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Synthesis, crystal structures and magnetic properties of tetrakis(μ_2-carboxylate)-bridged dimeric gadolinium(III) complexes

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ABSTRACT Four dimeric gadolinium(III) complexes, $[Gd_2(pybet)_4(H_2O)_8](ClO_4)_6$ (**1**), $[Gd_2(pybet)_4(phen)_4](ClO_4)_6\cdot 3H_2O$ (**3**), $[Gd_2(pybet)_6(phen)_2(H_2O)_2](ClO_4)_6\cdot 2H_2O$ (**4**), and $[Gd_2(ppbet)_6(bpy)_2](ClO_4)_6\cdot 3H_2O$ (**5**) (pybet = $C_5H_5N^+CH_2CO_2^-$, ppbet = $C_5H_5N^+CH_2CH_2CO_2^-$, phen = 1,10-phenanthroline, bpy = 2,2′-bipyridine) have been prepared and structurally characterized by X-ray crystallography. The complexes comprise discrete quadruply carboxylate-*O,O′* bridged $[Gd_2(carboxylate)_4]^{6+}$ dimeric cores in which each metal atom is further coordinated by four terminal aqua ligands, one monodentate pybet carboxylate group and three aqua ligands, two phen ligands and a bpy ligand and a chelate ppbet carboxylate group for **1, 3, 4** and **5**, respectively. In the four complexes, the metal atoms all adopt distorted square-antiprismatic coordination geometries. The variable-temperature (4-300 K) magnetic susceptibility of **5** has been determined and the observed susceptibility data were fitted to the theoretical magnetic equation. The exchange integral J was found to be 0.037 cm^{-1}, indicating very weak ferromagnetic spin-exchange interaction between the pair of Gd(III) ions in the dimers.

ABSTRAK Empat kompleks berdimer gadolinium(III), $[Gd_2(pybet)_4(H_2O)_{18}](ClO_4)_6$ (**1**), $[Gd_2(pybet)_4(phen)_4](ClO_4)_6\cdot 3H_2O$ (**3**), $[Gd_2(pybet)_4(phen)_4(H_2O)_2](ClO_4)_6\cdot 2H_2O$ (**4**) dan $[Gd_2(ppbet)_6(bpy)_2](ClO_4)_6\cdot 3H_2O$ (**5**) (pybet = $C_5H_5N^+CH_2CO_2^-$, ppbet = $C_5H_5CH_2CH_2CO_2^-$, phen = 1,10-fenantrolina, bpy = bipridina) telah disediakan dan strukturnya dikaji secara kristalografi sinar-X. Kompleks-kompleks terdiri dari teras berdimer $[Gd_2(carboxylat)_4]^{6+}$ diskrit yang mempunyai ikatan karboksil-*O,O′* dimana tiap-tiap atom logamnya dikoordinat oleh empat ligan air, dua ligan fenantrolina, dan satu ligan bpy dan satu kumpulan karboxylat ppbet berkelat untuk **1,3,4** dan **5**, masing-masing. Dalam keempat-empat komplek ini, atom logam mengambil geometri koordinat antiprismatik empatsegi-sama terherot. Kerentanan magnet ubah-suhu (4 - 300 K) untuk **5** telah ditentukan dan data kerentanan disesuaikan ke persamaan magnet teori. Kamilan penukaran J adalah 0.037 cm^{-1}, yang menunjukkan interaksi penukaran spin yang terlalu lemah diantara pasangan ion Gd(III) dalam dimer.

INTRODUCTION

Bridged polynuclear complexes have attracted considerable interest in recent years [1]. Synthesis, spectroscopic and magnetic investigations of new polynuclear complexes are of significance for understanding the magnetic interaction between metal ions and for further design of molecular magnetic materials. The studies on magnetism of binuclear lanthanide(III) complexes will provide first hand information of the magnetic interactions between the *f* electrons [2].

The coordination chemistry of lanthanide(III) carboxylates has been widely studied, and several types of coordination modes of carboxylate ligands have been established [2-5]. Lanthanide(III) carboxylates are commonly found in polymeric forms including dimeric forms, however, magnetic properties of lanthanide(III) carboxylates are rarely known so far. The first report on magnetic properties of dimeric lanthanide(III) carboxylates appeared very recently, in which two of the acetate act in the bidentate bridging mode and the others two in the bidentate bridging plus chelate mode [6]. Furthermore, lanthanide(III) carboxylate complexes containing other nitrogen ligands are less well known [5].

Betaine derivatives, as neutral analogues of carboxylates, have been extensively used in the preparation of transition metal complexes [7]. We have recently synthesized some interesting heterometallic copper(II)-lanthanide(III) complexes [8-10]. We now report the preparation, structures and magnetic properties of five tetrakis(μ_2-carboxylate)-bridged dimeric Gd(III) complexes, namely $[Gd_2(pybet)_4(H_2O)_8](ClO_4)_6$ (**1**), $[Gd_2(pybet)_6(H_2O)_6](ClO_4)_6\cdot 2H_2O$ (**2**), $[Gd_2(pybet)_4(phen)_4](ClO_4)_6\cdot 3H_2O$ (**3**), $[Gd_2(pybet)_4(phen)_2(H_2O)_2](ClO_4)_6\cdot 2H_2O$ (**4**) and $[Gd_2(ppbet)_6(bpy)_2](ClO_4)_6\cdot 3H_2O$ (**5**).

EXPERIMENTAL

The ligands pybet and ppbet were synthesized by the

literature method [11]. All other reagents were commercially available and used as received. The C, H, N microanalyses were carried out with a Perkin-Elmer 240 elemental analyzer. The FT-IR spectra were recorded from KBr pellets in range 4000-400 cm^{-1} on a Nicolet 5DX spectrometer. Variable-temperature magnetic susceptibility data were obtained on a Quantum Design SQUID magnetometer. Diamagnetic corrections were performed with Pascal's constants [12] for all the constituent atoms and the effective molar magnetic moments were calculated with the equation $\mu_{eff} = 2.828(\chi_M T)^{1/2}$.

Preparation of complexes

$[Gd_2(pybet)_4(H_2O)_8](ClO_4)_6$ (**1**). To an aqueous solution (5 ml) containing pybet (0.274 g, 2.0 mmol) was added $Gd(NO_3)_3 \cdot nH_2O$ (1.0 mmol) and $NaClO_4 \cdot H_2O$ (0.42 g, 3.0 mmol), the mixture was then stirred at 50-60 °C for 10 min. The resulting solution was allowed to stand in a desiccator charged with silica gel. After a few days, colorless block crystals were deposited. The yield was about 80%. Anal. calcd for $C_{28}H_{44}Cl_6Gd_2N_4O_{40}$: C, 21.0; H, 2.8; N, 3.5%. Found: C, 20.7; H, 2.7; N, 3.4%. IR (KBr, cm^{-1}): 3402m, 3135m, 3057m, 2934m, 1630s, 1489s, 1440s, 1398s, 1314m, 1152vs, 1100w, 1089vs, 976w, 941w, 850w, 779s, 702s, 674s, 632vs.

$[Gd_2(pybet)_6(H_2O)_6](ClO_4)_6 \cdot 2H_2O$ (**2**). This complex was prepared with the same procedure described for **1** using 1:3 molar ratio of $Gd(NO_3)_3$ and pybet. The product was isolated as colorless block crystals. Anal. calcd for $C_{42}H_{58}Cl_6Gd_2N_6O_{44}$: C, 26.8; H, 3.1; N, 4.5%. Found: C, 26.3; H, 2.9; N, 4.2%. IR (KBr, cm^{-1}): 3399m, 3085m, 3015m, 2903m, 1651vs, 1630s, 1482s, 1447s, 1398s, 1314m, 1115vs, 1100w, 1082vs, 976w, 941w, 850w, 779s, 702s, 674s, 632vs.

$[Gd_2(pybet)_4(phen)_4](ClO_4)_6 \cdot 3H_2O$ (**3**). To an aqueous solution (5 ml) containing pybet (0.274 g, 2.0 mmol) was added $Gd(NO_3)_3 \cdot nH_2O$ (1.0 mmol), the mixture was then stirred at 50-60 °C for 10 min. After that a 1:1 aqueous ethanol solution (5 ml) of phen (0.198 g, 1.0 mmol) was added, followed with an aqueous solution (3 ml) of $NaClO_4 \cdot H_2O$ (0.42 g, 3.0 mmol). The resulting solution was allowed to stand in a desiccator charged with silica gel. After a few days, colorless block crystals were deposited. The yield was about 88%. Anal. calcd for $C_{76}H_{66}Cl_6Gd_2N_{12}O_{35}$: C, 40.9; H, 3.0; N, 7.5%. Found: C, 40.6; H, 2.7; N, 7.2%. IR (KBr, cm^{-1}): 3402m, 3135m, 3057m, 2934m, 1630s, 1489s, 1440s, 1398s, 1314m, 1152vs, 1100w, 1089vs, 976w, 941w, 850w, 779s, 702s, 674s, 632vs.

