Polish J. Chem., **75**, 1195–1202 (2001) **INORGANIC CHEMISTRY**

Synthesis and Magnetic Properties of Binuclear Lanthanide(III) Complexes Bridged by μ-2-Chloroterephthalato Groups

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(Received December 4th, 2000)

Ten new binuclear lanthanide(III) complexes described by the overall formula $[Ln_2(CTPHA)(Mephen)_4(ClO_4)_2](ClO_4)_2$ (Ln = La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er), where Mephen stands for 5-methyl-1,10-phenanthroline, and CTPHA represents the 2-chloroterephthalate dianions, have been synthesized and characterized by elemental analyses, molar conductance measurements, IR, ESR and electronic spectra. It is proposed that these complexes present CTPHA-bridged structures consisting of two lanthanide(III) ions. The $[Gd_2(CTPHA)(Mephen)_4(ClO_4)_2](ClO_4)_2$ complex has been further characterized by variable-temperature magnetic susceptibilities (4~300 K), demonstrating a very weak antiferromagnetic spin-exchange interaction between Gd(III)–Gd(III) ions within the complex. Based on the spin Hamiltonian operator, $\hat{H} = -2J\hat{S}_1\cdot\hat{S}_2$, the exchange parameter (J) was evaluated as -0.16 cm^{-1}.

Key words: μ-2-chloroterephthalato-bridge, binuclear lanthanide(III) complexes, magnetism, synthesis

The syntheses and magnetic properties of rare earth metal binuclear complexes have been an active field of research in recent years, not only for the relevant theoretical interest to investigate the spin-exchange mechanism on the involvement of the *f* orbitals in magnetic interactions, but also for understanding chemical properties, and application of rare earth metal, and the exploitation of the synthesis of novel molecular magnetic materials [1–6]. The benzene dicarboxylate dianions, due to both their versatile bonding mode with metal ions and their peculiar structure – involving carboxylato groups that are non-coplanar relative to each other and with the benzene ring – could be good candidates in supporting long-distance magnetic exchange interactions. Many binuclear transition-metal complexes, containing the bridging phenyl dicaboxylate ligands, have been synthesized and their magnetic properties have been studied [7–11]. It has been revealed by X-ray diffraction analyses [7,11] and variable-temperature magnetic susceptibility investigations that the long-range magnetic coupling can occur between the two transition-metal ions centers bridged by the dicarboxylate groups. However, to the best of our knowledge, no 2-chlorotere-

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phthalato-bridged binuclear lanthanide(III) complexes have been reported. Owing to the importance mentioned above and to understand the feature of this kind of binuclear lanthanide(III) complexes propagated by 2-chloroterephthalato (abbreviated as CTPHA) bridge, in this paper, we describe the syntheses and magnetic properties of ten new μ-2-chloroterephthalato lanthanide(III) binuclear complexes of general formula $[Ln_2(CTPHA)(Mephen)_4(ClO_4)_2](ClO_4)_2$ (Ln = La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er; Mephen = 5-methyl-1,10-phenanthroline). The ESR spectra and magnetic properties of $[Gd_2(CTPHA)(Mephen)_4(ClO_4)_2](ClO_4)_2$ complex have been studied in detail.

EXPERIMENTAL

Materials: Piperidinium 2-chloroterephthalate was synthesized by the literature [7] method. $Ln(ClO_4)_3{\cdot}6H_2O$ (Ln = La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er) was prepared by dissolving the respective lanthanide oxides (99.99% pure) in *ca*. 50% $HClO_4$ and then recrystallizing the resulting salt by evaporating the solution on a steam bath. The terminal ligand 5-methyl-1,10-phenanthroline (Mephen) (analytical grade) was purchased from the Beijing Chemical Company.

