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Notes

Syntheses, Structures and Magnetic Behaviors of Di- and Trinuclear Pivalate Complexes Containing Both Cobalt(II) and Lanthanide(III) Ions

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Introduction

In the past few years, the magnetic properties of complexes simultaneously comprising lanthanide and transition metal ions have attracted increasing interest.[1−9] Attention has been largely focused on the Cu(II)−Gd(III) couple, which was found to be directly ferromagnetic irrespective of the structural details.[1−4] Recent studies further revealed that the magnitude of this interaction is exponentially dependent on the Cu−Gd distance.[3] In comparison, there are few reports on the magnetic interactions between other 3d−4f mixtures, and further model compounds are required to determine the nature of the magnetic couplings.[5−8] In a previous paper,[8] we reported several tri- and tetranuclear Co−Ln (Ln = a lanthanide ion) pivalate compounds showing weak antiferromagnetic couplings. Herein, we describe the syntheses and structures of four new di- and trinuclear Co−Ln pivalates, $[C_9H_7NH][CoTb(Piv)_3(C_9H_7N)(NO_3)_3]\cdot 0.5H_2O$, $[CoLn(Piv)_5(C_9H_7N)(H_2O)]\cdot 0.5C_9H_7N$ (Ln = Gd, Dy), and $[Co_2Gd(Piv)_6(C_9H_7N)_2(NO_3)]$ (Piv = $^-O_2CCMe_3$), all of which exhibit weak ferromagnetic interactions between their corresponding heterometallic ions.

Experimental Section

All chemicals were used as received. IR spectra were recorded on a Nicolet Magna 750 FT-IR spectrometer with the KBr disk method. Magnetic measurements were carried out with a Quantum Design model 6000 magnetometer using a dc field of 1 T. Elemental analyses were performed in the elemental analysis laboratory of the Fujian Institute of Research on the Structure of Matter.

Synthesis of $[C_9H_7NH][CoTb(Piv)_3(C_9H_7N)(NO_3)_3]\cdot 0.5H_2O$ (1). A mixture of $Co(NO_3)_2$ (0.291 g, 1 mmol), $Tb(NO_3)_3\cdot 6H_2O$ (0.453 g, 1 mmol), and pivalic acid (0.306 g, 3 mmol) was dissolved in EtOH (80 mmol), followed by addition of quinoline (2 mmol). The resulting mixture was refluxed for 10 h and then filtered while hot, after which the filtrate was concentrated to 15 mL. Red-brown prismatic crystals were collected after slow evaporation at room temperature for 10 days. Yield: 20% (on a cobalt basis). Anal. Calcd (found): C, 20.32 (19.57); H, 2.22 (2.28); N, 3.59 (3.64). IR (KBr pellet; cm^{-1}): 1598 vs, 1512 s, 1471 s, 1420 vs, 1384 vs, 1362 m, 1291 m, 1230 m, 812 w, 788 m, 784 w.

Synthesis of $[CoGd(Piv)_5(C_9H_7N)(H_2O)]\cdot 0.5C_9H_7N$ (2). $Co(NO_3)_2\cdot 6H_2O$ (0.291 g, 1 mmol), $Gd(NO_3)_3\cdot 6H_2O$ (0.451 g, 1 mmol), and pivalic acid (0.511 g, 5 mmol) were dissolved in EtOH (60 mmol), followed by addition of quinoline (0.24 mL). The resulting mixture was refluxed for 10 h and then filtered while hot. The filtrate was concentrated to 20 mL and allowed to stand at room temperature. Red-brown prismatic crystals deposited over a period of 1 week. Yield: 40% (on a cobalt basis). Anal. Calcd (found): C, 24.77 (23.95); H, 3.11 (2.96); N, 1.13 (1.10). IR (KBr pellet; cm^{-1}): 1602 vs, 1512 s, 1486 s, 1429 vs, 1414 s, 1378 vs, 1362 m, 1228 m, 810 m, 788 w.

Synthesis of $[CoDy(Piv)_5(C_9H_7N)(H_2O)]\cdot 0.5C_9H_7N$ (3). This complex was synthesized identically to **2**, but with $Dy(NO_3)_3\cdot 6H_2O$ used in place of $Gd(NO_3)_3\cdot 6H_2O$. Yield: 15% (on a cobalt basis). Anal. Calcd (found): C, 24.63 (23.33); H, 3.09 (3.02); N, 1.12 (1.09). IR (KBr pellet; cm^{-1}): 1533 vs, 1510 s, 1486 m, 1429 vs, 1417 s, 1311 m, 1230 m, 810 m, 792 m, 783 m. Cell parameters: $a = 12.2457(5)$ Å, $b = 13.3210(5)$ Å, $c = 15.0938(6)$ Å, $\alpha = 68.426(1)°$, $\beta = 93.486°$, $\gamma = 77.60(2)°$.

