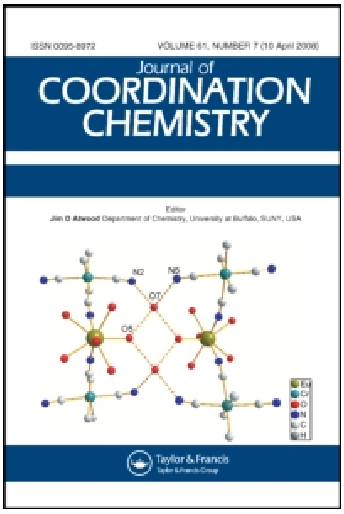

**Journal of Coordination Chemistry**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

# Synthesis and magnetic characterization of Ln(III)-Co(II) complexes with 1,10-phenanthroline ligands

Fang Chen[a]; Weimin Lu[a]; Yue Zhu[b]; Bin Wu[c]; Xiaoming Zheng[a]
[a] Chemistry Department, Zhejiang University (Xixi Campus), Hangzhou 310028, P.R. China [b] Department of Basic Medical Sciences, Hangzhou Normal University, Hangzhou 310018, P.R. China [c] Department of Chemistry, Zhejiang Sci-Tech University, Hangzhou 310018, P.R. China

**To cite this Article** Chen, Fang , Lu, Weimin , Zhu, Yue , Wu, Bin and Zheng, Xiaoming(2009) 'Synthesis and magnetic characterization of Ln(III)-Co(II) complexes with 1,10-phenanthroline ligands', Journal of Coordination Chemistry, 62: 5, 808 — 816

**To link to this Article: DOI:** 10.1080/00958970802308367

**URL:** http://dx.doi.org/10.1080/00958970802308367

*Journal of Coordination Chemistry*
Vol. 62, No. 5, 10 March 2009, 808–816

Taylor & Francis
Taylor & Francis Group

# Synthesis and magnetic characterization of Ln(III)–Co(II) complexes with 1,10-phenanthroline ligands

FANG CHEN†, WEIMIN LU*†, YUE ZHU‡, BIN WU§ and XIAOMING ZHENG†

†Chemistry Department, Zhejiang University (Xixi Campus),
Hangzhou, 310028, P.R. China
‡Department of Basic Medical Sciences, Hangzhou Normal University,
Hangzhou, 310018, P.R. China
§Department of Chemistry, Zhejiang Sci-Tech University, Hangzhou, 310018, P.R. China

(*Received 3 April 2008; in final form 12 May 2008*)

Four heteronuclear complexes, $[Ln_2Co_2L_{10}(H_2O)(phen)_2]\cdot n(H_2O)$ (Ln = La **1**, $n = 2$; Ln = Nd **2**, Sm **3**, Gd **4**, $n = 0$; HL = α-methylacrylic acid, phen = 1,10-phenanthroline), have been synthesized and characterized by elemental analysis, IR and X-ray diffraction. The complexes with a discrete Co–Ln–Ln–Co tetranuclear molecule are isomorphous in the triclinic space group $P\bar{1}$ and $Z = 1$, in which all metal ions are bridged by bidentate α-methylacrylato groups. Magnetic measurements of **1**, **2** and **3** show antiferromagnetic exchange interaction between paramagnetic centers.

*Keywords*: Rare earth; Cobalt; α-Methylacrylic acid; Crystal structure; Magnetic property

## 1. Introduction

Preparation and structures of heteronuclear complexes containing 4f and 3d ions have attracted special attention in view of their magnetic and electronic properties. Magnetism of such compounds is an active field of research involving chemistry, physics, biology and material science [1–6]. Efforts to obtain molecular magnets with rare-earth ions is comparatively less numerous because interactions in pairs of electrons are expected to be small, but the number of new compounds in which rare-earth ions are magnetically coupled to transition-metal ions and/or organic radicals is rapidly increasing [7–16]. It is difficult to clarify what contributes most to the magnetic interaction between rare earth and transition metal ions, because many facts are related to changes in magnetic properties such as the different ions, the coordination environments of the ions, etc. Generally, rare earth ions are trivalent and sometimes isostructural if their central ions possess almost the same coordination,

---

*Corresponding author. Email: weimwlu@mail.hz.zj.cn

*Journal of Coordination Chemistry*
ISSN 0095-8972 print/ISSN 1029-0389 online © 2009 Taylor & Francis
DOI: 10.1080/00958970802308367

propitious to elucidate magnetic properties of different 4f or 3d metallic ions in heteronuclear complexes.