Synthesis of $[Ln_2(CTPHA)(Mephen)_4(ClO_4)_2](ClO_4)_2$ (Ln = La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er): All the ten binuclear complexes were prepared in a similar fashion and only the typical preparation of $[Gd_2(CTPHA)(Mephen)_4(ClO_4)_2](ClO_4)_2$ is given here. To a solution of piperidinium 2-chloroterephthalate (74.3 mg, 0.2 mmol) stirred in absolute ethanol (15 cm^3) was added successively a solution of $Gd(ClO_4)_3{\cdot}6H_2O$ (225.6 mg, 0.4 mmol) in absolute ethanol (10 cm^3), followed by a solution of ethyl orthoformate (10 cm^3) and Mephen (1250 mg, 0.8 mmol) in the same solvent (20 cm^3) at room temperature. After the reaction mixture was further refluxed for *ca*. 12 h, white microcrystals, thus obtained, were filtered, washed several times with absolute ethanol and diethyl ether, and dried over P_2O_5 under reduced pressure. Recrystallization was carried out from a hot DMF solution. All yields and melting points of the binuclear complexes are listed in Table 1. In the solid states all of the complexes are fairly stable in air so as to facilitate physical measurements.

Physical measurements: Carbon, hydrogen and nitrogen elemental analyses were performed with a Perkin-Elmer elemental analyzer Model 240 confirming the formula given in Table 1. The metal contents were determined by EDTA titration. IR spectra were recorded with a NICOLET FT-IR 5DX spectrophotometer using KBr pellets. ESR spectra were recorded with a JES-FEIXG ESR apparatus using an X-band and Mn-reference. The electronic spectra (DMF solution) were measured on a Perkin-Elmer Hitachi-240 spectrophotometer. Molar conductances were measured with a DDS-11A conductometer. Variable- temperature magnetic susceptibilities (4~300 K) were measured at the Institute of Physics, Chinese Academy of Sciences, using a vibrating magnetometer Model CF-1 (sensitivity $m = 10^{-4}$ emu.). Diamagnetic corrections were made with Pascal's constants [12] for all the constituent atoms and effective magnetic moments were calculated using the equation $\mu_{eff} = 2.828(\chi_M T)^{1/2}$, where χ_M is the molar magnetic susceptibility corrected for diamagnetism of the constituting atoms.

RESULTS AND DISCUSSION

Composition and coordination environment of the complexes: Elemental analyses have indicated that the reaction of CTPHA with $Ln(ClO_4)_3{\cdot}6H_2O$ and the terminal ligand Mephen in 1:2:4 mole ratio in absolute ethanol readily forms binuclear complexes of general formula $[Ln_2(CTPHA)(Mephen)_4(ClO_4)_2](ClO_4)_2$ (Ln = La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er), as expected. They are the first examples of Ln(III)–Ln(III) binuclear complexes bridged by 2-chloroterephthalato group, which are presumed to have the coordination environment shown in Figure 1.

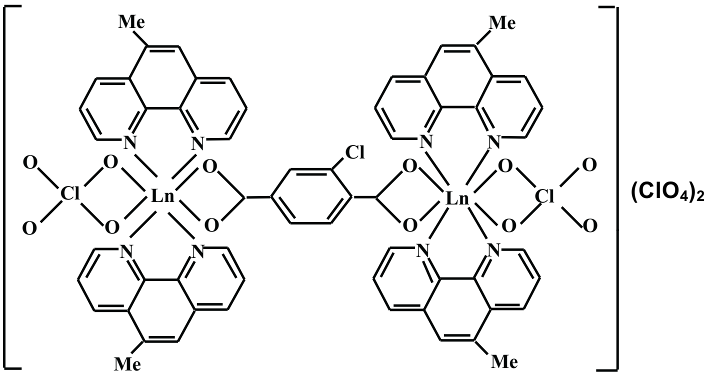

Figure 1. Plausible coordination environment of the complexes ($\overset{\frown}{N\ N}$ = Mephen; Ln = La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er).

Solubility and molar conductances of the complexes: All of the binuclear complexes are sparingly soluble in water, ethanol, methanol, carbon tetrachloride, chloroform and benzene, but very soluble in acetonitrile, DMF and DMSO to give stable solutions at room temperature. For the ten binuclear complexes, the molar conductance values in DMF solution (see Table 2) fall in the expected for 1:2 electrolytes [13], indicating that only two perchlorate anions lie outside the coordination sphere and the two perchlorate anions are inside the coordination sphere. This is in accord with the presumed structure of the complexes shown in Figure 1. In spite of our many efforts, single crystals suitable for X-ray crystallography have not been obtained for any of these complexes. However, the binuclear complexes were further characterized by the following results.

Table 1. Compositions, yields, colors and melting points (M.p.) of the binuclear complexes.