Synthesis of $[Co_2Gd(Piv)_6(C_9H_7N)_2(NO_3)]$ (4). A mixture of $Co(NO_3)_2\cdot 6H_2O$ (0.582 g, 2 mmol), $Gd(NO_3)_3\cdot 6H_2O$ (0.441 g, 1 mmol), and pivalic acid (0.613 g, 6 mmol) was dissolved in EtOH (100 mmol), followed by addition of quinoline (0.24 mL). The resultant mixture was refluxed for 10 h and then filtered while hot. The filtrate was concentrated to 30 mL and allowed to stand at room temperature. Red-brown prismatic crystals deposited over a period of 2 weeks. Yield: 20% (on a cobalt basis). Anal. Calcd (found): C, 47.96 (47.12); H, 5.70 (5.54); N, 3.50 (3.35). IR (KBr pellet, cm^{-1}): 1598 vs, 1560 s, 1512 s, 1485 s, 1421 vs, 1379 vs, 1362 m, 1303 m, 1228 m, 816 w, 789 m, 783 w.

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Table 1. Crystallographic Data for **1**, **2**, and **4**

	1	**2**	**4**
empirical formula	$C_{33}H_{43}CoN_5O_{15.5}Tb$	$C_{38.5}H_{57.5}CoGd\,N_{1.5}O_{11}$	$C_{48}H_{68}Co_2GdN_3O_{15}$
fw	975.57	933.54	1202.16
crystal system	monoclinic	triclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$C2/c$
a, Å	19.7813(3)	12.2338(2)	22.282(5)
b, Å	12.4875(3)	13.3670(3)	11.644(2)
c, Å	20.3735(4)	15.0987(3)	24.301(5))
α, deg		111.606(2)	
β, deg	118.191(6)	93.393(3)	115.79(3)
γ, deg		102.323(3)	
V, Å^3	4435.7(2)	2216.76(8)	5677(2)
Z	4	2	4
D_c, g cm^{-3}	1.461	1.399	1.407
μ(Mo Kα), cm^{-1}	20.22	19.10	17.94
R^a	0.0801	0.0441	0.0558
$R_w{}^b$	0.2203	0.1190	0.1315

^{a} $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. ^{b} $R_w = [\sum w(F_o{}^2 - F_c{}^2)^2/\sum w(F_o{}^2)^2]^{1/2}$.

X-ray Crystallography. The crystallographic data for **1**, **2**, and **4** are listed in Tables 1. Diffraction data were collected on a Siemens SMART CCD diffractometer for **1** and **2** and on an Enraf-Nonius CAD4 diffractometer for **4**. The structures were solved by direct methods and refined by full-matrix least-squares calculations using the SHELXTL-PC program[10] and anisotropic thermal parameters for all non-hydrogen atoms except the disordered atoms. The *tert*-butyl groups of the pivalate ligands involving C(12), C(22), and C(32) for **1** and **4** and C(32), C(42), and C(52) for **2** were split into two parts, each having a site occupancy factor of 0.5. The chelating nitrate anion in **4** displays a *C*2 rotational disorder around the N(1)−O(2) bond. The geometry of the protonated quinoline rings of **1** and the C−C bond distances involving the disordered carbon atoms were constrained reasonably. No attempts were made to locate the hydrogen atoms of water and the protonated quinoline in **1** and of the disordered carbon atoms; the other hydrogen atoms were added in a riding model and not refined.