Here, four isostructural heteronuclear complexes, $[Ln_2Co_2L_{10}(H_2O)_2(phen)_2] \cdot n(H_2O)$ (Ln = La, Nd, Sm and Gd), are reported, undertaken in order to determine the structures and magnetic properties. It is part of our research investigating structures and properties of heteronuclear complexes of rare earth and transition metals bridged by carboxylates.

## 2. Experimental

### 2.1. *General*

$LnL_3$ compounds were synthesized according to the literature [17]. All other chemicals of reagent grade were obtained from commercial sources and used without further purification. Elemental analyses were performed on a Carlo–Erba 1110 instrument. IR spectra were recorded using KBr pellets from 4000 ~ 400 $cm^{-1}$ on a Nicolet 560 IR spectrophotometer. The variable temperature susceptibility of **1**, **2** and **3** were measured by physical property measurement system PPMS-9 in the temperature range from 5 to 300 K at a magnetic field of 20 kOe for **1** and **2** or 10 kOe for **3**. The molar susceptibility was corrected from the sample holder and diamagnetic contributions of all constituent atoms by using Pascal's constants.

### 2.2. *Preparation of the title complexes*

$LnL_3$ (0.4 mmol) and $Co(NO_3)_2 \cdot 6H_2O$ (0.3 mmol) were dissolved in 5 mL $H_2O$ and the pH adjusted to 4.1 with HL (0.1 M). Ethanol (2.5 mL) solution of phen (0.3 mmol) was added with stirring. After filtration, the filtrate was allowed to stand at room temperature and single crystals suitable for X-ray work were obtained after three weeks. Anal. Calcd for **1**, $C_{64}H_{74}N_4O_{24}La_2Co_2$ (%): C, 45.78; H, 4.44; N, 3.34. Found: C, 46.06; H, 4.41; N, 3.61. IR (KBr, $cm^{-1}$): $\nu_{as(COO)}$ 1549, $\nu_{s(COO)}$ 1419, $\nu_{(C=C)}$ 1645, $\nu_{(phen\ ring)}$ 1516. Anal. Calcd for **2**, $C_{64}H_{70}N_4O_{22}Nd_2Co_2$ (%): C, 46.49; H, 4.27; N, 3.39. Found: C, 46.19; H, 4.23; N, 3.12. IR (KBr, $cm^{-1}$): $\nu_{as(COO)}$ 1549, $\nu_{s(COO)}$ 1421, $\nu_{(C=C)}$ 1645, $\nu_{(phen\ ring)}$ 1518. Anal. Calcd for **3**, $C_{64}H_{70}N_4O_{22}Sm_2Co_2$ (%): C, 46.15; H, 4.24; N, 3.36. Found: C, 46.20; H, 4.31; N, 3.28. IR (KBr, $cm^{-1}$): $\nu_{as(COO)}$ 1558, $\nu_{s(COO)}$ 1427, $\nu_{(C=C)}$ 1647, $\nu_{(phen\ ring)}$ 1518. Anal. Calcd for **4**, $C_{64}H_{70}N_4O_{22}Gd_2Co_2$ (%): C, 45.77; H, 4.20; N, 3.34. Found: C, 45.92; H, 4.25; N, 3.41. IR (KBr, $cm^{-1}$): $\nu_{as(COO)}$ 1558, $\nu_{s(COO)}$ 1429, $\nu_{(C=C)}$ 1647, $\nu_{(phen\ ring)}$ 1518.

### 2.3. *Determination of crystal structures*

Each crystal was mounted on a glass fiber. Determination of the unit cell and the intensity data were measured on a Rigaku RIGAKU-RAPID diffractometer with graphite-monochromated Mo-K$\alpha$ radiation ($\lambda = 0.71073$ Å) by the $\omega = 2\theta$ scan technique at room temperature. Usual Lp and empirical absorption corrections were applied. The structures were solved by the direct method and then by Fourier syntheses expanded using the Fourier technique. The structure refinement was carried out by full-matrix least-squares procedures on $F^2$ with anisotropic thermal parameters for all non-hydrogen atoms using the SHELXTL/PC program package [18]. Some H atoms were located on a difference Fourier map, others were geometrically fixed and allowed to ride on the parent carbon atoms with isotropic displacement parameters. Atomic scattering factors were taken from International Tables for X-ray Crystallography [19]. Crystal data collection and refinement parameters are summarized in table 1.