$[Gd_2(pybet)_6(phen)_2(H_2O)_2](ClO_4)_6 \cdot 2H_2O$ (**4**). This complex was prepared with the same procedure described for **3** using 1:3 molar ratio of $Gd(NO_3)_3$ and pybet. The product was isolated as colorless block crystals. Anal. calcd for $C_{66}H_{66}Cl_6Gd_2N_{10}O_{40}$: C, 36.6; H, 3.1; N, 6.5%. Found: C, 36.1; H, 3.0; N, 6.4%. IR (KBr, cm^{-1}): 3399m, 3085m, 3015m, 2903m, 1651vs, 1630s, 1482s, 1447s, 1398s, 1314m, 1115vs, 1100w, 1082vs, 976w, 941w, 850w, 779s, 702s, 674s, 632vs.

$[Gd_2(ppbet)_6(bpy)_2](ClO_4)_6 \cdot 3H_2O$ (**5**). The complex was prepared with the same procedure described for **3** using ppbet and bpy in stead of pybet and phen, respectively, and using 1:3 molar ratio of $Gd(NO_3)_3$ and ppbet. The product was isolated as colorless block crystals. Anal. calcd for $C_{68}H_{76}Cl_6Gd_2N_{10}O_{39}$: C,37.4; H, 3.5; N, 6.4%. Found: C, 37.3; H, 3.3; N, 6.2%. IR (KBr, cm^{-1}): 3409m, 3105m, 3057m, 2923m, 1651vs, 1630s, 1482s, 1447s, 1398s, 1314m, 1115vs, 1100w, 1082vs, 976w, 941w, 850w, 779s, 702s, 674s, 632vs.

X-ray diffraction analyses

The intensity data of the four complexes **1**, **3**, **4** and **5** were collected on a Siemens P4 diffractometer with graphite-monochromated MoKα radiation using the ω-scan technique. Data processing, absorption corrections and structure solutions were made with SHELXTL-PC program package [13]. Full-matrix least-squares refinement were performed with SHELXL-93 [14]. Details of the crystallographic studies are given in Table 1, atomic coordinates and thermal parameters are given in Table 2, selected bond lengths and bond angles in Table 3.

RESULTS AND DISCUSSION

The five complexes **1** - **5** were conveniently obtained in good yields from the following scheme. The isolation of complexes **1** - **4** from the similar reaction systems implies that there should be an equilibrium in the solution with the quadruply carboxylate-*O,O'* bridged $[Gd_2(pybet)_4]^{6+}$ dimeric core as an intermediate. Hence without the presence of additional ligands other than water molecules complex **1** can be isolated; when additional ligands such as excessive pybet or phen ligands in the reaction systems, complexes **2** and **3** can be ob-

Table 1. Crystallographic data.

	1	3	4	5
Empirical formula	$C_{28}H_{44}Cl_6Gd_2N_4O_{40}$	$C_{76}H_{66}Cl_6Gd_2N_{12}O_{35}$	$C_{66}H_{66}Cl_6Gd_2N_{10}O_{40}$	$C_{68}H_{76}Cl_6Gd_2N_{10}O_{39}$
Formula weight	1603.87	2230.6	2166.49	2184.59
Temperature (K)	293	294	293	293
Wavelength l (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	triclinic	Orthorhombic	triclinic	monoclinic
Space group	$P\bar{1}$	*Imm2*	$P\bar{1}$	$P2_1/c$
a (Å)	9.081(1)	22.468(4)	13.081(2)	14.344(2)
b (Å)	11.253(1)	14.216(3)	13.3820(10)	24.669(4)
c (Å)	15.203(2)	14.963(3)	14.3170(10)	12.259(3)
α (°)	97.534(7)	90	62.760(10)	90
β (°)	105.427(9)	90	79.780(10)	93.590(10)
g (°)	112.579(3)	90	74.450(10)	90
Volume (Å^3)	1334.1(3)	4779(2)	2142.3(4)	4329.4(14)
Z	1	2	1	2
Density (calculated)	1.996 Mg/m^3	1.550 Mg/m^3	1.679 Mg/m^3	1.676 Mg/m^3
Absorption coefficient	2.878 mm^{-1}	1.630 mm^{-1}	1.819 mm^{-1}	1.80 mm^{-1}
F(000)	790	2224	1082	2192
Crystal size	0.20 x 0.32 x 0.36 mm	0.2 x 0.2 x 0.24 mm	0.22 x 0.32 x 0.34 mm	0.20 x 0.30 x 0.40 mm
θ range for data collection	2.03 to 27.50°	3.0 to 52.0°	1.60 to 25.00°	1.64 to 25.89
Reflections collected	6997	2876	7257	7562
unique reflections	5924 [R(int) = 0.0088]	2746	7257	7150
Data/restraints/parameters	5924 / 20 / 397	2741/26/357	7257 / 34 / 553	7136 / 40 / 560
Goodness-of-fit on F^2	0.872	1.31	1.016	1.003
Final *R* indices [$I > 2\sigma$]	$R_1 = 0.0295$, $wR_2 = 0.0924$	$R_1 = 0.0676$, $wR_2 = 0.1811$	$R_1 = 0.0516$, $wR_2 = 0.1429$	$R_1 = 0.0527$, $wR_2 = 0.1314$
Largest diff. peak and hole	0.909/-1.464 e·Å^{-3}	0.79/-1.34 e·Å^{-3}	1.342/-1.204 e·Å^{-3}	1.013/-1.340 e·Å^{-3}

Table 2. Atomic coordinates ($\times 10^4$) and thermal parameters($U_{eq} \times 10^3$).

(a) Complex **1**

atom	*x*	*y*	*z*	U_{eq}	atom	*x*	*y*	*z*	U_{eq}
Gd(1)	1614(1)	118(1)	4105(1)	21(1)	C(25)	2489(9)	4293(7)	9198(4)	78(2)
O(1w)	916(5)	-410(3)	2435(2)	47(1)	C(26)	3405(9)	3616(7)	9082(4)	77(2)
O(2w)	2486(4)	2168(3)	3609(2)	42(1)	C(27)	3711(8)	3455(6)	8269(4)	59(1)
O(3w)	2340(4)	-1675(3)	3653(2)	43(1)	Cl(1)	3810(2)	2366(1)	1544(1)	47(1)
O(4w)	4584(4)	1055(3)	4419(2)	44(1)	O(13)	2316(7)	1161(5)	1302(4)	97(2)
O(11)	2494(4)	-617(3)	5457(2)	38(1)	O(14)	4973(7)	2247(6)	1119(4)	101(2)
O(12)	721(4)	-601(3)	6222(2)	40(1)	O(15)	4632(6)	2833(6)	2548(3)	93(2)
C(11)	1913(5)	-802(4)	6116(3)	31(1)	O(16)	3378(8)	3368(6)	1256(5)	109(2)
C(12)	2816(8)	-1326(7)	6842(4)	59(2)	Cl(2)	7446(2)	2779(1)	8637(1)	60(1)
N(1)	2277(5)	-1375(4)	7666(2)	37(1)	O(23)	8764(5)	2356(4)	8785(3)	68(1)
C(13)	3126(9)	-353(6)	8420(4)	71(2)	O(24)	6181(6)	2003(5)	7712(3)	77(1)
C(14)	2667(15)	-353(11)	9188(5)	114(4)	O(25)	6668(6)	2542(6)	9316(3)	82(1)
C(15)	1320(16)	-1381(15)	9193(6)	121(5)	O(26)	8082(10)	4153(5)	8663(6)	129(3)
C(16)	423(10)	-2452(10)	8422(8)	98(3)	Cl(3)	2260(2)	5402(1)	4554(1)	66(1)
C(17)	921(7)	-2441(6)	7641(4)	61(1)	O(33)*	1193(16)	5683(12)	3828(9)	107(7)
O(21)	2474(4)	1875(3)	5388(2)	43(1)	O(34)*	3923(14)	5849(20)	4472(16)	303(22)
O(22)	729(4)	1865(3)	6173(2)	42(1)	O(35)*	1568(13)	4045(7)	4511(9)	55(3)
C(21)	2087(5)	2349(4)	6024(3)	32(1)	O(36)*	2439(23)	6134(14)	5463(7)	185(11)
C(22)	3463(6)	3691(4)	6688(3)	44(1)	O(33')*	951(16)	5776(17)	4163(11)	117(7)
N(2)	3143(5)	3960(3)	7572(2)	37(1)	O(36')*	3370(17)	6297(10)	5455(7)	117(6)
C(23)	2227(8)	4616(5)	7659(5)	60(1)	O(35')*	1527(22)	4094(9)	4667(12)	139(10)
C(24)	1923(10)	4800(7)	8514(6)	82(2)	O(34')*	3208(23)	5451(19)	3922(13)	215(13)

