PEoxd)] [scheme 1(b)]. Magnetic studies for two $[Gd^{III}Cu^{II}_4]$ complexes show ferromagnetic interactions between Cu(II) and Gd(III) bridged by *N*-substituted oxamide containing pyridyl

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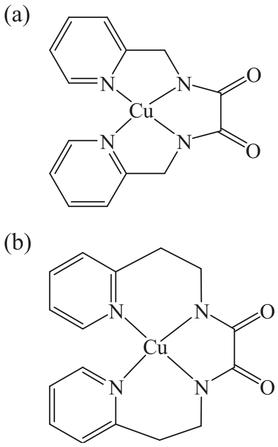


Scheme 1. (a) Structure for [Cu(PMoxd)], (b) Structure for [Cu(PEoxd)].

group, stronger than previously reported [$Gd^{III}Cu_4^{II}$] complexes bridged by *N*-substituted oxamide containing amino group. Fluorescent quenching of [$Eu^{III}Cu_4^{II}$] and [$Tb^{III}Cu_4^{II}$] complexes and the super sensitive transitions of [$Nd^{III}Cu_4^{II}$] and [$Ho^{III}Cu_4^{II}$] complexes are also discussed in this article.

2. Experimental

2.1. *Physical measurements*

Elemental analyses for C, H, and N were carried out on a Perkin–Elmer elemental analyzer (model 240). Thermogravimetric analyses were surveyed on a DUPOND 109 Calorimeter and PCT-1 Calorimeter. Molar conductance was measured on a DDS-11 apparatus. Infrared (IR) spectra in the 4000–400 cm^{-1} region were recorded on a Tensor 27 spectrophotometer using KBr pellets. Electronic spectra were measured on a Shimadzu UV-2101 PC spectrophotometer using water from 225 to 900 nm. Cyclic voltammograms were obtained by BAS-100B using a single electrode vessel system, saturated calomel electrode as the reference electrode, Platinum as working electrode, $Bu_4N(ClO_4)$ (0.1 mol L^{-1}) as supporting electrolyte, Dimethylformamide (DMF) as solvent, at 0.1 mmol L^{-1} (scanning rate is 200 mV s^{-1}). Fluorescence spectra were carried out on a Shimadzu RF-540 fluorimeter. Variable temperature magnetic susceptibilities were carried out on a SQUID magnetometer MPMS-7 in the range 4.2 ~ 300 K; magnetic moments were calculated by $\mu_{\mathrm{eff}} = 2.828\ (\chi_M T)^{1/2}$, where χ_M is the molar magnetic susceptibility, and diamagnetic corrections were made with Pascal's constants.

2.2. *Materials and synthesis*

All the starting chemicals are of AR grade and used as received. The fragments [Cu(PMoxd)] and [Cu(PEoxd)] have been prepared by a modified literature method [13, 14]. The syntheses of $Ln[Cu(PMoxd)]_4(ClO_4)_3 \cdot 5H_2O$ and $Ln[Cu(PEoxd)]_4(ClO_4)_3 \cdot 5H_2O$ are similar; $Gd[Cu(PMoxd)]_4(ClO_4)_3 \cdot 5H_2O$ (**7**) can serve as an example: An aqueous solution (10 mL) of $Gd(ClO_4)_3 \cdot 6H_2O$ (0.1 mmol) was added dropwise to stirred aqueous solution (30 mL) of Cu(PMoxd) (0.4 mmol). After the mixture was stirred for 6 ~ 8 h at room temperature, blue-violet microcrystals were filtered off and washed several times with absolute ethanol and absolute diethyl ether, then dried under vacuum. Other $Ln[Cu(PMoxd)]_4(ClO_4)_3 \cdot 5H_2O$ and $Ln[Cu(PEoxd)]_4(ClO_4)_3 \cdot 5H_2O$ complexes can be obtained in the same way by using other $Ln(ClO_4)_3 \cdot 6H_2O$ in place of $Gd(ClO_4)_3 \cdot 6H_2O$.