## 3. Results and discussion

### 3.1. *IR spectra*

Published infrared data for ligands and unsaturated carboxylates [20] are used to assign the IR spectra of the complexes. A comparison between the spectrum of $CH_2C(CH_3)COOH$ and those of the complexes reveals considerable changes due to coordination. A peak assigned to C=O at $1710\,cm^{-1}$ in $CH_2C(CH_3)COOH$ disappears. Carboxylate groups give rise to very strong IR absorptions, which can be used to distinguish between different coordination modes of the ligands (ionic, monodentate or bidentate) [21]. The stretching vibration of carboxylate was observed about 1549–$1558\,cm^{-1}$ [$\nu_{as(COO)}$] and 1419–$1429\,cm^{-1}$ [$\nu_{s(COO)}$] for **1**–**4**. The separation between $\nu_{as(COO)}$ and $\nu_{s(COO)}$ is about $130\,cm^{-1}$, similar to the previously reported ($127\,cm^{-1}$) [22], indicative of bidentate coordination of the carboxylate because it is smaller than the $146\,cm^{-1}$ value for the corresponding sodium salt. However, spectroscopic techniques could not correctly identify the bridging or chelating bidentate coordination.

### 3.2. *Crystal structures*

Complexes **1**–**4** are triclinic space group $P\bar{1}$ and $Z=1$. Selected bond distances and angles are listed in table 2. Figures 1 and 2 show the ORTEP diagrams of **1** and **2**; the ORTEP diagrams of **3** and **4** are the same as **2** with different lanthanides. Complex **1** consists of a discrete tetranuclear Co–La–La–Co because the coordination of phen ligands with Co ions prevents formation of an infinite structure. The Co and La ions are bridged by three carboxylates with $\mu$-2(COO)-mode, and the symmetry-related La ions are linked by two carboxylates. Each La(III) has a distorted square antiprism environment with one O from water and seven oxygens from one chelating and five bridging carboxylates. Each cobalt(II) is five-coordinate by three oxygens from three bridging carboxylates and two N atoms from a phen. The configuration around Co ion is a slightly distorted pyramid. N2, O1, O3 and O5 occupy the square, while N1 occupies the vertex of the pyramid. The carboxylato groups in **1** exhibit the chelating and bridged bidentate modes with corresponding average La–O distances of 2.618 and 2.430 Å, respectively. The former is longer because of the strain in the four-member La/O7/C51/O8 ring with the O–La–O angle of 50.51°. The Co–O bond distances are similar at 2.029(2), 2.059(2), 2.018(2) Å, respectively, but the Co–N bond lengths differ significantly [Co(1)–N(1) 2.162(2) and Co(1)–N(2) 2.095(2) Å]. The separation of 4.484 Å in La–La is significantly longer than that of 4.046 Å in $[La(CH_2C(CH_3)COO)_3(phen)(HL)]_2$, in which there are four bridging carboxylates between La ions [20].

Table 1. Crystal data and details of experiment for **1**–**4**.