Complex	Empirical Formula (Formula Weight)	Color	M.p. (°C)	Yield (%)
(1)	$La_2C_{60}H_{43}N_8O_{20}Cl_5$ (1651.09)	white	329	45
(2)	$Ce_2C_{60}H_{45}N_8O_{21}Cl_5$ (1671.51)	white	288	52
(3)	$Nd_2C_{60}H_{45}N_8O_{21}Cl_5$ (1679.71)	violet	291	68
(4)	$Sm_2C_{60}H_{43}N_8O_{20}Cl_5$ (1674.09)	pale-purple	343	43
(5)	$Eu_2C_{60}H_{47}N_8O_{22}Cl_5$ (1713.32)	white	339	71
(6)	$Gd_2C_{60}H_{43}N_8O_{20}Cl_5$ (1687.89)	white	313	89

Table 1 (continuation)

(7)	$Tb_2C_{60}H_{45}N_8O_{21}Cl_5$ (1709.11)	pale-violet	308	76
(8)	$Dy_2C_{60}H_{43}N_8O_{20}Cl_5$ (1698.29)	ruby	347	85
(9)	$Ho_2C_{60}H_{43}N_8O_{20}Cl_5$ (1703.09)	pale-red	324	67
(10)	$Er_2C_{60}H_{43}N_8O_{20}Cl_5$ (1707.89)	red-brown	356	72

(1) = $La_2(CTPHA)(Mephen)_4(ClO_4)_4$, **(2)** = $Ce_2(CTPHA)(Mephen)_4(ClO_4)_4 \cdot H_2O$,
(3) = $Nd_2(CTPHA)(Mephen)_4(ClO_4)_4 \cdot H_2O$, **(4)** = $Sm_2(CTPHA)(Mephen)_4(ClO_4)_4$,
(5) = $Eu_2(CTPHA)(Mephen)_4(ClO_4)_4 \cdot 2H_2O$, **(6)** = $Gd_2(CTPHA)(Mephen)_4(ClO_4)_4$,
(7) = $Tb_2(CTPHA)(Mephen)_4(ClO_4)_4 \cdot H_2O$, **(8)** = $Dy_2(CTPHA)(Mephen)_4(ClO_4)_4$,
(9) = $Ho_2(CTPHA)(Mephen)_4(ClO_4)_4$, **(10)** = $Er_2(CTPHA)(Mephen)_4(ClO_4)_4$.

Table 2. Conductance data and important infrared spectral bands (cm^{-1}) of the binuclear complexes.

Complex						$\nu(ClO_4^-)$ (coordinated)					$\nu(ClO_4^-)$ (ionic)	
	$\Lambda_M{}^a$	$\nu_{as}(COO)$	$\nu_s(COO)$	$\nu(C{=}N)$	$\nu(Ln–N)$	ν_8	ν_6	ν_1	ν_2	ν_3	ν_3	ν_4
(1)	140	1580	1420	1530	385	1140	1100	1020	940	636	1089	620
(2)	145	1582	1426	1530	380	1143	1108	1020	942	633	1088	620
(3)	150	1585	1428	1530	382	1140	1109	1020	940	635	1090	620
(4)	152	1578	1430	1532	380	1144	1100	1020	940	635	1090	620
(5)	155	1575	1420	1531	380	1141	1100	1020	940	634	1090	620
(6)	160	1580	1425	1530	380	1145	1100	1020	940	635	1087	620
(7)	158	1584	1420	1530	384	1140	1100	1020	940	633	1090	620
(8)	156	1585	1425	1528	385	1140	1100	1020	940	635	1085	620
(9)	144	1590	1430	1529	383	1142	1100	1020	940	635	1090	620
(10)	146	1588	1420	1530	382	1145	1100	1020	940	635	1090	620

[a] Values for 1×10^{-3} $mol \cdot L^{-1}$ DMF solution; unit: $S \cdot cm^2 \cdot mol^{-1}$.