Results and Discussion

It is well-known that cobalt(II) is reluctant to form carboxylate-bridged di- and trinuclear complexes;[11,12], there are many examples of rhodium(II) and copper(II) binuclear species, but it is the mononuclear complexes of cobalt(II) that abound.[13] The major factor able to promote di- and trinuclear complex formation with cobalt(II) is the presence of steric crowding around the metal ions due to coordination of sterically demanding carboxylate groups and heterocyclic amines, this arrangement restricting the formation of bis(amine) adducts.[11] On the basis of this information, the bulky species pivalic acid and quinoline were chosen as ligands to prepare heterometallic cobalt−lanthanide assemblies with the aim of studying their magnetic and structural properties. As might be expected, complexes **1**−**4**, as well as the complexes $[Co_2Ln(Piv)_6(C_9H_7N)_2(NO_3)]$ (Ln = Nd, Ce) and $[Co_2Ln_2(Piv)_8(C_9H_7N)_2(NO_3)_2]$ (Ln = Er, Y) reported previously, were all obtained readily as well-formed red-brown crystals in moderate yields from the self-assembly reactions of $Co(NO_3)_2{\cdot}6H_2O$, $Ln(NO_3)_3{\cdot}6H_2O$, pivalic acid, and quinoline in stoichiometric molar ratios in refluxing ethanol. However, all attempts to prepare heterotetranuclear Co_2Ln_2 pivalates with Ln = Nd, Gd, and Dy having structures similar to those of the Co_2Er_2 and Co_2Y_2 pivalates have so far been unsuccessful. The change in structure from Co_2Ln to Co_2Ln_2 probably results from the reduction in ionic radius in going from Nd to Er. Similar effects have been recorded.[5a] It is worth mentioning that, as anticipated, no heteronuclear Co−Ln carboxylates could be prepared by employing small carboxylic acids, such as CH_3CO_2H and $CH_3CH_2CO_2H$, and/or small heterocyclic bases, such as imidazole and pyridine, indicating that the factors promoting di- and tricobalt carboxylate formation (carboxylate and amine steric hindrance) are also necessary for generation of mixed-metal cobalt−lanthanide carboxylates. All complexes are air stable and soluble in common organic solvents such as MeOH, EtOH, THF, and DMSO. Single crystals of these compounds suitable for X-ray crystallography were collected by slow evaporation of their ethanolic solutions at room temperature. Complexes **1**, **2**, and **4** were structurally characterized completely by X-ray crystallography, While elemental analyses and a cell determination suggested that the Dy analogue had a structure similar to that of **2**.

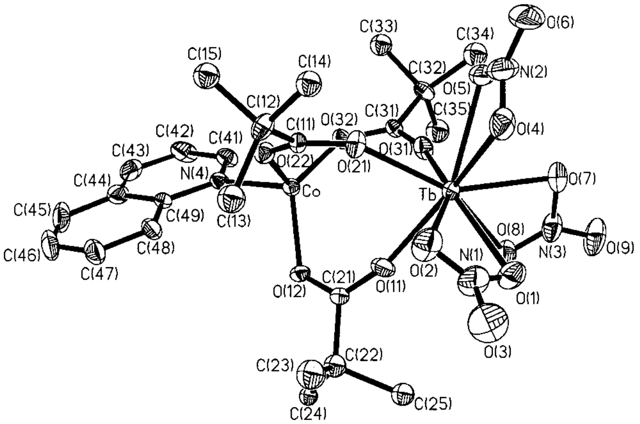

Figure 1. X-ray crystal structure of the complex anion in **1**. For simplicity, only one part of the disordered *tert*-butyl groups are presented.

Complex **1** comprises protonated quinoline $C_9H_7NH^+$ cations, dinuclear $[CoTb(Piv)_3(C_9H_7N)(NO_3)_3]^-$, anions and water molecules of crystallization. As shown in Figure 1, the Co^{II} and Tb^{III} ions in the complex anion are bridged by three pivalate groups in a *syn-syn* fashion with a Co···Tb distance of 4.011(2) Å. The Co atom is coordinated to three carboxyl oxygen atoms [Co−O = 1.941(7)−1.945(8) Å] and a quinoline nitrogen atom [Co−N = 2.041(10) Å], forming a distorted tetrahedron, where the most distorted bond angle is O(32)−Co-N(4) at 97.4(4)°. The Tb ion is coordinated by three bridging pivalate groups

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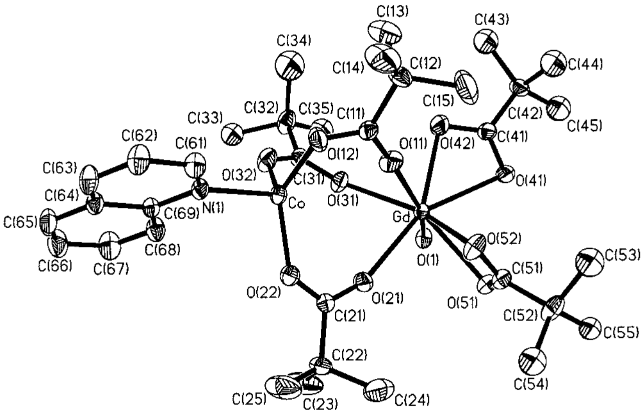

Figure 2. X-ray crystal structure of $[CoGd(Piv)_5(C_9H_7N)(H_2O)]$ in **2**. For simplicity, only one part of the disordered *tert*-butyl groups are presented.