(a) Complex **3**

atom	*x*	*y*	*z*	U_{eq}	atom	*x*	*y*	*z*	U_{eq}
Gd(1)	0	0	0	54(1)	C(36)	1637(5)	466(10)	-2999(8)	81(1)
Gd(2)	0	0	2968(1)	53(1)	N(41)	603(4)	1072(7)	4010(6)	61(1)
O(11)	877(3)	0	796(7)	63(1)	C(41)	1199(5)	1182(8)	3983(8)	73(1)
O(12)	986(6)	0	2295(8)	77(1)	C(42)	1529(7)	1735(10)	4561(9)	87(1)
C(11)	1161(6)	0	1509(13)	66(1)	C(43)	1266(5)	2127(8)	5250(7)	69(1)
C(12)	1852(5)	0	1537(12)	67(1)	C(44)	621(6)	2111(9)	5343(7)	76(1)
N(11)	2068(6)	0	2435(8)	71(1)	C(45)	318(5)	1560(7)	4713(7)	63(1)
C(13)	2217(8)	851(10)	2849(8)	94(1)	C(46)	309(7)	2568(9)	6021(9)	85(1)
C(14)	2425(9)	876(10)	3685(10)	100(1)	Cl(1)	3705(3)	0	1475(8)	144(1)
C(15)	2558(8)	0	4135(10)	80(1)	O(13)	3354(7)	758(9)	1265(10)	165(1)
O(21)	0	1476(5)	722(5)	48(1)	O(14)	4229(6)	0	1017(11)	199(1)
O(22)	0	1322(12)	2162(12)	116(1)	O(15)	3810(9)	0	2397(7)	159(1)
C(21)	0	1839(8)	1424(9)	57(1)	Cl(2)	1972(2)	2824(4)	1812(3)	133(1)
C(22)	0	2902(7)	1477(13)	68(1)	O(23)*	2522(5)	2535(11)	1522(11)	124(1)
N(21)	0	3276(8)	2438(8)	67(1)	O(24)*	1577(6)	2089(9)	1876(11)	116(1)
C(23)	518(9)	3453(12)	2831(12)	116(1)	O(25)*	1744(8)	3490(9)	1210(9)	137(1)
C(24)	518(10)	3693(12)	3711(12)	123(1)	O(26)*	2030(8)	3270(10)	2637(7)	125(1)
C(25)	0	3926(12)	4153(12)	98(1)	O(23')*	2360(6)	2877(10)	1088(8)	99(1)
N(31)	706(6)	959(8)	-1045(7)	75(1)	O(24')*	1457(4)	2374(8)	1557(10)	81(1)
C(31)	748(7)	1884(8)	-985(9)	86(1)	O(25')*	1854(7)	3715(7)	2131(10)	112(1)
C(32)	1089(9)	2401(11)	-1561(11)	106(1)	O(26')*	2253(7)	2299(10)	2481(8)	135(1)
C(33)	1401(10)	1961(13)	-2229(12)	124(1)	O(1w)	606(11)	5000	1199(12)	141(1)
C(34)	1334(6)	1004(9)	-2339(8)	78(1)	O(2w)*	0	0	6253(12)	118(1)
C(35)	983(4)	482(8)	-1668(6)	62(1)					

(a) Complex **4**

atom	*x*	*y*	*z*	U_{eq}	atom	*x*	*y*	*z*	U_{eq}
Gd(1)	363(1)	3196(1)	1272(1)	36(1)	C(43)	-1999(9)	1(9)	3384(9)	80(3)
O(1w)	923(5)	1762(5)	555(5)	62(1)	C(44)	-1616(7)	467(7)	3917(7)	63(2)

O(11)	966(4)	4601(4)	1494(4)	48(1)	C(45)	-1008(6)	1307(6)	3328(6)	50(2)
O(12)	739(4)	6303(5)	83(4)	55(1)	C(46)	-1827(9)	123(9)	5029(8)	82(3)
C(11)	1108(6)	5603(6)	953(5)	42(2)	C(47)	-1486(9)	593(10)	5508(7)	79(3)
C(12)	1796(7)	6054(7)	1344(6)	55(2)	C(48)	-864(7)	1458(8)	4947(6)	60(2)
N(11)	2162(5)	5235(5)	2411(5)	48(1)	C(49)	-606(6)	1791(6)	3862(5)	46(2)
C(13)	1717(7)	5428(9)	3246(7)	65(2)	C(50)	-474(9)	1974(9)	5428(7)	76(3)
C(14)	2038(9)	4638(11)	4241(7)	82(3)	C(51)	136(9)	2769(10)	4844(6)	80(3)
C(15)	2806(10)	3681(10)	4351(7)	85(3)	C(52)	347(8)	3039(8)	3777(6)	64(2)
C(16)	3245(9)	3520(9)	3504(8)	81(3)	Cl(1)	5000	5000	0	76(1)
C(17)	2906(7)	4305(8)	2528(7)	62(2)	O(13)	4144(10)	4535(14)	121(14)	99(5)
O(21)	1484(5)	3976(5)	-213(4)	63(2)	O(14)	4968(18)	5957(13)	-960(11)	129(7)
O(22)	1254(4)	5677(5)	-1613(4)	54(1)	O(15)	4789(15)	5509(15)	708(12)	106(5)
C(21)	1772(6)	4703(7)	-1087(5)	47(2)	O(16)	6000(10)	4311(17)	139(18)	129(7)
C(22)	2861(6)	4331(7)	-1515(6)	57(2)	Cl(2)	5000	0	5000	79(1)
N(21)	3164(5)	5224(6)	-2529(5)	53(2)	O(23)	5511(26)	-932(28)	4691(26)	181(11)
C(23)	3430(7)	6121(9)	-2559(8)	70(2)	O(24)	5695(23)	430(25)	5340(22)	160(9)
C(24)	3675(9)	6985(10)	-3505(10)	90(3)	O(25)	4151(21)	725(24)	4528(22)	152(9)
C(25)	3656(10)	6900(12)	-4410(9)	98(4)	O(26)	5443(14)	716(15)	3896(15)	102(5)
C(26)	3381(14)	6014(14)	-4370(9)	122(5)	Cl(3)	1191(2)	2955(2)	7351(2)	71(1)
C(27)	3145(11)	5140(11)	-3411(8)	92(4)	O(33)*	2256(9)	2951(17)	6864(14)	135(8)
O(31)	2013(4)	2087(5)	1982(4)	63(2)	O(34)*	729(15)	4054(11)	7339(17)	158(9)
O(32)	2881(7)	1086(11)	1095(10)	139(5)	O(35)*	575(14)	2631(17)	6861(16)	143(8)
C(31)	2834(7)	1572(8)	1646(7)	67(2)	O(36)*	1292(17)	2091(15)	8449(8)	166(10)
C(32)	3872(8)	1627(12)	1955(10)	92(4)	O(33')*	1430(14)	2798(16)	8321(9)	145(8)
N(31)	4798(5)	935(6)	1594(5)	56(2)	O(34')*	350(9)	2382(11)	7434(12)	85(4)
C(33)	5054(9)	-160(10)	2158(12)	104(4)	O(35')*	837(11)	4167(7)	6648(11)	101(5)
C(34)	5884(12)	-800(13)	1800(20)	131(7)	O(36')*	2097(9)	2496(13)	6810(12)	110(6)
C(35)	6352(14)	-373(19)	894(16)	129(7)	Cl(4)	4089(3)	6897(3)	2608(3)	111(1)
C(36)	6158(12)	800(20)	295(11)	159(9)	O(43)	4983(7)	7112(10)	1892(8)	151(4)
C(37)	5298(11)	1481(12)	665(11)	123(6)	O(44)	3150(9)	7231(13)	2036(12)	266(11)
N(41)	-773(5)	1674(5)	2274(5)	51(2)	O(45)	4209(9)	5730(6)	3353(8)	148(4)
N(42)	0(5)	2581(5)	3285(4)	49(1)	O(46)	3915(14)	7623(10)	3139(9)	246(10)
C(41)	-1160(8)	1225(8)	1791(7)	67(2)	O(2w)*	1617(23)	9101(24)	1995(23)	165(9)
C(42)	-1764(9)	375(9)	2325(10)	81(3)	O(3w)*	661(23)	9006(26)	626(24)	167(10)

(d) Complex **5**

atom	*x*	*y*	*z*	U_{eq}	atom	*x*	*y*	*z*	U_{eq}
Gd(1)	9626(1)	276(1)	8389(1)	33(1)	C(40)	11183(8)	1051(4)	7100(10)	51(3)
O(11)	10862(5)	-256(3)	9048(8)	61(2)	C(41)	11828(9)	1231(5)	6381(12)	67(4)
O(12)	11522(5)	-669(3)	10500(6)	50(2)	C(42)	12071(10)	884(6)	5566(11)	69(4)
C(11)	11402(6)	-601(4)	9478(10)	41(3)	C(43)	11694(9)	377(5)	5484(10)	54(3)
C(12)	11923(8)	-967(4)	8734(10)	53(3)	C(44)	11059(7)	223(4)	6261(9)	44(2)
C(13)	12157(9)	-1520(5)	9197(12)	64(3)	C(45)	10638(8)	-330(4)	6207(9)	44(2)
N(1)	11323(7)	-1874(4)	9221(8)	53(2)	C(46)	10970(10)	-736(5)	5569(13)	72(4)
C(14)	10791(9)	-1852(5)	10094(11)	57(3)	C(47)	10554(11)	-1240(6)	5584(13)	80(5)
C(15)	9996(10)	-2152(5)	10099(13)	67(4)	C(48)	9802(10)	-1325(6)	6191(13)	76(4)
C(16)	9753(13)	-2495(7)	9241(16)	89(5)	C(49)	9524(9)	-896(5)	6790(10)	57(3)
C(17)	10326(17)	-2528(8)	8412(18)	119(7)	Cl(1)	6979(2)	2251(1)	3890(3)	64(1)
C(18)	11090(14)	-2212(7)	8403(14)	93(5)	O(13)	6874(11)	2281(5)	5012(10)	124(5)
O(21)	8844(5)	-488(3)	8993(5)	43(2)	O(14)	7615(16)	2618(10)	3571(17)	233(12)
O(22)	9430(5)	-874(3)	10537(6)	46(2)	O(15)	6134(15)	2406(11)	3449(19)	233(11)
C(21)	8816(7)	-809(4)	9790(8)	35(2)	O(16)	7131(14)	1737(6)	3497(16)	179(8)
C(22)	7950(8)	-1164(5)	9777(12)	63(4)	Cl(2)	7577(3)	-2682(2)	11896(4)	85(1)
C(23)	7079(9)	-853(6)	9644(16)	87(5)	O(23)*	7475(15)	-2624(9)	13082(9)	112(8)
N(2)	6239(7)	-1199(5)	9457(11)	72(3)	O(24)*	6774(11)	-2426(8)	11387(17)	132(10)
C(24)	5909(16)	-1470(12)	10238(18)	167(13)	O(25)*	8397(10)	-2408(8)	11665(18)	120(9)
C(25)	5183(14)	-1828(10)	10052(19)	138(9)	O(26)*	7593(14)	-3235(4)	11669(18)	115(8)
C(26)	4722(10)	-1845(7)	9114(18)	93(5)	O(23')*	7720(19)	-2834(12)	10769(12)	162(13)