Infrared spectra: The IR spectra taken in the region of 350–4000 cm^{-1} provide some information regarding the mode of coordination in the complexes and were analyzed in comparison with that of the free ligand. The most relevant IR absorption bands due to the complexes along with their assignments are shown in Table 2 and we will discuss here only selected bands. The spectrum of 2-chloroterephthalic acid (H_2CTPHA) shows a broad band near 1705 cm^{-1}, attributed to $\upsilon(C{=}O)$ of the carboxylic groups. However, in the IR spectra of all complexes this band had disappeared and is accompanied by the appearance of two characteristic strong and broad bands at *ca.* 1580 cm^{-1} and 1420 cm^{-1}, attributed to $\upsilon_{as}(COO)$ (1575~1590 cm^{-1}) and $\upsilon_s(COO)$ (1420~1430 cm^{-1}) stretching vibrations of the coordinated carboxylate groups. The absence of any splitting of the $\upsilon_{as}(COO)$ and $\upsilon_s(COO)$ bands strongly suggests end-to-end linking of the 2-chloroterephthalato ligand in an equivalent way at both sites [14]. According to the literature [15], the coordination modes of carboxylate groups have been determined by a separation between $\upsilon_{as}(COO)$ and $\upsilon_s(COO)$, *i.e.*, bidentate carboxylate groups show a separation smaller than 200 cm^{-1}, whereas unidentate carboxylate groups show a larger separation. Thus, for the present complexes these two bands were separated by *ca.* 160 cm^{-1} (see Table 2), suggesting a bidentate coordination mode for both carboxylate groups of the CTPHA ligand. The bidentate coordination modes of the carboxylates in bridging ligand (CTPHA) have been revealed by X-ray diffraction analysis of the μ-terephthalato nickel(II) binuclear complex [11] $[Ni_2(TPHA)(bpy)_4](ClO_4)_2$ (TPHA = terephthalato dianions). On the other hand, the -N=C- stretching vibration for the terminal ligand (Mephen) is shifted to higher frequencies (*ca.* 1530 cm^{-1}) in their binuclear complexes, suggesting that the N atoms of the terminal ligand coordinated with the Ln(III) ions. The broad band observed around 380 cm^{-1}, due to ν_{Ln-N}, supports further this view. In addition, the IR spectra of all the complexes exhibit absorption bands, characteristic of both the ionic and bidentately coordinated perchlorate groups. The band maxima, observed at around 1140, 1100 and 1020 cm^{-1} are due to the ν_8, ν_6 and ν_1 vibrations of the perchlorate groups of C_{2V} symmetry [16,17], which indicate that the perchlorate groups are coordinated to Ln(III) ions as a chelation bidentate ligand. The band at *ca.* 1090 cm^{-1} is assigned to the ν_3 vibration of the ionic perchlorate of T_d symmetry. The vibrational frequencies, observed about 940 and 635 cm^{-1}, corresponding to the ν_2 and ν_3 vibrations of the perchlorate group of C_{2V} symmetry, and the band at 620 cm^{-1} due to the ν_4 vibration of the ionic perchlorate further support the co-existence of both ionic and bidentately coordinated perchlorate groups in these binuclear complexes. These observations are consistent with the conductance data, which suggest that two of the perchlorate groups are coordinated. Thus, on the basis of IR and molar conductance measurements, the complexes may be formulated as $[Ln_2(CTPHA)(Mephen)_4(ClO_4)_2](ClO_4)_2$ (Ln = La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er).

Electronic spectra: Since the electronic absorption spectra of the ten complexes in DMF solutions are similar, the discussion is confined to the most important of the structure. For all the complexes, a strong absorption at *ca.* 37×10^3 cm^{-1} found may be attributed to the charge-transfer absorption band arising from the CTPHA ligand [18]. Further investigation of these and similar systems is still required in order to obtain a detailed assignment for charge transfer. In addition, the f-f transitions were observed [19] for binuclear complexes of Nd(III), Sm(III), Dy(III), Ho(III), Er(III). As shown in Table 3, these f-f transitions are found to be red-shifted with respect to the aquo ions. According to relevant absorption peaks of their aquo ions of Ln(III) (Ln = Nd, Sm, Dy, Ho, Er), the parameters $\overline{\beta}$ and $b^{1/2}$ were obtained [20,21], where $\overline{\beta}$ is the nephelauxetic ratio which is defined as: $\overline{\beta} = 1/n\sum\left(\nu_{complex}/\nu_{aquo}\right)$, and $b^{1/2}$ measures the amount of 4f orbital mixing, *i.e.* covalency. The bonding parameter is related to the nephelauxetic ratio ($\overline{\beta}$) by the relation: $b^{1/2} = [(1 - \overline{\beta})/2]^{1/2}$. The covalency parameters calculated are also given in Table 3. This result suggests some covalent character of the metal–ligand bond, and the covalency decreases as the atomic number of the rare earth metal increases for the same ligand. This is in agreement with the general observation that the nepheloauxetic effect is more pronounced in the beginning of the 4f group than for the later members.