Blue-violet crystals of $La[Cu(PMoxd)]_4(ClO_4)_3 \cdot 5H_2O$ (**1**) have been obtained by vaporization of the mother liquid, but were not sufficiently stable for X-ray diffraction. In spite of many attempts, we have not been able to grow crystals suitable for X-ray structure analysis, so we tried to use alternative techniques (elemental analysis, the molar conductance, IR spectra, etc.) to get structural information for all the complexes.

Warning! Perchlorate salts are potentially explosive and should be handled in small amounts only, and with great caution.

3. Results and discussion

3.1. *Elemental analysis*

Metal ions were determined by ethylenediaminetetraacetic acid titration [15]. The elemental analytical results of all the complexes are in Supplementary Material. [Cu(PMoxd)] and [Cu(PEoxd)] form pentanuclear complexes with the corresponding lanthanide cations.

3.2. *Thermogravimetric analysis*

Thermogravimetric analyses for all the complexes have been carried out (table 1). In the range 50–135°C the complexes lost 1.69–5.20% of their weight, indicating 2–5 H_2O in the complexes. These results are in accord with the elemental analyses. Heated to 250°C, the complexes decompose.

3.3. *Molar conductance*

The molar conductance data of all the complexes (Λ_m, DMF as solvent) in table 1 show that all the samples are 1 : 3 electrolytes, with all ClO_4^- not coordinated.

3.4. *IR spectra*

IR spectra of **1**–**24** show a band at 3350–3400 cm^{-1}, attributed to the ν(H–O); the strong band of 1610–1640 cm^{-1} is due to ν(C=O), characteristic of the bridging [PMoxd] and [PEoxd] [16, 17]. The appearance of a strong and broad band occurring at 1090–1100 cm^{-1} indicates the presence of ClO_4^-.

Table 1. Physical data of all the complexes.

Complexes	Color	DGA (%) Found (Calcd)	Λ_M (Ω^{-1} cm^2 mol^{-1})	IR (cm^{-1}) $\nu_{C=O}$	$\nu_{-C=N}$	$\nu^{-1}_{ClO_4}$
1	Blue-violet	5.20 (4.85)	215	3400	1640	1090
2	Blue-violet	5.15 (4.85)	214	3400	1640	1090
3	Blue-violet	4.90 (4.85)	215	3400	1635	1090
4	Blue-violet	4.96 (4.84)	202	3350	1640	1100
5	Blue-violet	4.71 (4.82)	233	3350	1640	1100
6	Blue-violet	5.15 (4.82)	212	3350	1635	1090
7	Blue-violet	5.05 (4.81)	230	3350	1635	1095
8	Blue-violet	5.13 (4.80)	215	3400	1640	1090
9	Blue-violet	4.95 (4.79)	209	3400	1635	1100
10	Blue-violet	4.80 (4.79)	212	3400	1640	1100
11	Blue-violet	4.96 (4.78)	203	3350	1635	1090
12	Blue-violet	4.65 (4.77)	205	3400	1640	1090
13	Blue-violet	4.61 (4.58)	220	3400	1620	1100
14	Blue-violet	4.29 (4.57)	216	3400	1610	1090
15	Blue-violet	2.87 (2.79)	218	3400	1610	1090
16	Blue-violet	3.68 (3.93)	209	3400	1610	1090
17	Blue-violet	1.69 (1.87)	217	3400	1610	1090
18	Blue-violet	1.87 (1.91)	208	3400	1610	1090
19	Blue-violet	2.05 (1.86)	210	3400	1610	1090
20	Blue-violet	4.56 (4.53)	216	3400	1610	1090
21	Blue-violet	4.83 (4.52)	232	3400	1620	1100
22	Blue-violet	4.26 (4.52)	230	3400	1610	1090
23	Blue-violet	5.05 (4.51)	225	3400	1610	1090
24	Blue-violet	4.95 (4.50)	218	3400	1620	1095

Note: DGA: *N*,*N'*-diphenyl-diglycolamide.

