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Synthesis and Magnetic Properties of μ-2-Nitroterephthalato-Bridged Binuclear Lanthanide(III) Complexes

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Nine new binuclear lanthanide(III) complexes described by the overall formula $[Ln_2(NTPHA)(Me_2bpy)_4(ClO_4)_2](ClO_4)_2$ (Ln = La, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er), where Me_2bpy stands for 4,4′-dimethyl-2,2′-bipyridine, and NTPHA represents the 2-nitroterephthalate dianions, have been synthesized and characterized by elemental analyses, IR, ESR and electronic spectra, and molar conductance measurements. It is proposed that these complexes present NTPHA-bridged structures consisting of two lanthanide(III) ions. The variable-temperature magnetic susceptibilities (4~300 K) of complex $[Gd_2(NTPHA)(Me_2bpy)_4(ClO_4)_2](ClO_4)_2$ were measured and studied, 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 $-0.12\ cm^{-1}$.

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

The syntheses and magnetic properties of rare earth metal binuclear complexes are important, 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 [1–7].

So far, much effort has been devoted to the development of multiatom bridging ligands that can afford magnetic interactions. Among other more elaborate ligands employed in the study of magnetic interactions, 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 dicarboxylate ligands have been synthesized and their magnetic properties have been studied [8–13]. It has been revealed by X-ray diffraction analyses [8,12] and variable-temperature magnetic susceptibility investigations that

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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-nitroterephthalato-bridged binuclear lanthanide(III) complexes have been reported. Owing to the importance mentioned above, it is considerable interest to synthesize and study rare earth metal binuclear complexes propagated by 2-nitroterephthalato (abbreviated as NTPHA) bridge in order to understand the feature and the molecular magnetism of this kind of complexes.

In this paper, we describe the syntheses and characterization of nine new μ-2-nitroterephthalato lanthanide(III) binuclear complexes of general formula $[Ln_2(NTPHA)(Me_2bpy)_4(ClO_4)_2](ClO_4)_2$ (Ln = La, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er; Me_2bpy = 4,4′-dimethyl-2,2′-bipyridine). The ESR spectra and magnetic properties of $[Gd_2(NTPHA)(Me_2bpy)_4(ClO_4)_2](ClO_4)_2$ complex have been studied in detail.

EXPERIMENTAL

Materials: Piperidinium 2-nitroterephthalate was synthesized by the literature method [8]. $Ln(ClO_4)_3 \cdot 6H_2O$ (Ln = La, 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 4,4′-dimethyl-2,2′-bipyridine (Me_2bpy) was analytical grade and used as commercially obtained.

Synthesis of $[Ln_2(NTPHA)(Me_2bpy)_4(ClO_4)_2](ClO_4)_2$ (Ln = La, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er): All the nine binuclear complexes were prepared in a similar fashion and only the typical preparation of $[Gd_2(NTPHA)(Me_2bpy)_4(ClO_4)_2](ClO_4)_2$ is given here. To a solution of piperidinium 2-nitroterephthalate (417 mg, 1 mmol) stirred in absolute ethanol (20 cm^3) was added successively a solution of $Gd(ClO_4)_3 \cdot 6H_2O$ (1128 mg, 2 mmol) in absolute ethanol (25 cm^3), followed by a solution of ethyl orthoformate (15 cm^3) and Me_2bpy (737 mg, 4 mmol) in the same solvent (20 cm^3) at the 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 DMF/ethanol (1:2) mixture.

All the analytical data, 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. 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 using a Quantum Design MPMS SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants [14] for all the constituent atoms and effective magnetic moments were calculated by the equation $\mu_{eff} = 2.828(\chi_M T)^{1/2}$, where χ_M is the molar magnetic susceptibility corrected for diamagnetisms of the constituting atoms.

RESULTS AND DISCUSSION

Composition and coordination environment of the complexes: Elemental analyses and physical data (see Tables 1, 2 and 3) have indicated that the reaction of NTPHA with $Ln(ClO_4)_3 \cdot 6H_2O$ and the terminal ligand Me_2bpy in 1:2:4 mole ratio in absolute ethanol readily forms binuclear complexes of general formula

$Ln_2(NTPHA)(Me_2bpy)_4(ClO_4)_4$ (Ln = La, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er), as expected. These complexes are the first examples of Ln(III)–Ln(III) binuclear complexes bridged by 2-nitroterephthalato group. Based on the stoichiometric determinations, spectroscopic characterization and magnetic studies (*vide infra*) these complexes are presumed to have the coordination environment as shown in Figure 1.