Table 3. f-f transitions and some covalency parameters of the binuclear complexes.

Ln^{3+}	f-f transitions (cm^{-1})		Assignments		$\bar{\beta}$	$b^{1/2}$
	Aquo ions	Complex	Ground state	Exciting state		
Nd^{3+}	12650	12510	$^4I_{9/2}$	$^4F_{5/2}$	0.9899	0.0711
	13570	13410		$^4F_{7/2}$		
	17600	17400		$^4G_{5/2}$, $^2G_{7/2}$		
	19280	19160		$^4G_{7/2}$		
Sm^{3+}	21150	20900	$^4H_{5/2}$	$^4I_{11/2}$	0.9902	0.0700
	24400	24210		$^4I_{9/2}$		
Dy^{3+}	35336	35200	$^6H_{15/2}$	$^4L_{17/2}$	0.9922	0.0624
	27946	27620		$^6P_{5/2}$		
Ho^{3+}	29820	29750	$^5I_8$	$^3L_9$	0.9942	0.0539
	27910	27780		$^3G_6$		
	24250	24155		$^5G_5$		
	22770	22520		$^5F_1$		
	22310	22218		$^5G_6$		
	18750	18590		$^5F_4$		
Er^{3+}	31800	31780	$^4I_{15/2}$	$^2K_{13/2}$	0.9962	0.0436
	26500	26410		$^4G_{11/2}$		
	25180	24980		$^2H_{9/2}$		
	19330	19290		$^2H_{11/2}$		
	15480	15400		$^4F_{9/2}$		

Based on the above discussion and the crystal structure study [11] on the $[Ni_2(TPHA)(bpy)_4](ClO_4)_2$ complex, we conclude that these complexes have extended CTPHA-bridged binuclear structures, in which the CTPHA ligand bridges in a *bis*-bidentate fashion, as shown in Figure 1. It should be pointed out that the most direct and forceful evidence for the above assumption may come from X-ray crystallographic studies. Unfortunately, all our efforts to grow crystals of these binuclear complexes suitable for X-ray structure determination so far have been unsuccessful. However, the plausible binuclear structure is proved by the following ESR and magnetic studies.

ESR spectra: In order to obtain further structural information, the X-band powder ESR spectra of $[Gd_2(CTPHA)(Mephen)_4(ClO_4)_2](ClO_4)_2$ and $Gd(ClO_4)_3{\cdot}6H_2O$ were measured at room temperature. The spectrum of the former is obviously different from that of the latter and exhibits a broad band, which further proves the formation of a binuclear complex and also indicates a magnetic spin-exchange interaction between Gd(III) ions [22]. Due to lack of structural data of this type complexes, it is difficult to quantitatively interpret this broad band. Qualitatively, however, it is clear that these features reflect the exchange coupling between Gd(III) ions. According to Kambe's approach [23], two spin states of Gd(III) ($S_1 = S_2 = 7/2$) coupled to yield the total spin states, $S_T = 7, 6, 5, 4, 3, 2, 1, 0$. On the basis of Boltzmann's distribution [24], all these states are thermally populated at room temperature owing to very weak interaction ($J = -0.16\ cm^{-1}$) (*vide infra*); thus, the broad signals may be ascribed to the complex in these spin states.