| Complex no. | **1** | **2** | **3** | **4** |
|---|---|---|---|---|
| Empirical formula | $C_{64}H_{74}N_4O_{24}La_2Co_2$ | $C_{64}H_{70}N_4O_{22}Nd_2Co_2$ | $C_{64}H_{70}N_4O_{22}Sm_2Co_2$ | $C_{64}H_{70}N_4O_{22}Gd_2Co_2$ |
| Formula weight | 1678.95 | 1653.58 | 1665.82 | 1679.60 |
| Color, crystal shape | Purple, prism | Pink, prism | Brown, prism | Red, prism |
| Crystal system | Triclinic | Triclinic | Triclinic | Triclinic |
| Space group | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ |
| Unit cells and dimensions (Å, °) | | | | |
| $a$ | 12.142(5) | 11.499 (4) | 11.434(2) | 11.409(2) |
| $b$ | 12.566(4) | 11.594 (3) | 11.578(2) | 11.599 (3) |
| $c$ | 14.430(4) | 14.752 (4) | 14.707(3) | 14.707 (7) |
| $\alpha$ | 66.357(12) | 73.951 (10) | 73.863(3) | 73.762(4) |
| $\beta$ | 70.077(13) | 79.878 (10) | 79.748(3) | 79.699(3) |
| $\gamma$ | 64.609(14) | 75.747 (10) | 75.843(3) | 75.926(2) |
| $V$ (Å$^3$) | 1783.8(10) | 1819.71(9) | 1800.8(2) | 1799.66(10) |
| $Z$, $D_{\mathrm{Cacld}}$ (g cm$^{-3}$) | 1, 1.563 | 1, 1.507 | 1, 1.536 | 1, 1.550 |
| $\mu$ (Mo-K$\alpha$) (mm$^{-1}$) | 1.708 | 1.919 | 2.132 | 2.345 |
| $F$ (000) | 846 | 812 | 836 | 840 |
| Crystal size (mm$^3$) | 0.33 × 0.28 × 0.27 | 0.53 × 0.41 × 0.22 | 0.30 × 0.20 × 0.20 | 0.29 × 0.27 × 0.22 |
| $\theta$ range (°) | 3.09 – 27.48 | 3.04 – 27.44 | 2.34 – 24.98 | 1.45 – 25.55 |
| Limiting indices | $-15 \le h \le 15$ | $-14 \le h \le 14$ | $-14 \le h \le 13$ | $-13 \le h \le 13$ |
| | $-16 \le k \le 16$ | $-15 \le k \le 15$ | $-14 \le k \le 12$ | $-12 \le k \le 14$ |
| | $-18 \le l \le 18$ | $-19 \le l \le 18$ | $-18 \le l \le 15$ | $-17 \le l \le 17$ |
| Total/unique reflections | 17613, 8095 | 17799, 8186 | 9916, 6964 | 14167, 6596 |
| $T_{\min}$ and $T_{\max}$ | 0.603, 0.656 | 0.430, 0.678 | 0.605, 0.679 | 0.580, 0.580 |
| Data/restraints/params. | 8095/0/433 | 8186/0/424 | 6964/2/437 | 6596/2/438 |
| Goodness of Fit ($F^2$) | 1.096 | 1.141 | 0.942 | 1.241 |
| $R$ [$I > 2.0\ \sigma(I)$] | 0.0270 | 0.0354 | 0.0417 | 0.0456 |
| $wR$ | 0.0714 | 0.0924 | 0.0733 | 0.1040 |
| $\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å$^3$) | 0.560, −0.577 | 0.899, −0.802 | 1.293, −0.401 | 0.985, −0.852 |

Table 2. Selected bond lengths (Å) and angles (°) for **1**–**4**.