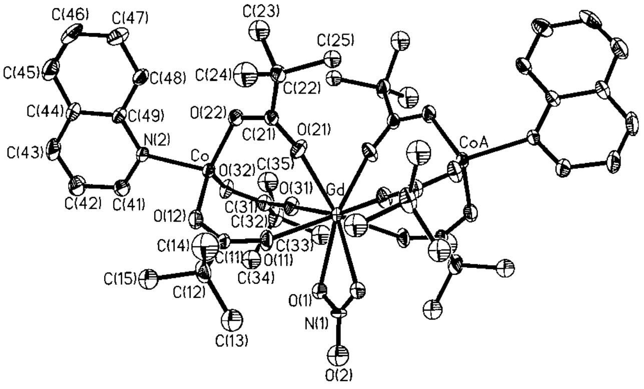

Figure 3. X-ray crystal structure of **4**. For simplicity, only one part of the disordered *tert*-butyl groups are presented. Symmetry code: A $= -x + 1, y, z$.

and three chelating nitrate anions, forming a tricapped trigonal prism with Tb−O bond lengths ranging from 2.254(10) to 2.493(13) Å. The two outer triangular faces are formed by O(11), O(21), O(31) and O(1), O(4), O(7), and the three capping positions are occupied by O(2), O(5), and O(8).

Complex **2** contains a neutral dinuclear $[CoGd(Piv)_5(C_9H_7N)(H_2O)]$ molecule (Figure 2), in which the Co and Gd ions are linked by three pivalate bridges with Co in a tetrahedral geometry analogous to that of **1**. The Co−O bond lengths are in the range 1.935(5)−1.964(5) Å, and the Co−N bond length is 2.070(5) Å. The neighboring Co···Gd separation of 3.998(1) Å is slightly shorter than the Co···Tb distance in **1**. The Gd ion is coordinated by eight oxygen atoms, from three bridging and two chelating pivalate groups, and a water molecule, resulting in a distorted dodecahedron with Gd−O bond lengths ranging from 2.295(4) to 2.475(4) Å, and the two trapezia defined by O(11), O(42), O(1), O(52) and O(31), O(21), O(51), O(41) intersecting at an angle of 83.3°.

As shown in Figure 3, complex **4** consists of a discrete trinuclear $[Co_2Gd(O_2CCMe_3)_6(C_9H_7N)_2(NO_3)]$ molecule with a crystallographic C_2 axis passing through the Gd and N(1) atoms. This molecule also contains a triply pivalate-bridged dinuclear Co···Gd motif with a quinoline molecule ligated to the Co ion to form a distorted tetrahedron. In its essential features the structure of **3** closely resembles the structure of the Co_2Nd pivalate,[8] although the latter does not possess a crystallographic symmetry. The bond distances of Co−O [1.922(5)−1.956(6) Å] and Co−N [2.097(6) Å] compare well with those of **1**, **2**, and the Nd analogue. The Co···Gd separation of 4.032(1) Å is shorter than the average Co···Nd distances of 4.0687(1) Å in the Nd analogue but slightly longer than the Co−Ln distances in complexes **1** and **2**. The arrangement of the three metals is quasi-linear with the Co(1)···Gd···Co(2) angle being 137.84(4)°. The eight-coordination sphere of Gd is completed by a chelating nitrate anion forming with the six carboxyl oxygen atoms a distorted dodecahedron with Gd−O bond distances varying from 2.299(5) to 2.463(7) Å and the two trapezia defined by O(21), O(1), O(1A), O(21A) and O(11), O(31), O(31A), O(11A) intersecting at an angle of 86.4°.

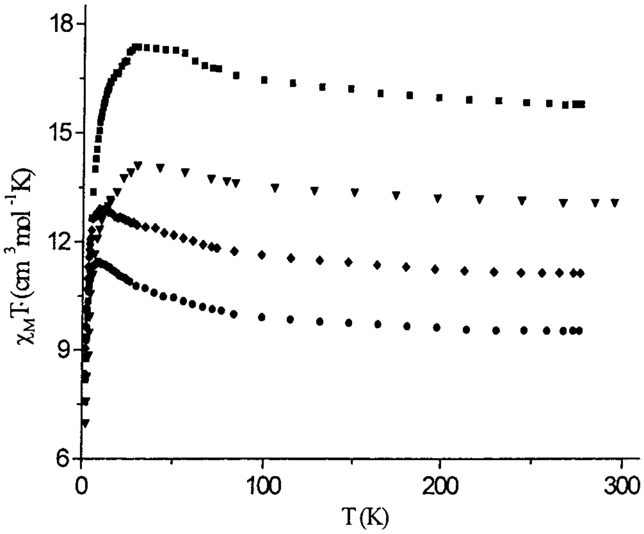

Figure 4. Plots of $\chi_M T$ versus T for **1** (▼), **2** (●), **3** (■), and 4 (◆).