C(27)	5045(16)	-1546(12)	8337(20)	169(13)	O(24')*	7932(20)	-3106(9)	12574(22)	226(20)
C(28)	5821(15)	-1237(10)	8497(17)	139(10)	O(25')*	6622(8)	-2597(11)	11990(23)	147(12)
O(31)	8269(5)	397(3)	7120(6)	52(2)	O(26')*	8099(18)	-2199(8)	12104(24)	183(16)
O(32)	9033(5)	1145(3)	7551(6)	47(2)	Cl(3)	4128(9)	39(4)	7437(13)	174(7)
C(31)	8327(7)	912(4)	7157(8)	42(2)	O(33)*	3449(31)	-157(21)	6639(37)	155(34)
C(32)	7494(8)	1235(5)	6701(11)	58(3)	O(34)*	4051(32)	611(6)	7523(39)	189(22)
C(33)	6639(9)	894(6)	6456(16)	89(5)	O(35)*	5035(19)	-100(17)	7134(44)	182(22)
N(3)	5805(7)	1225(5)	6147(12)	73(3)	O(36)*	3968(39)	-199(17)	8470(24)	182(30)
C(34)	5385(12)	1201(9)	5146(18)	113(7)	O(33')*	3460(28)	361(19)	7954(52)	190(35)
C(35)	4576(13)	1490(10)	4936(19)	121(8)	O(34')*	4456(53)	324(21)	6530(34)	144(75)
C(36)	4211(11)	1793(8)	5673(18)	96(6)	O(35')*	3685(28)	-450(12)	7057(39)	122(21)
C(37)	4650(11)	1817(8)	6656(18)	98(5)	O(36')*	4884(35)	-83(21)	8197(50)	145(66)
C(38)	5433(11)	1525(8)	6889(15)	92(5)	O(1w)	6900(14)	-494(7)	6793(16)	171(7)
N(41)	10807(6)	552(3)	7044(7)	42(2)	O(2w)*	13631(20)	-773(13)	10974(23)	137(11)
N(42)	9911(6)	-413(3)	6861(8)	47(2)					

*Site occupancy factor 0.5.

Table 3. Selected bond lengths (Å) and bond angles (°).

(a) Complex **1**

Gd(1)-O(21)	2.306(3)	Gd(1)-O(2w)	2.426(3)
Gd(1)-O(22a)	2.304(3)	O(12)-Gd(1a)	2.330(3)
Gd(1)-O(12a)	2.330(3)	O(22)-Gd(1a)	2.304(3)
Gd(1)-O(11)	2.370(3)	O(21)-C(21)	1.234(5)
Gd(1)-O(4w)	2.368(3)	O(22)-C(21)	1.238(5)
Gd(1)-O(1w)	2.379(3)	O(11)-C(11)	1.256(5)
Gd(1)-O(3w)	2.422(3)	O(12)-C(11)	1.232(5)
O(21)-Gd(1)-O(22a)	120.96(11)	O(22a)-Gd(1)-O(12a)	73.78(11)
O(21)-Gd(1)-O(12a)	78.19(12)	O(21)-Gd(1)-O(11)	74.36(11)
O(22a)-Gd(1)-O(12a)	73.78(11)	O(22a)-Gd(1)-O(11)	78.47(11)
O(21)-Gd(1)-O(11)	74.36(11)	O(12a)-Gd(1)-O(11)	122.13(10)
O(22a)-Gd(1)-O(11)	78.47(11)	O(21)-Gd(1)-O(4w)	81.04(12)
O(12a)-Gd(1)-O(11)	122.13(10)	O(22a)-Gd(1)-O(4w)	142.78(11)
O(21)-Gd(1)-O(4w)	81.04(12)	O(12a)-Gd(1)-O(4w)	143.29(11)
O(22a)-Gd(1)-O(4w)	142.78(11)	O(11)-Gd(1)-O(4w)	79.90(11)
O(12a)-Gd(1)-O(4w)	143.29(11)	O(21)-Gd(1)-O(1w)	141.51(11)
O(11)-Gd(1)-O(4w)	79.90(11)	O(22a)-Gd(1)-O(1w)	85.59(12)
O(21)-Gd(1)-O(1w)	141.51(11)	O(12a)-Gd(1)-O(1w)	84.37(12)
O(22a)-Gd(1)-O(1w)	85.59(12)	O(11)-Gd(1)-O(1w)	142.56(10)
O(12a)-Gd(1)-O(1w)	84.37(12)	O(4w)-Gd(1)-O(1w)	93.70(13)
O(22a)-Gd(1)-O(3w)	72.62(11)	O(21)-Gd(1)-O(3w)	138.97(12)
O(12a)-Gd(1)-O(3w)	139.91(12)	O(22a)-Gd(1)-O(3w)	72.62(11)
O(11)-Gd(1)-O(3w)	71.05(10)	O(12a)-Gd(1)-O(3w)	139.91(12)
O(4w)-Gd(1)-O(3w)	71.86(11)	O(11)-Gd(1)-O(3w)	71.05(10)
O(1w)-Gd(1)-O(3w)	71.90(11)	O(4w)-Gd(1)-O(3w)	71.86(11)
O(21)-Gd(1)-O(2w)	71.62(11)	O(1w)-Gd(1)-O(3w)	71.90(11)
O(22a)-Gd(1)-O(2w)	141.54(11)	O(21)-Gd(1)-O(2w)	71.62(11)
O(12a)-Gd(1)-O(2w)	74.12(11)	O(22a)-Gd(1)-O(2w)	141.54(11)
O(11)-Gd(1)-O(2w)	137.71(11)	O(12a)-Gd(1)-O(2w)	74.12(11)
O(4w)-Gd(1)-O(2w)	70.72(11)	O(11)-Gd(1)-O(2w)	137.71(11)
O(1w)-Gd(1)-O(2w)	70.69(11)	O(4w)-Gd(1)-O(2w)	70.72(11)
O(3w)-Gd(1)-O(2w)	124.07(10)	O(1w)-Gd(1)-O(2w)	70.69(11)
C(11)-O(11)-Gd(1)	130.9(2)	O(3w)-Gd(1)-O(2w)	124.07(1)
C(11)-O(12)-Gd(1a)	159.8(3)	C(11)-O(11)-Gd(1)	130.9(2)
O(12)-C(11)-O(11)	127.0(4)	C(11)-O(12)-Gd(1a)	159.8(3)

C(21)-O(21)-Gd(1)	146.1(3)	O(12)-C(11)-O(11)	127.0(4)
C(21)-O(22)-Gd(1a)	142.8(3)	C(21)-O(21)-Gd(1)	146.1(3)
O(22)-C(21)-O(21)	127.4(4)	C(21)-O(22)-Gd(1a)	142.8(3)
O(21)-Gd(1)-O(12a)	78.19(12)	O(22)-C(21)-O(21)	127.4(4)

(b) Complex **3**

Gd(1)-O(11)	2.302(8)	Gd(2)-N(41)	2.568(9)
Gd(1)-O(21)	2.361(8)	O(11)-C(11)	1.243(20)
Gd(1)-N(31)	2.610(12)	O(12)-C(11)	1.241(22)
Gd(2)-O(12)	2.432(14)	O(21)-C(21)	1.170(15)
Gd(2)-O(22)	2.233(18)	O(22)-C(21)	1.325(22)
N(31)-Gd(1)-O(11b)	146.0(3)	O(22)-Gd(2)-O(22a)	114.7(9)
O(21)-Gd(1)-O(21a)	125.5(4)	N(41)-Gd(2)-O(22a)	145.9(3)
N(31)-Gd(1)-O(21a)	137.6(3)	N(41)-Gd(2)-N(41a)	105.2(4)
O(11)-Gd(1)-N(31a)	146.0(3)	N(41)-Gd(2)-N(41c)	72.9(4)
O(21)-Gd(1)-N(31a)	137.6(3)	N(41)-Gd(2)-N(41b)	63.6(4)
N(31)-Gd(1)-N(31b)	106.4(5)	Gd(1)-O(11)-C(11)	152.1(9)
N(31)-Gd(1)-N(31a)	63.0(5)	Gd(2)-O(12)-C(11)	133.1(11)
N(31)-Gd(1)-N(31c)	74.8(5)	Gd(1)-O(21)-C(21)	143.4(8)
O(12)-Gd(2)-O(22)	77.1(2)	Gd(2)-O(22)-C(21)	156.3(13)
O(12)-Gd(2)-N(41)	76.8(3)	Gd(1)-N(31)-C(31)	121.6(9)
O(22)-Gd(2)-N(41)	80.1(4)	Gd(1)-N(31)-C(35)	116.4(8)
O(12)-Gd(2)-O(12b)	131.1(6)	Gd(2)-N(41)-C(41)	125.0(7)
O(22)-Gd(2)-O(12b)	77.1(2)	Gd(2)-N(41)-C(45)	120.4(6)
N(41)-Gd(2)-O(12b)	137.0(2)	O(11)-C(11)-O(12)	130.4(13)
O(21)-C(21)-O(22)	120.2(12)		