| Bond lengths | **1** | **2** | **3** | **4** |
|---|---|---|---|---|
| Co(1)–O(1) | 2.029(2) | 2. 069(3) | 2.068(3) | 2.070(4) |
| Co(1)–O(3) | 2.059(2) | 2.057(2) | 2.054(3) | 2.058(4) |
| Co(1)–O(5) | 2.018(2) | 2.004(2) | 2.003(3) | 1.998(4) |
| Co(1)–N(1) | 2.162(2) | 2.133(3) | 2.126(3) | 2.122(4) |
| Co(1)–N(2) | 2.095(2) | 2.101(3) | 2.093(3) | 2.100(4) |
| Ln(1)–O(2) | 2.505(2) | 2.390(2) | 2.361(3) | 2.333(3) |
| Ln(1)–O(4) | 2.430(2) | 2.345(2) | 2.310(3) | 2.290(3) |
| Ln(1)–O(6) | 2.476(2) | 2.517(2) | 2.490(3) | 2.474(3) |
| Ln(1)–O(7) | 2.618(2) | 2.562(2) | 2.530(3) | 2.505(3) |
| Ln(1)–O(8) | 2.529(2) | 2.471(2) | 2.435(2) | 2.418(3) |
| Ln(1)–O(9) | 2.558(2) | 2.454(2) | 2.414(2) | 2.388(3) |
| Ln(1)–O(10) | 2.452(2) | 2.384(2) | 2.322(3) | 2.298(3) |
| Ln(1)–O(11) | 2.594(2) | 2.561(2) | 2.520(2) | 2.489(4) |
| O(1)–Co(1)–O(3) | 163.72(8) | 164.93(9) | 164.60(11) | 164.10(13) |
| O(1)–Co(1)–N(1) | 87.24(9) | 85.47(10) | 85.57(12) | 85.75(15) |
| O(1)–Co(1)–N(2) | 104.07(9) | 101.02(10) | 101.47(11) | 101.86(14) |
| O(3)–Co(1)–N(1) | 85.54(8) | 86.57(10) | 86.29(11) | 86.18(14) |
| O(3)–Co(1)–N(2) | 88.67(8) | 89.94(10) | 89.73(11) | 89.95(14) |
| O(5)–Co(1)–O(1) | 94.97(9) | 95.05(11) | 95.32(12) | 95.37(16) |
| O(5)–Co(1)–O(3) | 93.34(9) | 93.99(11) | 93.97(12) | 94.00(16) |
| O(5)–Co(1)–N(1) | 175.29(8) | 174.98(10) | 174.82(12) | 174.37(14) |
| O(5)–Co(1)–N(2) | 97.46(9) | 96.22(10) | 96.01(12) | 95.66(14) |
| N(1)–Co(1)–N(2) | 77.95(8) | 78.79(10) | 78.82(12) | 78.71(14) |
| O(2)–Ln(1)–O(7) | 67.45(7) | 71.59(9) | 71.99(9) | 72.16(12) |
| O(2)–Ln(1)–O(8) | 80.32(7) | 83.15(9) | 83.34(9) | 83.72(12) |
| O(2)–Ln(1)–O(9) | 135.59(7) | 143.83(9) | 144.88(10) | 145.45(12) |
| O(2)–Ln(1)–O(11) | 140.17(7) | 138.86(9) | 139.41(10) | 139.71(13) |
| O(4)–Ln(1)–O(2) | 84.53(7) | 86.21(9) | 87.56(10) | 88.08(13) |
| O(4)–Ln(1)–O(6) | 79.24(8) | 74.95(9) | 75.50(9) | 75.82(12) |
| O(4)–Ln(1)–O(7) | 79.31(7) | 76.00(8) | 76.40(9) | 76.41(11) |
| O(4)–Ln(1)–O(8) | 129.64(7) | 127.23(8) | 128.07(9) | 128.43(11) |
| O(4)–Ln(1)–O(9) | 75.47(7) | 78.61(8) | 79.82(9) | 80.51(11) |
| O(4)–Ln(1)–O(10) | 157.47(7) | 156.11(8) | 155.69(9) | 155.50(13) |
| O(4)–Ln(1)–O(11) | 79.68(7) | 84.95(8) | 84.99(9) | 85.22(12) |
| O(6)–Ln(1)–O(2) | 69.22(8) | 74.80(9) | 75.28(10) | 75.35(13) |
| O(6)–Ln(1)–O(7) | 132.96(8) | 136.47(8) | 137.27(9) | 137.49(11) |
| O(6)–Ln(1)–O(8) | 135.97(8) | 147.82(10) | 147.69(10) | 147.67(12) |
| O(6)–Ln(1)–O(9) | 141.08(8) | 130.48(9) | 131.17(9) | 131.55(13) |
| O(6)–Ln(1)–O(11) | 72.00(8) | 64.10(9) | 64.22(10) | 64.48(12) |
| O(8)–Ln(1)–O(7) | 50.50(6) | 51.59(7) | 52.15(8) | 52.60(10) |
| O(8)–Ln(1)–O(9) | 82.73(8) | 80.47(8) | 79.19(9) | 78.37(11) |
| O(8)–Ln(1)–O(11) | 136.72(6) | 132.56(7) | 131.13(9) | 130.09(11) |
| O(9)–Ln(1)–O(7) | 70.07(7) | 72.95(8) | 73.22(9) | 73.47(11) |
| O(9)–Ln(1)–O(11) | 74.70(8) | 72.58(8) | 72.28(10) | 71.99(12) |
| O(10)–Ln(1)–O(2) | 100.28(7) | 91.83(9) | 91.05(10) | 90.97(13) |
| O(10)–Ln(1)–O(6) | 81.95(7) | 81.55(9) | 80.71(10) | 80.26(12) |
| O(10)–Ln(1)–O(7) | 122.95(6) | 125.82(8) | 126.04(9) | 126.38(12) |
| O(10)–Ln(1)–O(8) | 72.86(6) | 75.95(8) | 75.73(9) | 75.68(12) |
| O(10)–Ln(1)–O(9) | 113.33(6) | 114.82(8) | 113.44(9) | 112.48(12) |
| O(10)–Ln(1)–O(11) | 82.82(7) | 80.93(8) | 80.34(10) | 79.75(13) |
| O(11)–Ln(1)–O(7) | 142.44(7) | 143.20(9) | 143.09(9) | 143.01(12) |