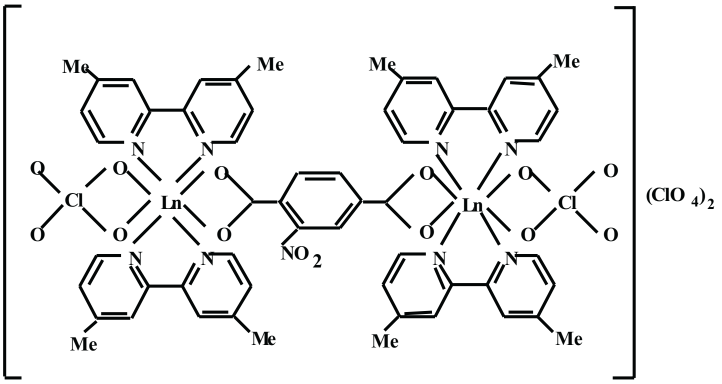

Figure 1. Plausible coordination environment of the complexes (Ln = La, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er).

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 nine binuclear complexes, the molar conductance values in acetonitrile solution (see Table 2) fall in the expected for 1:2 electrolytes [15], indicating that only two perchlorate anions lie outside the coordination sphere and the other 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.

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. It is noteworthy that the spectrum of 2-nitroterephthalic acid (H_2NTPHA) shows a broad band near 1705 cm^{-1}, which may be attributed to υ(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 1400 cm^{-1}, attributed to υ_{as}(COO) (1575~1590 cm^{-1}) and υ_s(COO) (1420~1430 cm^{-1}) stretching vibrations of the coordinated carboxylate groups. The absence of any splitting of the υ_{as}(COO) and υ_s(COO) bands strongly suggests end-to-end linking of the 2-nitroterephthalato ligand in an equivalent way at both sites [16]. According to the literature [17], the coordination modes of carboxylate groups have been determined by a separation between v_{as}(COO) and v_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 the difference in asymmetric and symmetric carboxylate groups frequencies ($\Delta = v_{as}(COO) - v_s(COO) \approx 160\ cm^{-1}$) indicates that the ligand (NTPHA) is acting as a bidentate chelating coordination mode for both carboxylate groups. The coordination mode of the carboxylates in bridging ligand (NTPHA) has been revealed by X-ray diffraction analysis of the μ-terephthalato nickel(II) binuclear complex [12] $[Ni_2(TPHA)(bpy)_4](ClO_4)_2$ (TPHA = terephthalato dianions). On the other hand, the -N=C- stretching vibration for the terminal ligand (Me_2bpy) 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 $\nu_{Ln\text{-}N}$, 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 bands 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 [18,19], 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, these complexes may be formulated as $[Ln_2(NTPHA)(Me_2bpy)_4(ClO_4)_2](ClO_4)_2$ (Ln = La, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er).

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

Complex	Empirical Formula (Formula Weight)	Color	M.p. (°C)	Yield (%)
(1)	$La_2C_{56}H_{51}N_9O_{22}Cl_4$ (1621.69)	white	313.5	73
(2)	$Nd_2C_{56}H_{53}N_9O_{23}Cl_4$ (1650.37)	violet	306.2	66
(3)	$Sm_2C_{56}H_{51}N_9O_{22}Cl_4$ (1644.68)	pale-purple	298.0	70
(4)	$Eu_2C_{56}H_{55}N_9O_{24}Cl_4$ (1683.83)	white	253.7	78
(5)	$Gd_2C_{56}H_{51}N_9O_{22}Cl_4$ (1658.38)	white	302.6	86
(6)	$Tb_2C_{56}H_{53}N_9O_{23}Cl_4$ (1679.74)	pale-violet	319.2	85
(7)	$Dy_2C_{56}H_{51}N_9O_{22}Cl_4$ (1668.88)	white	339.1	80
(8)	$Ho_2C_{56}H_{51}N_9O_{22}Cl_4$ (1673.74)	pale-red	313.5	68
(9)	$Er_2C_{56}H_{51}N_9O_{22}Cl_4$ (1678.40)	brown	343.6	77

(1) = $La_2(NTPHA)(Me_2bpy)_4(ClO_4)_4$, **(2)** = $Nd_2(NTPHA)(Me_2bpy)_4(ClO_4)_4 \cdot H_2O$,
(3) = $Sm_2(NTPHA)(Me_2bpy)_4(ClO_4)_4$, **(4)** = $Eu_2(NTPHA)(Me_2bpy)_4(ClO_4)_4 \cdot 2H_2O$,
(5) = $Gd_2(NTPHA)(Me_2bpy)_4(ClO_4)_4$, **(6)** = $Tb_2(NTPHA)(Me_2bpy)_4(ClO_4)_4 \cdot H_2O$,
(7) = $Dy_2(NTPHA)(Me_2bpy)_4(ClO_4)_4$, **(8)** = $Ho_2(NTPHA)(Me_2bpy)_4(ClO_4)_4$,
(9) = $Er_2(NTPHA)(Me_2bpy)_4(ClO_4)_4$.