3.5. *Electronic spectra*

The spectra show that all the complexes have two bands, one is a weak band in visible region (560–590 nm), ascribed to the spin allowed $^2B_{1g} \rightarrow {}^2E_g$ of square planar Cu(II) [18]. The strong band in ultraviolet-light (210–260 nm, $\log \varepsilon > 4$) may be due to the charger transfer band from the ligands. The electronic spectral data of all the complexes are in table 2.

In the electronic spectra of Ho[Cu(PEoxd)]$_4$(ClO$_4$)$_3 \cdot 5$H$_2$O (**22**) (Supplementary Material), the sensitive transition of Ho(III) $^5I_8 \rightarrow {}^5G_6$ at 450 nm also occurs [19]. Using the absorption peaks of Ho(III) and the following formulas [20], the nephelauxetic parameters were evaluated: $\beta = 0.985$, $b^{1/2}_{\mathrm{Ho}} = 0.0867$, $\delta = 6.53$.

$$\beta = 1/n \Sigma \nu_{\mathrm{complex}} / \nu_{\mathrm{aqueous\,ion}}$$

$$b^{1/2} = [1/2(1-\beta)]^{1/2}$$

$$\%\,\delta = [(1-\beta)/\beta] * 100$$

$b^{1/2}$ measures the amount of 4f orbital mixing, for example, covalency [21]. The $b^{1/2}$ value of Ho(III) ($b^{1/2}_{\mathrm{Ho}} = 0.0867$) in Ho[Cu(PEoxd)]$_4$(ClO$_4$)$_3 \cdot 5H_2$O (**22**) indicates covalency between Ho(III) and ligands. The calculated results for other [Ln$^{\mathrm{III}}$Cu$^{\mathrm{II}}_4$] complexes are shown in table 3.

3.6. *Cyclic voltammograms*

The cyclic voltammetric data for **1**–**24** are similar (Supplementary Material); Tb[Cu(PEoxd)]$_4$(ClO$_4$)$_3 \cdot 5$H$_2$O (**20**) can serve as an example. The data (scanning

Table 2. Electronic spectrum data of all the complexes.

UV (λ, nm, $\log \varepsilon$)			UV (λ, nm, $\log \varepsilon$)		
	d–d	CT		d–d	CT
1	564 (1.70)	257 (4.21)	13	581 (1.72)	258 (4.25)
2	562 (1.71)	210 (4.24)	14	585 (1.70)	227 (4.24)
3	566 (1.74)	211 (4.35)	15	586 (1.71)	228 (4.35)
4	564 (1.72)	235 (4.25)	16	579 (1.71)	210 (4.26)
5	562 (1.71)	211 (4.20)	17	566 (1.72)	211 (4.23)
6	559 (1.72)	256 (4.10)	18	578 (1.73)	228 (4.25)
7	562 (1.72)	210 (4.29)	19	585 (1.70)	211 (4.28)
8	566 (1.72)	210 (4.29)	20	578 (1.74)	227 (4.21)
9	562 (1.72)	256 (4.19)	21	586 (1.70)	225 (4.17)
10	550 (1.77)	211 (4.07)	22	578 (1.70)	259 (4.19)
11	561 (1.70)	223 (4.15)	23	578 (1.72)	227 (4.23)
12	560 (1.71)	210 (4.31)	24	583 (1.72)	226 (4.21)

Note: UV: Ultra/violet; CT: Charge Transfer.

Table 3. β, $b^{1/2}$ and Sinha parameter (δ) of some complexes.