The Co–La separation is 3.989 Å and exceeds the sum of the corresponding ionic radii. Uncoordinated water molecules are linked to the complex via O(12)–H(122)–O(3) and O(12)–H(111)–O(11) hydrogen bonds at 2.908(5) and 2.817(5) Å (table 3), respectively, forming a two-dimensional network structure along the *b* axis. Except for lacking non-coordinated water, the structures of [$Ln_2Co_2L_{10}(H_2O)(phen)_2$] (Ln=Nd, Sm, Gd) are the same as **1**. Distances of 4.514, 4.566 and 4.615 Å are observed for Ln–Ln in **2**, **3** and **4**, respectively, along with the distances of 3.943, 3.904 and 3.885 Å for Co–Ln. These Co–Ln (Ln from La to Gd) heteronuclear complexes are isostructural with central ions possessing the same coordination, allowing comparison of their

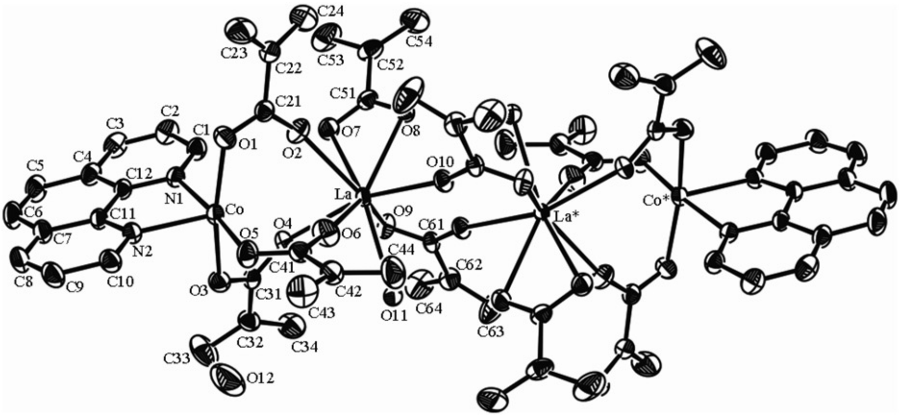

Figure 1. ORTEP plot of [$La_2Co_2L_{10}(H_2O)_2(phen)_2$]$\cdot 2H_2O$. The hydrogen atoms have been omitted for clarity. Thermal ellipsoids are at the 30% level.

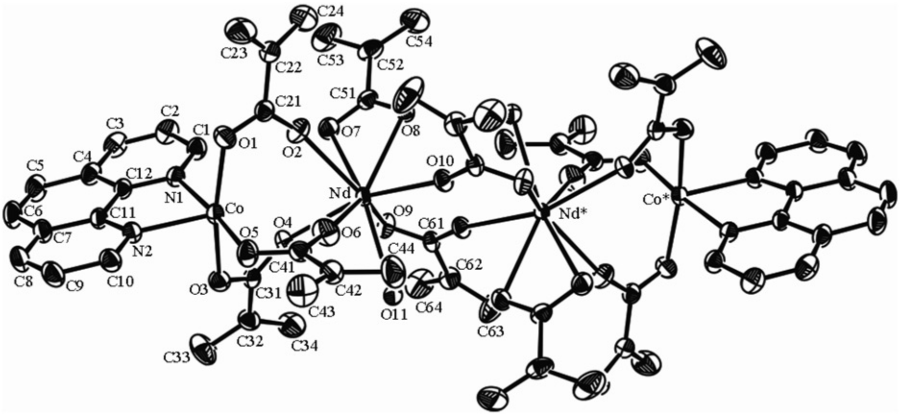

Figure 2. ORTEP plot of [$Nd_2Co_2L_{10}(H_2O)_2(phen)_2$]. The hydrogen atoms have been omitted for clarity. Thermal ellipsoids are at the 30% level.