Magnetic properties of $[Gd_2(CTPHA)(Mephen)_4(ClO_4)_2](ClO_4)_2$: From the above discussion of ESR spectra, it has shown that a spin-coupled interaction exists

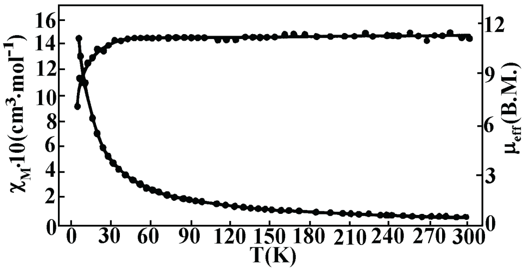

Figure 2. Variable-temperature magnetic susceptibility (lower curve) and magnetic moment (upper curve) for the complex $[Gd_2(CTPHA)(Mephen)_4(ClO_4)_2](ClO_4)_2$. The curve is based on Eq. (2) using the parameters given in the text. (•), experimental data; (-), calculated curve as described in the text.

between gadolinium(III) and gadolinium(III). Being interested in the magnetic behavior of the complexes, variable-temperature (4~300 K) magnetic susceptibility data were collected for $[Gd_2(CTPHA)(Mephen)_4(ClO_4)_2](ClO_4)_2$ complex, and the results are shown in Figure 2 in the form of plots of χ_M *vs.* T and μ_{eff} *vs.* T, where χ_M, μ_{eff} and T denote magnetic susceptibility per molecule, effective magnetic moment per molecule, and temperature, respectively. The reason for the choice of gadolinium is because Gd(III) ion and its complex are quite simple for a magnetic study. The Gd^{3+} ion has a $^8S_{7/2}$ ground state, which is located at some 3×10^4 cm^{-1} below the first excited state and is not perturbed by crystal field effects, and has no orbital angular momentum and the anisotropic effect [22,25,26]. Based on the inherent nature of Gd(III), the complex $[Gd_2(CTPHA)(Mephen)_4(ClO_4)_2](ClO_4)_2$ is an ideal model for studying the magnetic interaction between Ln(III) and Ln(III) ions among the ten binuclear complexes. As shown in Figure 2, the effective magnetic moment at room temperature is 11.15 B.M., which is slightly less than the spin-only value, 11.23 B.M., calculated from the equation $\mu_{eff} = (\mu^2_{Gd(III)} + \mu^2_{Gd(III)})^{1/2}$, in the absence of exchange interaction for a binuclear Gd(III) ($S_1 = S_2 = 7/2$) system, and nearly keeps constant over the 30–300 K region, but it sharply decreases below *ca.* 30 K. This behavior is characteristic for weak intramolecular antiferromagnetic spin-exchange interaction between the paramagnetic ions in the complex.

In order to further assess the strength of this magnetic interaction quantitatively, a magnetic analysis was performed with the susceptibility equation based on the Heisenberg spin-exchange operator:

$$\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2 \tag{1}$$

where the exchange parameter J is negative for an antiferromagnetic and positive for a ferromagnetic interaction. For the Gd(III)–Gd(III) ($S_1 = S_2 = 7/2$) system, the theoretical expression of magnetic susceptibility is easily derived from (1):

$$\chi_M = \frac{N\beta^2 g^2}{3kT}\left[\frac{A}{B}\right] \tag{2}$$

$$\begin{aligned} \text{where } A &= 840 + 546\exp(14x) + 330\exp(26x) + 180\exp(36x) + 84\exp(44x) + \\ &\quad 30\exp(50x) + 6\exp(54x), \\ B &= 15 + 13\exp(14\exp(26x) + 9\exp(36x) + 7\exp(44x) + 5\exp(50x) + \\ &\quad 3\exp(54x) + \exp(56x), \\ x &= -J/kT, \end{aligned}$$

and χ_M is the molecular susceptibility per binuclear complex and the remaining symbols have their usual meanings. As shown in Figure 2, good least-square fits to the experimental data were obtained for $J = -0.16\ \mathrm{cm}^{-1}$ and $g = 2.00$. The agreement factor F, defined here as $F = \Sigma[(\chi_M)_{obs.} - (\chi_M)_{calc.}]^2/\Sigma(\chi_M)_{obs.}$, is 1.9×10^{-5}. This result (small and negative J value) indicates that the complex is essentially binuclear and undergoes a very weak antiferromagnetic superexchange interaction between Gd(III)–Gd(III) ions. The very weak antiferromagnetic behavior of the complex may result mainly from the properties of the bridged ligand [18] and lanthanide(III) ions [26].

Acknowledgments

This project was supported by the Natural Science Foundation of Shandong Province and the National Natural Science Foundation of China.

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