Complexes	Ln^{3+}	β	$b^{1/2}$	δ
3	Pr	0.9865	0.0823	1.37
5	Sm	0.9746	0.1126	2.60
6	Eu	0.9238	0.1952	8.25
7	Gd	0.9632	0.1356	3.82
10	Ho	0.9856	0.0846	1.45
11	Er	0.9843	0.0885	1.59
15	Pr	0.9855	0.0852	1.08
17	Sm	0.9677	0.1290	3.44
18	Eu	0.9718	0.1188	2.90
19	Gd	0.9581	0.1448	4.38
22	Ho	0.985	0.0867	6.53
23	Er	0.9631	0.1921	3.83

range: $1.0 \sim -1.9$ V) of $Tb[Cu(PEoxd)]_4(ClO_4)_3 \cdot 5H_2O$ (**20**) show the irreversible redox peak of Cu(II)/Cu(I) at −1.02, and the irreversible redox peak of Cu(II)/Cu(I) for [Cu(PMoxd)] at −0.99. According to the literature [22, 23], changing the coordination environment leads to potential electrode property changes for the core ion. Comparing $E_{1/2}$ of all the pentanuclear compounds, Cu(II) in the mononuclear fragment has the same coordination environment as Cu(II) in the pentanuclear compounds [24]; [Cu(PMoxd)] retains *cis*-structure, and in the oxamide, the C=O coordinates with Ln(III).

3.7. *Fluorescent properties*

The fluorescence spectra of $Eu[Cu(PMoxd)]_4(ClO_4)_3 \cdot 5H_2O$ (**6**)/$Eu(ClO_4)_3$ and $Tb[Cu(PMoxd)]_4(ClO_4)_3 \cdot 5H_2O$ (**8**)/$Tb(ClO_4)_3$ in DMF solution ($10^{-6}\,mol\,L^{-1}$), with excitation at 394 and 355 nm, respectively, are shown in figure 1 and Supplementary Material. In figure 1, curve (a) shows the fluorescent spectra of $Eu(ClO_4)_3$ with the peaks of 593, 615, 653, and 700 nm, for the ${}^5D_0$–${}^7F_1$, ${}^5D_0$–${}^7F_2$, ${}^5D_0$–${}^7F_3$, ${}^5D_0$–${}^7F_4$ transitions of Eu(III) [25]. However, the peaks for Eu(III) disappear in Eu[Cu(PMoxd)]$_4$(ClO$_4$)$_3 \cdot 5H_2O$ (**6**) as shown in curve (b). Similarly, the three peaks of Tb(III) in Tb(ClO$_4$)$_3$ [26] are at 491, 546, and 622 nm, which correspond to the ${}^5D_4 \rightarrow {}^7F_6$, ${}^5D_4 \rightarrow {}^7F_5$, ${}^5D_4 \rightarrow {}^7F_4$ transitions. However, for complex Tb[Cu(PMoxd)]$_4$(ClO$_4$)$_3 \cdot 5H_2O$ the fluorescence emissions are also totally quenched. Fluorescence quenching for the two complexes may be due to energy transmission from the excited Ln(III) to Cu(II) ions through the oxamide ligands [27–29]. The strong absorption at 450 nm perhaps comes from impurity in methanol.

3.8. *Magnetic properties*

Variable-temperature magnetic susceptibility data for Gd[Cu(PMoxd)]$_4$(ClO$_4$)$_3 \cdot 5H_2O$ (**7**) (figure 2) and Gd[Cu(PEoxd)]$_4$(ClO$_4$)$_3 \cdot 2H_2O$ (**19**) (figure 3) in the temperature range 6–300 K, at a magnetic field of 5000 G, were collected. The μ_{eff} values at room temperature of 8.77 and 8.78 B.M., respectively, are slightly larger than the spin-only value (8.66 B.M. with $S_{\mathrm{Cu}} = 1/2$, $S_{\mathrm{Gd}} = 7/2$). Upon cooling, the μ_{eff} value increases slowly, suggesting ferromagnetic interaction between the Gd(III) and Cu(II) in the pentanuclear [GdCu$_4$] systems. For complex Gd[Cu(PEoxd)]$_4$(ClO$_4$)$_3 \cdot 2H_2O$ (**19**) in figure 3, at low temperature, μ_{eff} decreases with decreasing temperature, indicating intermolecular antiferromagnetic interactions.