(c) Complex **4**

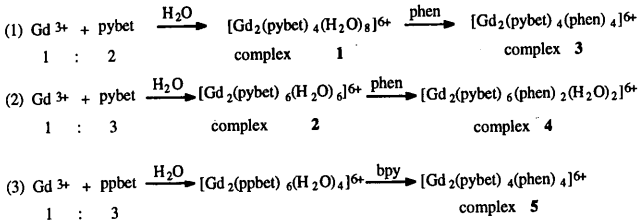
Gd(1)-O(21)	2.334(5)	O(11)-C(11)	1.251(8)
Gd(1)-O(31)	2.361(5)	O(12)-C(11)	1.250(8)
Gd(1)-O(22a)	2.362(5)	O(12)-Gd(1a)	2.362(5)
Gd(1)-O(12a)	2.362(5)	O(22)-Gd(1a)	2.362(5)
Gd(1)-O(11)	2.385(5)	O(21)-C(21)	1.252(9)
Gd(1)-O(1w)	2.461(5)	O(22)-C(21)	1.238(9)
Gd(1)-N(41)	2.570(6)	O(31)-C(31)	1.257(10)
Gd(1)-N(42)	2.599(6)	O(32)-C(31)	1.217(12)
O(21)-Gd(1)-O(31)	81.0(2)	O(1w)-Gd(1)-N(41)	72.8(2)
O(21)-Gd(1)-O(22a)	121.4(2)	O(21)-Gd(1)-N(42)	146.1(2)
O(31)-Gd(1)-O(22a)	142.4(2)	O(31)-Gd(1)-N(42)	75.7(2)
O(21)-Gd(1)-O(12a)	79.2(2)	O(22a)-Gd(1)-N(42)	69.8(2)
O(31)-Gd(1)-O(12a)	143.6(2)	O(12a)-Gd(1)-N(42)	133.0(2)
O(22a)-Gd(1)-O(12a)	73.7(2)	O(11)-Gd(1)-N(42)	77.8(2)
O(21)-Gd(1)-O(11)	74.3(2)	O(1w)-Gd(1)-N(42)	121.3(2)
O(31)-Gd(1)-O(11)	80.5(2)	N(41)-Gd(1)-N(42)	63.4(2)
O(22a)-Gd(1)-O(11)	78.1(2)	C(11)-O(11)-Gd(1)	138.3(4)
O(12a)-Gd(1)-O(11)	122.2(2)	C(11)-O(12)-Gd(1a)	150.2(5)
O(21)-Gd(1)-O(1w)	74.4(2)	O(12)-C(11)-O(11)	126.7(7)
O(31)-Gd(1)-O(1w)	74.7(2)	C(21)-O(21)-Gd(1)	157.7(6)
O(22a)-Gd(1)-O(1w)	136.9(2)	C(21)-O(22)-Gd(1a)	133.5(5)
O(12a)-Gd(1)-O(1w)	70.7(2)	O(22)-C(21)-O(21)	126.8(7)
O(11)-Gd(1)-O(1w)	142.5(2)	C(31)-O(31)-Gd(1)	133.5(5)
O(21)-Gd(1)-N(41)	145.9(2)	O(32)-C(31)-O(31)	127.5(9)
O(31)-Gd(1)-N(41)	99.1(2)	C(41)-N(41)-Gd(1)	121.9(5)
O(22a)-Gd(1)-N(41)	78.7(2)	C(45)-N(41)-Gd(1)	120.6(5)
O(12a)-Gd(1)-N(41)	81.4(2)	C(52)-N(42)-Gd(1)	122.6(5)
O(11)-Gd(1)-N(41)	139.7(2)	C(49)-N(42)-Gd(1)	119.8(5)

(d) Complex **5**

Gd(1)-O(11)	2.310(7)	Gd(1)-N(42)	2.581(10)
Gd(1)-O(21)	2.336(7)	O(12)-Gd(1a)	2.406(7)
Gd(1)-O(22a)	2.351(7)	O(22)-Gd(1a)	2.351(7)
Gd(1)-O(12a)	2.406(7)	O(11)-C(11)	1.246(12)
Gd(1)-O(31)	2.432(7)	O(12)-C(11)	1.265(13)
Gd(1)-O(32)	2.504(7)	O(21)-C(21)	1.260(11)
Gd(1)-N(41)	2.530(8)	O(22)-C(21)	1.241(12)
O(11)-Gd(1)-O(21)	78.7(3)	O(32)-Gd(1)-N(42)	109.4(3)
O(11)-Gd(1)-O(22a)	76.0(3)	N(41)-Gd(1)-N(42)	64.0(3)
O(21)-Gd(1)-O(22a)	126.9(2)	O(11)-Gd(1)-C(31)	167.3(3)
O(11)-Gd(1)-O(12a)	124.6(3)	O(21)-Gd(1)-C(31)	107.8(3)
O(21)-Gd(1)-O(12a)	77.7(3)	O(22a)-Gd(1)-C(31)	106.9(3)
O(22a)-Gd(1)-O(12a)	79.6(3)	O(12a)-Gd(1)-C(31)	67.9(3)
O(11)-Gd(1)-O(31)	149.3(3)	O(31)-Gd(1)-C(31)	27.0(3)
O(21)-Gd(1)-O(31)	85.5(3)	O(32)-Gd(1)-C(31)	26.2(3)
O(22a)-Gd(1)-O(31)	133.7(2)	N(41)-Gd(1)-C(31)	87.0(3)
O(12a)-Gd(1)-O(31)	76.3(3)	N(42)-Gd(1)-C(31)	96.2(3)
O(11)-Gd(1)-O(32)	149.7(3)	C(11)-O(11)-Gd(1)	168.3(8)
O(21)-Gd(1)-O(32)	131.6(3)	C(11)-O(12)-Gd(1a)	116.8(6)
O(22a)-Gd(1)-O(32)	82.0(2)	O(11)-C(11)-O(12)	123.5(10)
O(12a)-Gd(1)-O(32)	70.1(3)	C(21)-O(21)-Gd(1)	142.3(6)
O(31)-Gd(1)-O(32)	52.7(2)	C(21)-O(22)-Gd(1a)	133.6(6)
O(11)-Gd(1)-N(41)	81.4(3)	O(22)-C(21)-O(21)	126.7(9)
O(21)-Gd(1)-N(41)	141.0(3)	C(31)-O(31)-Gd(1)	93.0(6)
O(22a)-Gd(1)-N(41)	79.0(3)	C(31)-O(32)-Gd(1)	90.6(6)
O(12a)-Gd(1)-N(41)	140.4(3)	O(32)-C(31)-O(31)	121.9(9)
O(31)-Gd(1)-N(41)	95.3(3)	O(32)-C(31)-Gd(1)	63.3(5)
O(32)-Gd(1)-N(41)	74.1(3)	O(31)-C(31)-Gd(1)	60.0(5)
O(11)-Gd(1)-N(42)	74.2(3)	C(32)-C(31)-Gd(1)	167.4(8)
O(21)-Gd(1)-N(42)	78.5(3)	C(44)-N(41)-Gd(1)	122.2(7)
O(22a)-Gd(1)-N(42)	135.1(3)	C(40)-N(41)-Gd(1)	119.8(7)
O(12a)-Gd(1)-N(42)	145.3(3)	C(49)-N(42)-Gd(1)	124.0(8)
O(31)-Gd(1)-N(42)	76.9(3)	C(45)-N(42)-Gd(1)	119.2(6)

Symmetry codes: for **1**, -x, -y, 1-z; for **3**, a) x, -y, z, b) -x, y, z, c) -x, -y, z; for **4**, a) -z, 1-y, -z, b) 1-x, -1 y, z; c) -1x, -y, 1-z; for **5**, a) 2-x, -y, 2-z.

tained, respectively. Whereas the co-existence of both phen and excessive pybet ligands results in the formation of complex **4**. A similar mechanism may hold for the formation of complex **5**.