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

Complex						$\nu(ClO_4^-)$ (coordinated)					$\nu(ClO_4^-)$ (ionic)	
	$\Lambda_M{}^a$	$\nu_{as}(COO)$	$\nu_s(COO)$	$\nu(C=N)$	$\nu(Ln\text{-}N)$	ν_8	ν_6	ν_1	ν_2	ν_3	ν_3	ν_4
(1)	260	1580	1420	1530	380	1140	1100	1020	941	630	1089	615
(2)	265	1582	1426	1530	380	1140	1105	1020	942	635	1088	620
(3)	270	1585	1428	1530	382	1140	1109	1020	942	635	1090	618
(4)	262	1578	1430	1532	380	1142	1100	1020	940	635	1090	620
(5)	258	1575	1420	1531	380	1141	1100	1020	940	634	1090	617
(6)	272	1580	1425	1530	380	1143	1100	1020	940	635	1087	620
(7)	274	1584	1420	1530	385	1140	1100	1020	940	630	1090	614
(8)	278	1585	1425	1528	384	1140	1100	1020	940	630	1085	615
(9)	280	1590	1430	1529	380	1142	1100	1020	940	636	1090	612

[a] Values for 1×10^{-3} mol·L^{-1} acetonitrile solution; unit: S·cm^2·mol^{-1}.

Electronic spectra: Electronic spectral studies of these complexes have been carried out to elucidate their structure. Since the electronic absorption spectra of the nine complexes in DMF solutions are similar (see Table 3), 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 NTPHA ligand [20]. 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 also observed [21] for binuclear complexes of Nd(III), Sm(III), Tb(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, Tb, Ho, Er), the parameters $\bar{\beta}$ and $b^{1/2}$ were obtained [22,23], where $\bar{\beta}$ is the nephelauxetic ratio, which is defined as: $\bar{\beta} = \frac{1}{n}\sum\frac{\nu_{complex}}{\nu_{aquo}}$, and $b^{1/2}$ measures the amount of 4f orbital mixing, *i.e.* covalency. The bonding parameter is related to the nephelauxetic ratio ($\bar{\beta}$) by the relation: $b^{1/2} = [(1-\bar{\beta})/2]^{1/2}$. 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 ordinal number of the rare earth metal increases for the same ligand. This is in agreement with the general observation that the nephelauxetic effect is more pronounced in the beginning of the 4f ground than for the later members.

Based on the above discussion and the crystal structure of an analogous complex study [12] on the $[Ni_2(TPHA)(bpy)_4](ClO_4)_2$, we conclude that these complexes have extended NTPHA-bridged binuclear structures, in which the NTPHA 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.

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 ground		
Nd^{3+}	12650	12520	$^4I_{9/2}$	$^4F_{5/2}$	0.9903	0.0696
	13570	13415		$^4F_{7/2}$		
	17600	17390		$^4G_{5/2}$, $^2G_{7/2}$		
	19280	19180		$^4G_{7/2}$		
Sm^{3+}	21150	20950	$^4H_{5/2}$	$^4I_{11/2}$	0.9928	0.0600
	24400	24280		$^4I_{9/2}$		
Tb^{3+}	23450	23285	$^7F_6$	$^5F_4$	0.9930	0.0592
Ho^{3+}	29820	29760	$^5I_8$	$^3L_9$	0.9941	0.0543
	27910	27790		$^3G_6$		
	24250	24130		$^5G_5$		
	22770	22540		$^5F_1$		
	22310	22200		$^5G_6$		
	18750	18580		$^5F_4$		
Er^{3+}	31800	31750	$^4I_{15/2}$	$^2K_{13/2}$	0.9956	0.0469
	26500	26390		$^4G_{11/2}$		
	25180	24950		$^2H_{9/2}$		
	19330	19280		$^2H_{11/2}$		
	15480	15410		$^4F_{9/2}$		

ESR spectra: In order to obtain further structural information, the X-band powder ESR spectra of $[Gd_2(NTPHA)(Me_2bpy)_4(ClO_4)_2](ClO_4)_2$ and $Gd(ClO_4)_3 \cdot 6H_2O$ were measured at room temperature. It is noteworthy that the spectrum of the former is obviously different from that of the latter and exhibits a dissymmetric broad band, which further proves the formation of a binuclear complex and also indicates a magnetic spin-exchange interaction between Gd(III) ions [24]. Since there is a lack of structural data for this complex, it is difficult to interpret this broad band quantitatively. Qualitatively, however, it is clear that these features reflect the exchange coupling between Gd(III) ions. Thus, at this stage, the dissymmetric broad band appeared for the complex may be rationalized by the following reasons. According to Kambe's approach [25], 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 [26], all these states are thermally populated at room temperature owing to very weak interaction ($J = -0.12\ cm^{-1}$) (*vide infra*); thus, the broad signals may be ascribed to the complex in these spin states.