As sketched in scheme 2, there are two kinds of interactions in the [GdCu$_4$] systems, the Gd(III)–Cu(II) interaction and Cu(II)–Cu(II) interaction. In order to describe quantitatively the magnetic exchange interactions between paramagnetic

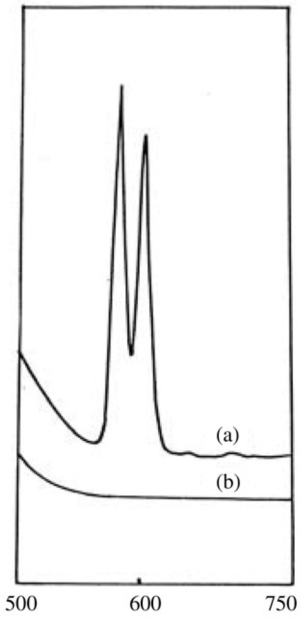


Figure 1. (a) Fluorescent spectra of Eu(ClO$_4$)$_3$ and (b) Eu[Cu(PMoxd)]$_4$(ClO$_4$)$_3$ (**6**).

ions in the complexes, the following spin Heisenberg Hamiltonian was used for both complexes:

$$\hat{H} = -2J\hat{S}_{\mathrm{Gd}}(\hat{S}_{\mathrm{Cu1}} + \hat{S}_{\mathrm{Cu2}} + \hat{S}_{\mathrm{Cu3}} + \hat{S}_{\mathrm{Cu4}}) - 2j(\hat{S}_{\mathrm{Cu1}}\hat{S}_{\mathrm{Cu2}} + \hat{S}_{\mathrm{Cu1}}\hat{S}_{\mathrm{Cu3}} + \hat{S}_{\mathrm{Cu1}}\hat{S}_{\mathrm{Cu4}} + \hat{S}_{\mathrm{Cu2}}\hat{S}_{\mathrm{Cu}} + \hat{S}_{\mathrm{Cu2}}\hat{S}_{\mathrm{Cu4}} + \hat{S}_{\mathrm{Cu3}}\hat{S}_{\mathrm{Cu4}}) \quad (1)$$

where J and j are the exchange integral of Cu(II)–Gd(III) and Cu(II)–Cu(II), respectively. Least-squares fitting of the experimental data with the calculated value derived from the theoretic susceptibility equation based on Hamiltonian (1) led to the magnetic parameters of complexes, shown in table 4.

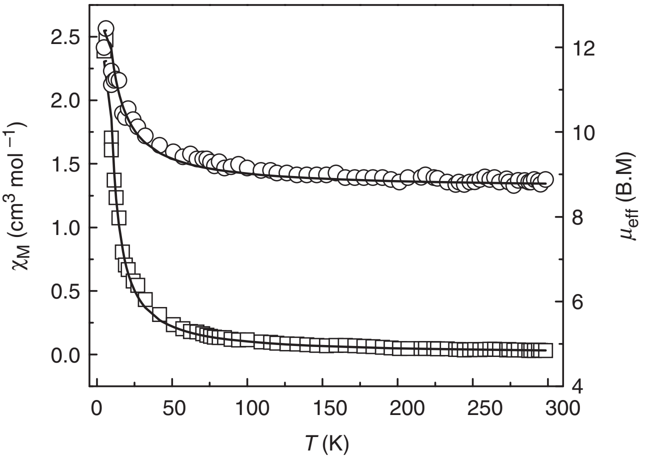


Figure 2. The magnetic susceptibility and magnetic moment of Gd[Cu(PMoxd)]$_4$(ClO$_4$)$_3$ (**7**).