$[Gd_2(pybet)_4(H_2O)_8](ClO_4)_6$ (**1**). Complex **1** comprises discrete $[Gd_2(pybet)_4(H_2O)_8]^{6+}$ cations, and perchlorate anions. As shown in Fig. 1, a pair of centrosymmetrically related Gd(III) atoms are quadruply bridged by the pybet carboxylate-*O,O'* groups in a centrosymmetrical dimeric structure. Each Gd(III) ion is further coordinated by four terminal aqua ligands, resulting in a distorted square-antiprismatic coordination sphere about the metal atom. The Gd–O(carboxy) bond lengths and Gd–O(aqua) fall in range of 2.304(3) to 2.370(3) Å and of 2.368(3) to 2.426(3) Å, respectively. In the square-antiprismatic coordination sphere (see Fig. 2), the upper square face consists of four oxygen atoms from the quadruple carboxylate bridges, which are very close to the least-squares plane with the deviations within ±0.006 Å. The lower square face comprises four aqua ligands, and the deviations of the oxygen atoms from the least-squares plane are quite significant (±0.243 Å). The angle between the square faces is 3.0°. Similar quadruply carboxylate-bridged

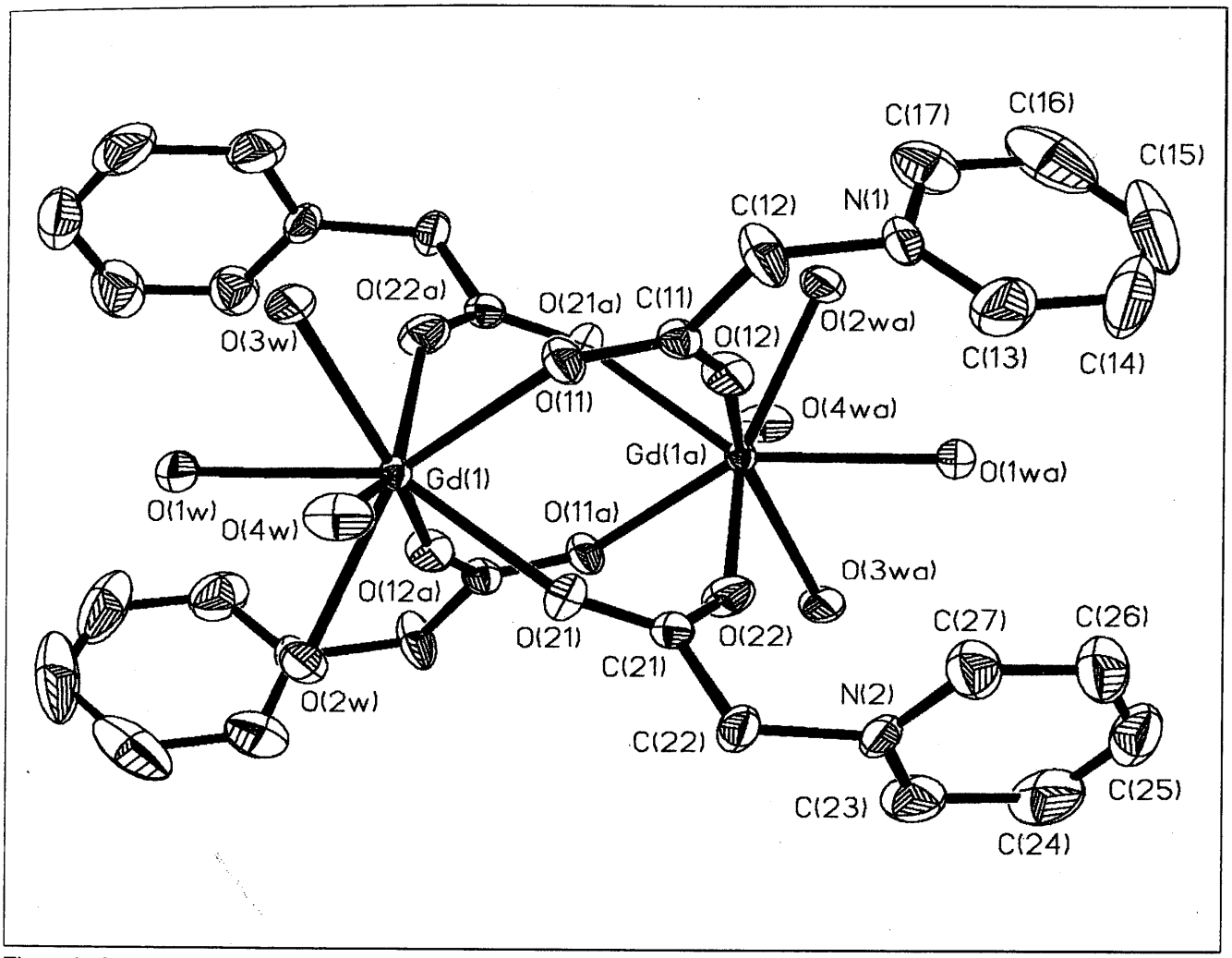


Figure 1. ORTEP drawing (35% probability) of the dimeric cation $[Gd_2(pybet)_4(H_2O)_8]^{6+}$ in complex **1**, and the atom-numbering scheme. Symmetric code (a) -x, -y ,1-z.

lanthanide(III) complexes have found in several lanthanide(III) carboxylates [5,15,16] which comprise similar dimeric structures with each metal atom being eight-coordinate, and having four aqua terminal.

$[Gd_2(pybet)_4(phen)_4](ClO_4)_6(3H_2O$ (**3**). Complex **3** contains discrete $[Gd_2(pybet)_4(phen)_4]^{6+}$ cations, perchlorate anions and lattice water molecules. The $[Gd_2(pybet)_4(phen)_4]^{6+}$ cation is bisected by a pair of vertically-related mirror planes in the solid. As shown in Fig. 3, a pair of Gd(III) atoms is linked by four μ_2-carboxylate-*O*,*O*' groups of pybet ligands into a dimeric structure. Each Gd(III) ion is further coordinated by two terminal bidentate phen ligands, forming a distorted square-antiprismatic coordination sphere about the metal atom, which is similar to that found for complex **1**. The Gd–O bond lengths and Gd–N bond lengths fall in range of 2.23(2) to 2.43(1) Å and of 2.568(9) to 2.61(1) Å, respectively. Noteworthy is the fact that no dinuclear lanthanide(III) complexes with each metal atom ligated by two terminal bidentate aromatic diamine ligands have been reported so far, although the dimeric lanthanide(III) complexes containing quadruple carboxylate bridge and phen as terminal ligands have previously been reported [17,18].

$[Gd_2(pybet)_6(phen)_2(H_2O)_2](ClO_4)_6{\cdot}2H_2O$ (**4**). Complex **4** also comprises discrete cations, namely $[Gd_2(pybet)_6(phen)_2(H_2O)_2]^{6+}$, perchlorate anions and lattice water molecules. As shown in Fig. 4, a pair of centrosymmetrically related Gd(III) atoms are connected by a quadruple bridge of the pybet carboxylate-*O*,*O*' groups into a centrosymmetrical dimeric structure. Each Gd(III) ion is further coordinated by a

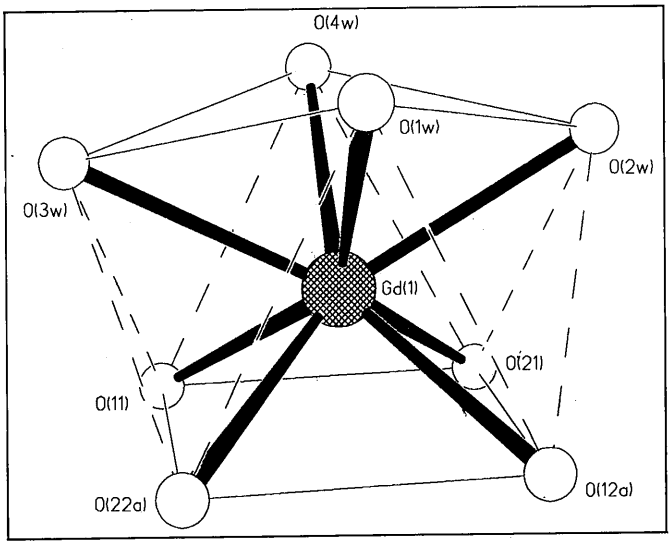


Figure 2. Perspective view showing the distorted square-antiprismatic evironment about the Gd(III) atom in the complex **1**.

bidentate phen ligands, a monodentate carboxylate group of a pybet ligand and an aqua ligand, resulting in a distorted square-antiprismatic coordination sphere about the metal atom. The Gd–O(carboxy) bond lengths and Gd–N bond lengths fall in range of 2.334(5) to 2.385(5) Å and of 2.570(6) to 2.599(6) Å, respectively. The square-antiprismatic coordination sphere about the Gd(III) atom is also similar to that found for complex **1** and **3**.

The other interesting feature is the formation of a hydrogen bond (2.61(1) Å) between the uncoordinated oxygen atom of the monodentate pybet ligand and the aqua ligand; this relatively strong interaction probably contributes to consolidating the dimeric structure.