Magnetic properties of $[Gd_2(NTPHA)(Me_2bpy)_4(ClO_4)_2](ClO_4)_2$: From the above discussion of ESR spectra, it has shown that a spin-coupled interaction exists 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 $[Gd_2(NTPHA)(Me_2bpy)_4(ClO_4)_2](ClO_4)_2$ complex, as an example, and the results are shown in Figure 2 as plots χ_M *versus* T and μ_{eff} *versus* T, where χ_M, μ_{eff} and T denote magnetic susceptibility per molecule, effective magnetic moment per molecule, and absolute temperature, respectively. Gadolinium is chosen because the gadolinium(III) ion and its complex are quite simple to study magnetically since the ground state of gadolinium(III) ion is $^8S_{7/2}$ and the energy level of the lowest excited state is very high, *i.e.*, the magnetic data usually can be interpreted without considering the contribution of the orbital angular momentum and the anisotropic effect [24,27,28]. Based on the inherent nature of the gadolinium(III), the complex $[Gd_2(NTPHA)(Me_2bpy)_4(ClO_4)_2](ClO_4)_2$ is an ideal model for studying the magnetic interaction between lanthanum(III) and lanthanum(III) ions among the nine binuclear complexes. As shown in Figure 2, the effective magnetic moment at room temperature is 11.10 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 gadolinium(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.

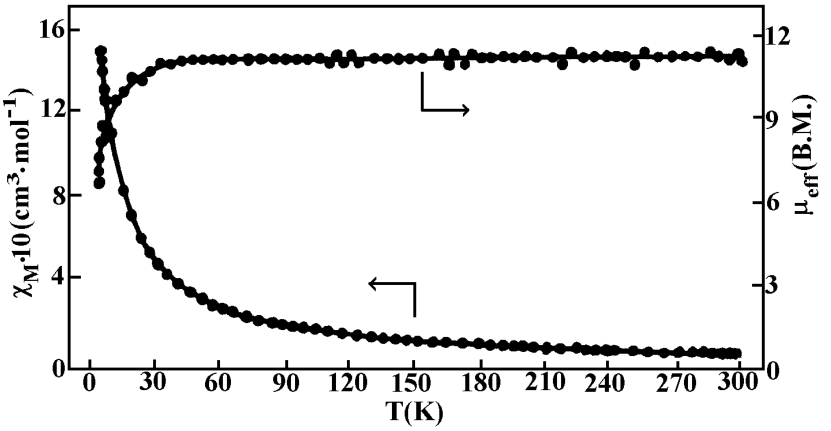

Figure 2. Variable-temperature magnetic susceptibility (lower curve) and magnetic moment (upper curve) for the complex $[Gd_2(NTPHA)(Me_2bpy)_4(ClO_4)_2](ClO_4)_2$. The curve is based on Eq. (2) using the parameters given in the text. (•), experimental data; (-), calculated curve as described in the text.

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

$$\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2 \qquad (1)$$

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

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

where A = 840 + 546exp(14x) + 330exp(26x) + 180exp(36x) + 84exp(44x) + 30exp(50x) + 6exp(54x), B = 15 + 13exp(14x) + 11exp(26x) + 9exp(36x) + 7exp(44x) +

5exp(50x) + 3exp(54x) + exp(56x), $x = -J/kT$, 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 $J = -0.12$ cm^{-1}, $g = 2.01$. The agreement factor F, defined here as $F = \Sigma[(\chi_M)_{obs.} - (\chi_M)_{calc.}]^2/\Sigma(\chi_M)_{obs.}$, is 1.5×10^{-5}. This result (small and negative J value) indicates that the complex is essentially binuclear and undergoes a very weak antiferromagnetic superexchange interaction between gadolinium(III)–gadolinium(III) ions. The small J value observed for the complex may be rationalized by the following reasons: (i) The distance between the two gadolinium(III) ions in the complex is long [20]; (ii) The 4f-electrons are shielded by the outershell electrons [28], therefore, the small J value is reasonable.

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