In complexes **1**, **2**, and **4**, the separations between metal ions belonging to neighboring molecules are large: the Co···Co separations are equal to 6.081(1), 5.755(1), and 6.628(1) Å for **1**, **2**, and **4**, respectively, while values of 9.034(1), 5.9309(1), and 11.644(1) Å are observed for Ln···Ln, along with 8.415(1), 8.519(1), and 9.001(1) Å for Co···Ln. These large separations preclude any significant intermolecular interaction of a magnetic nature.

The temperature dependences of the magnetic susceptibilities for complexes **1**−**4** were examined in the temperature range 2−300 K. The plots of $\chi_M T$ versus T are presented in Figure 4, where χ_M is the molar magnetic susceptibility and T is the temperature. The profiles of the plots are similar, indicating similar magnetic behaviors. The experimental $\chi_M T$ values at room temperature [13.11, 9.55, 15.80, and 11.15 $cm^3\ K\ mol^{-1}$ for **1**−**4**, respectively] are close to the $\chi_M T$ values calculated for noninteracting metal ions [13.68, 9.75, 16.04, and 11.63 $cm^3\ K\ mol^{-1}$ for **1**−**4**, respectively]. When the temperature is lowered, the $\chi_M T$ values increase slightly, reaching maxima of 13.98 $cm^3\ K\ mol^{-1}$ at 30 K for **1**, 11.44 $cm^3\ K\ mol^{-1}$ at 8 K for **2**, 17.37 $cm^3\ K\ mol^{-1}$ at 28 K for **3**, and 12.91 $cm^3\ K\ mol^{-1}$ at 9 K for **4**. The decreasing in $\chi_M T$ values at low temperatures for **1**−**4** are most likely attributable to saturation effects, zero-field splittings, and/or changes in the effective spin states of the Co(II) ions from $^3/_2$ to $^1/_2$. The observed behaviors indicate that ferromagnetic interactions take place between adjacent paramagnetic centers. Because **1**−**3** are discrete heterometallic dimers with longer intermolecular metal−metal distances, the magnetic exchange interaction between a Co(II) ion and Gd(III), Tb(III), or Dy(III) may be of the ferromagnetic type, as is further suggested by the ferromagnetic interaction occurring in the isolated quasi-linear CoGdCo complex **4**. This is obviously different from the magnetic behaviors of $[Co_2Nd(Piv)_6(C_9H_7N)_2(NO_3)]$ and $[Co_2Er_2(Piv)_8(C_9H_7N)_2]$, both of which present antiferromagnetic-type interactions.[8] The Co−Nd interaction in the former may be of the antiferromagnetic type as compared with the magnetic behavior of the Gd analogue, but it is difficult to discern the nature of the Co−Er interaction because, in the latter, two different interactions may occur: Co−Er and Er−Er. Thus, the magnetic behavior of the latter species corresponds not only to the Co−Er interaction but also to the overall behavior of the molecule, including both interactions as well as crystal field effects. Therefore, more detailed experiments are needed to better understand the Co−Er interaction. We note that a weakly ferromagnetic Co−Gd interaction was recently observed by Costes et al. for a Schiff base compound.[7] The dependence of the type of Co(II)−Ln(III) interaction (ferro- or antiferromagnetic) on the type of lanthanide ion in the pivalates is reminiscent of the relationship reported for the well-known Cu(II)−Ln(III) systems,[2] where the Cu−Ln interaction is ferromagnetic for Ln = Gd, Dy, or Tb and antiferromagnetic for Ln = Nd. To date, no unambiguous conclusion, however, has been drawn from these studied compounds[2] regarding the nature of the Cu−Er interaction

In summary, four discrete triply carboxylate-bridged di- and trinuclear Co(II)−Ln(III) assemblies were prepared using the metal ions and the bulky ligands pivalic acid and quinoline. Three of these complexes were structurally analyzed by X-ray diffraction crystallography. Variable-temperature magnetic studies indicate that the Co−Gd, Co−Tb, and Co−Dy interactions in these complexes are all ferromagnetic. Further studies of more isolated compounds with mixed cobalt(II) and lanthanide(III) ions are now in progress to fully understand the 3d−4f interactions.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for the structural determinations of complexes **1**, **2**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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