$[Gd_2(ppbet)_6(bpy)_2](ClO_4)_6 \cdot 3H_2O$ (**5**). Complex **5** also comprises discrete cations, namely $[Gd_2(ppbet)_6(bpy)_2]^{6+}$, perchlorate anions and lattice

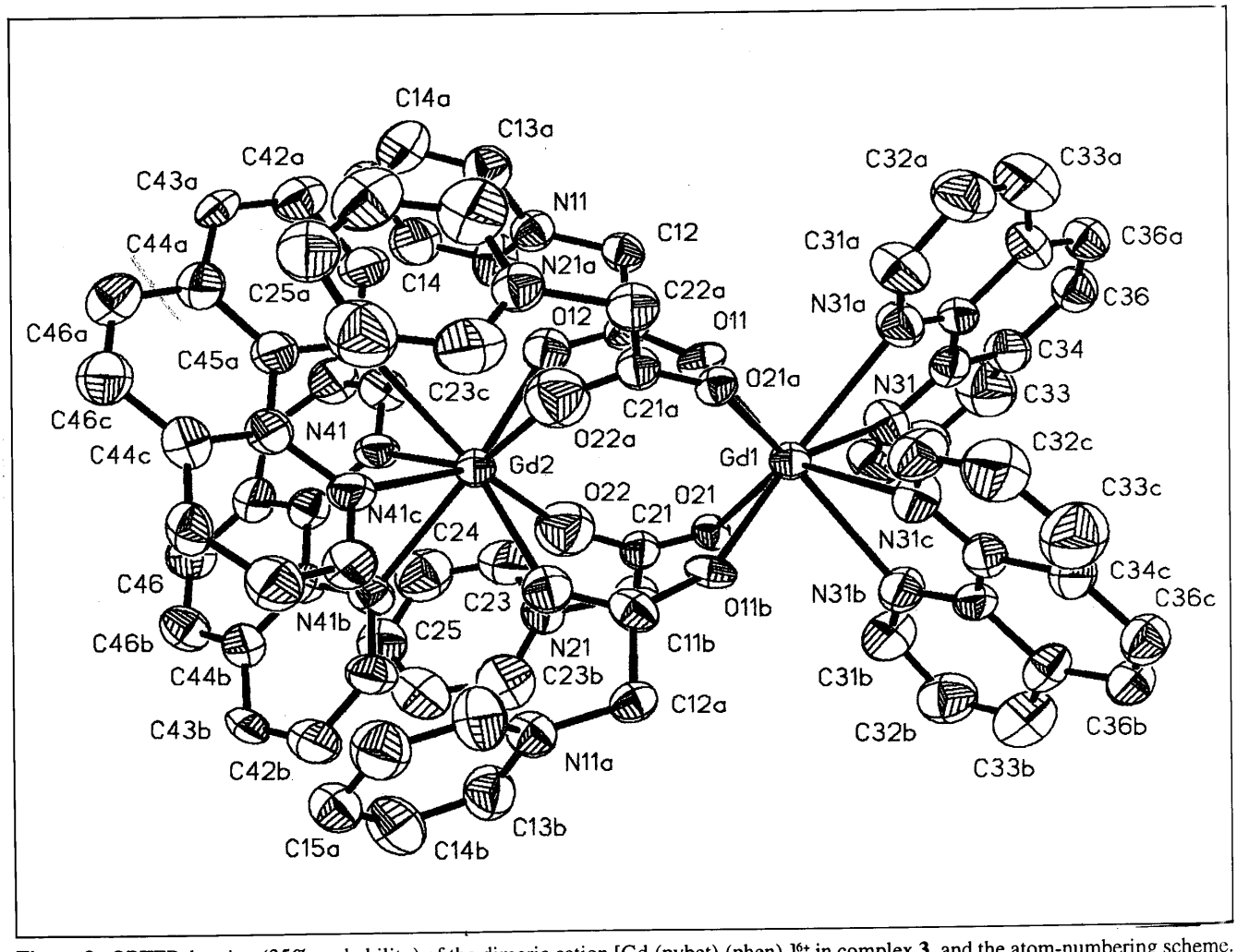


Figure 3. ORTEP drawing (35% probability) of the dimeric cation $[Gd_2(pybet)_4(phen)_4]^{6+}$ in complex **3**, and the atom-numbering scheme. Symmetric code (a) x, -y, z.

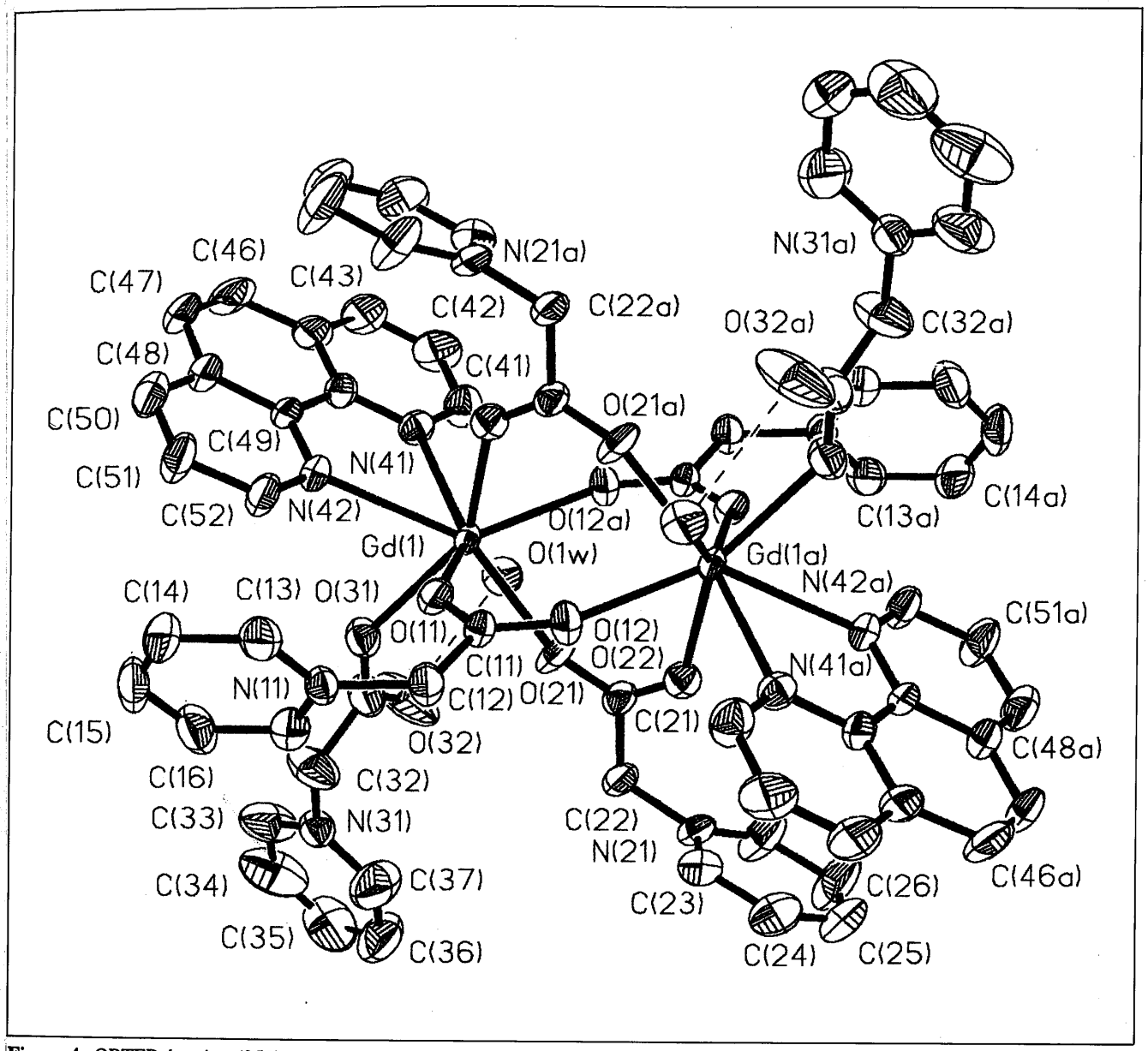


Figure 4. ORTEP drawing (35% probability) of the dimeric $[Gd_2(pybet)_6(phen)_2(H_2O)_2]^{6+}$ cation in complex **4**, and the atom-numbering scheme. Symmetric code: a) -x, 1-y, -z.

water molecules. As shown in Fig. 5, a pair of Gd(III) atoms are connected by a quadruple bridge of the ppbet carboxylate-*O*,*O*' groups into a dimeric structure. Each Gd(III) ion is further coordinated by a bidentate bpy ligands, a bidentate ppbet carboxylate group, resulting in a distorted square-antiprismatic coordination sphere about the metal atom. The Gd–O(carboxy) bond lengths and Gd–N bond lengths fall in range of 2.310(7) to 2.504(7) Å and of 2.530(8) to 2.58(1) Å, respectively. The square-antiprismatic coordination sphere about the metal atoms are analogous to those found for the above-mentioned complexes.