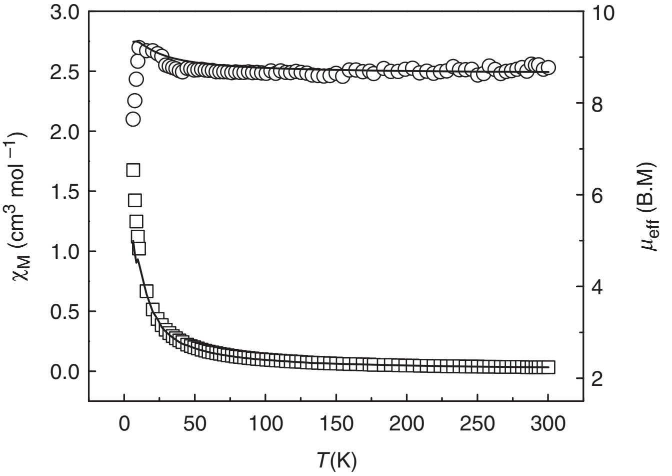
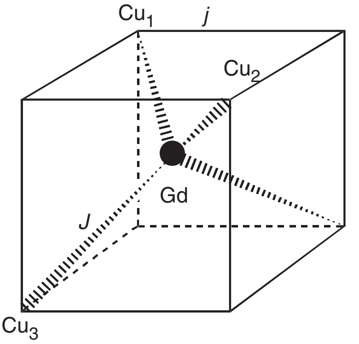


Figure 3. The magnetic susceptibility and magnetic moment of Gd[Cu(PEoxd)]$_4$(ClO$_4$)$_3$ (**19**).



Scheme 2. The sketched model of [GdCu$_4$] for magnetic analysis.

Table 4. Magnetic parameters of the two Cu(II)–Gd(III) complexes.

Complex	*g*	*J*	*j*	*F*
Gd[Cu(PMoxd)]$_4$(ClO$_4$)$_3 \cdot$ 5H$_2$O (**7**)	2.02 [7]	1.38	−0.19	7.38×10^{-5}
Gd[Cu(PEoxd)]$_4$(ClO$_4$)$_3 \cdot$ 2H$_2$O (**19**)	2.00 [7]	1.00	−0.45	5.22×10^{-4}

Note: The agreement factor is defined by $F = \sum[(\chi_M)_{obsd} - (\chi_M)_{Calcd}]^2/(\chi_M)_{obsd}$.

The fitting results confirm the ferromagnetic coupling between Gd(III) and Cu(II) in the two complexes, which can be explained by spin polarization theory [5]. The semi-full 4f orbital of Gd(III) ion cannot effectively overlap with the magnetic orbital of Cu(II), and because of the spin polarization, the unpaired electron of Cu(II) transfers partially to the 5d orbital of Gd(III). According to Hund's rule, the electrons in the 5d orbital and 4f orbital should remain parallel, leading to weak ferromagnetic interactions between Cu(II) and Gd(III). Comparing the [GdCu$_4$] system (with $J = 0.85$) containing *N*-substituted oxamide with amino group reported by Sanz *et al.* [7], the *J* values of Gd[Cu(PMoxd)]$_4$(ClO$_4$)$_3 \cdot$ 5H$_2$O (**7**) and Gd[Cu(PEoxd)]$_4$(ClO$_4$)$_3 \cdot$ 2H$_2$O (**19**) are higher, indicating the *N*-substituted oxamide containing pyridyl group in Gd[Cu(PMoxd)]$_4$(ClO$_4$)$_3 \cdot$ 5H$_2$O (**7**) and Gd[Cu(PEoxd)]$_4$(ClO$_4$)$_3 \cdot$ 2H$_2$O (**19**) complexes are better at transferring ferromagnetic exchange between Cu(II) andGd(III) than *N*-substituted oxamide containing amino groups.

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