One interesting feature of complex **5** is that the two carboxylate group of the pair of terminal ppbet ligands act in the chelate mode, which are different from the terminal pybet ligands in complex **4**. This fact further confirms that with additional methylene group, the inductive effect of the positively-charged nitrogen atom on the carboxylate group of ppbet is reduced in comparison to that in pybet, resulting that ppbet has a smaller O–C–O bond angle and hence a greater tendency to form the chelate mode in coordination with metal ions, in

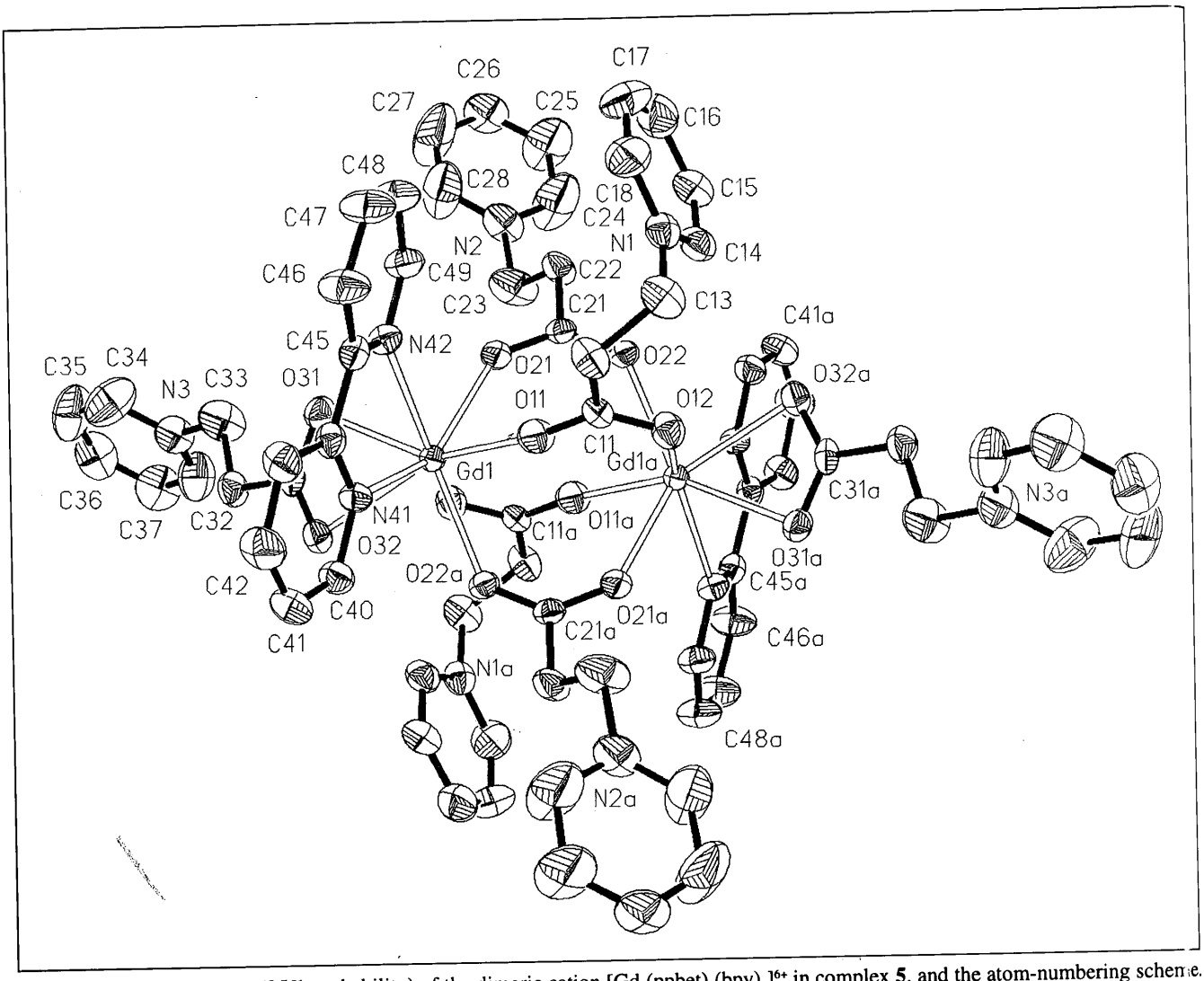


Figure 5. ORTEP drawing (35% probability) of the dimeric cation $[Gd_2(ppbet)_6(bpy)_2]^{6+}$ in complex **5**, and the atom-numbering scheme. Symmetric code: a) 2-x, -y, 2-z.

comparison with that of pybet [9,19].

The magnetic susceptibility data for **5** were measured over the temperature range 4-300 K. The effective magnetic moments per dimer (μ_{eff}) versus temperature are shown in Fig. 6. At 320 K, the μ_{eff} has the value of 10.82 B.M., and it increases slowly with decrease of temperature, and reaches the maximum of 11.26 B.M. at 7.0 K. This behavior is typical of a very weak ferromagnetic interaction.

These magnetic susceptibility data very closely follow the equation deduced from the isotropic spin Hamiltonian $\boldsymbol{H} = -J\mathbf{S}_{Gd1}\cdot\mathbf{S}_{Gd2}$ with the quantum numbers $S_{Gd1} = S_{Gd2} = 7/2$. This equation [6] is given by

$$\chi_M = \left(\frac{2N_A\beta^2 g^2}{kT}\right)\left(\frac{e^x + 5e^{3x} + 14e^{6x} + 30e^{10x} + 55e^{15x} + 91e^{21x} + 140e^{28x}}{1 + 3e^x + 5e^{3x} + 7e^{6x} + 9e^{10x} + 11e^{15x} + 13e^{21x} + 15e^{28x}}\right) \quad (1)$$

where $x = J/kT$, χ_M denotes the susceptibility per binuclear complex and the remaining symbols have their usual meanings. The good fitting to the experimental data was attained with eq. (1), giving the isotropic interaction parameter $J = 0.037$ cm^{-1}, the Zeeman factor $g = 1.95$ with the discrepancy factor R ($\Sigma(\chi_{obs}T - \chi_{calcd}T)^2/\Sigma(\chi_{obs}T)^2$) = 0.0056. The result ($J > 0$ and $|J|$ is very small) indicates a very weak ferromagnetic spin exchange interaction between the pair of Gd(III) ions. Our results are different from those found for a dimeric Gd(III) acetate, which has very weak antiferromagnetic exchange interaction ($J = -0.035$ cm^{-1}) [6]. This may, at least partially, be attributed to different geometry of the quadruple carboxylate bridges between the pair of Gd(III) ions in the dimeric structure, since in the acetate complex, two of the acetate groups act in the

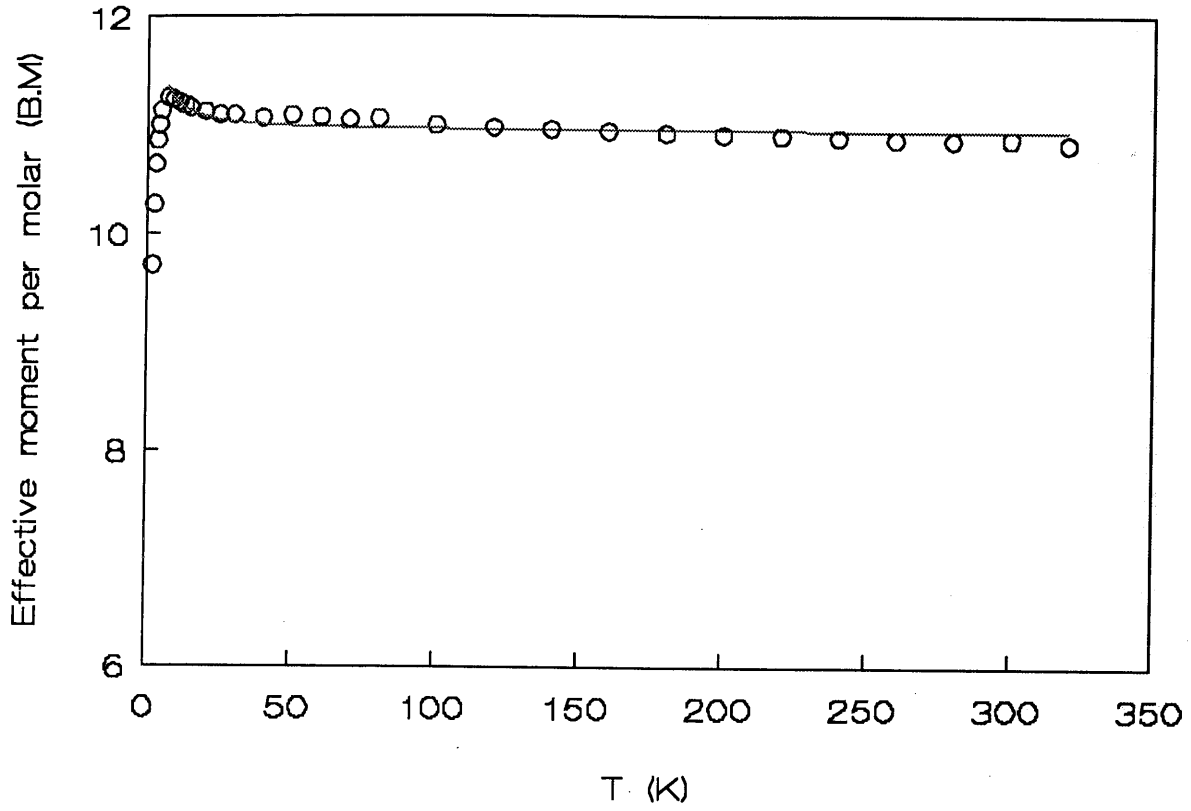


Figure 6. Temperature-dependence of molar effective moments (μ_M) for complex **5**. The solid line corresponds to the best theoretical fit using $J = 0.037$ cm^{-1} and $g = 1.95$ (see text).

bidentate bridging mode and the others two in the bidentate bridging plus chelate mode. Very weak magnetic spin-exchange interaction between lanthanide(III) ions may account for the fact that 4*f*-electrons are shielded by the outershell electrons [20]. Our findings further confirm that the intramolecular interaction between two 4*f* ions can be detected [6]. This interaction, however, is much smaller than those between 3*d* metal ions, or even those between 4*f* and 3*d* ions [20,22].

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