Table 3. Hydrogen bonding geometry for **1**.

| | D···A | H···A | D···A | D–H···A |
|---|---|---|---|---|
| O(11)–H(112)–O(8)$^{(I)}$ | 0.83 | 1.96 | 2.757(3) | 161.22 |
| O(11)–H(111)–O(12)$^{(I)}$ | 0.93 | 1.90 | 2.817(5) | 166.24 |
| O(12)–H(122)–O(3)$^{(II)}$ | 1.04 | 1.88 | 2.908(5) | 169.48 |

Symmetry code: (I) $-x$, $1-y$, $1-z$; (II) $x$, $1+y$, $z$.

magnetic properties. The phenanthroline ligands always coordinate with transition metal ions rather than with rare earth ions, as observed in other bidentate aromatic amine Ln–Cu, Ln–Zn heteronuclear complexes [23–27].

In the four complexes, a partially overlapped arrangement is observed between parallel phen ligands, with face-to-face separation of 3.595, 3.524, 3.531 and 3.540 Å for **1**, **2**, **3** and **4**, respectively, suggesting the existence of $\pi$–$\pi$ stacking.

### 3.3. *Magnetic properties*

The temperature dependences of the magnetic susceptibilities for **1**–**3** were examined from 5 to 300 K. The plot of $\chi_M T$ *versus* $T$ for **1** is presented in figure 3, where $\chi_M$ is molar magnetic susceptibility and $T$ is temperature. The experimental $\chi_M T$ value at room temperature is 5.27 $cm^3\,mol^{-1}\,K\,mol^{-1}$ and the corresponding magnetic moment is 6.52 µB, which is larger than that (5.47 µB) calculated for independent spins for two Co(II) ions ($S = 3/2$). Comparing the values between the experiment and calculation in **1**, significant paramagnetic interactions between the metal ions may be precluded due to the diamagnetic La(III) ions and large separations between Co(II) ions. Thus, excited states of Co(II) in **1** are occupied at room temperature and the effective magnetic moment comes from spin ($S = 3/2$) and orbital contributions of Co(II). When the temperature lowers, the $\chi_M T$ value of **1** decreases slowly, reaching to 3.05 $cm^3\,K\,mol^{-1}$ at 5 K. This value deviates from expectation, likely due to the spin-orbit coupling of the Co(II). The values of $\theta$ and C for **1** are obtained from the least squares fit of the data sets, which appear to follow the Curie–Weiss law. The low negative value (−2.693 K) of $\theta$ indicates weak antiferromagnetic interaction between metal centers.

The plots of $\chi_M T$ *versus* $T$ for **2** and **3** are also in figure 3. The $\chi_M T$ values at room temperature are 8.95 and 5.64 $cm^3\,mol^{-1}\,K\,mol^{-1}$ and the corresponding magnetic moments are 8.50 and 6.72 µB, respectively. These values are much more than those (7.50 and 5.63 µB) calculated for the sum of independent spins for two Co(II) ions ($S = 3/2$) and spin-orbit coupling for two Ln(III) ions ($S = n/2$) ($n = 3, 5$ for Nd, Sm, respectively). The differences of $\Delta\mu_{\mathrm{eff}}$ ($\mu_{\mathrm{eff}}$ **2** $-$ $\mu_{\mathrm{eff}}$ **1** or $\mu_{\mathrm{eff}}$ **3** $-$ $\mu_{\mathrm{eff}}$ **1**) at room temperature are 1.98 and 0.20 µB, respectively, close to the corresponding calculated values (2.03 and 0.16 µB), implying that paramagnetic interaction is very weak between Co and Ln ions or Ln and Ln ions, and that the effective magnetic moments for the two

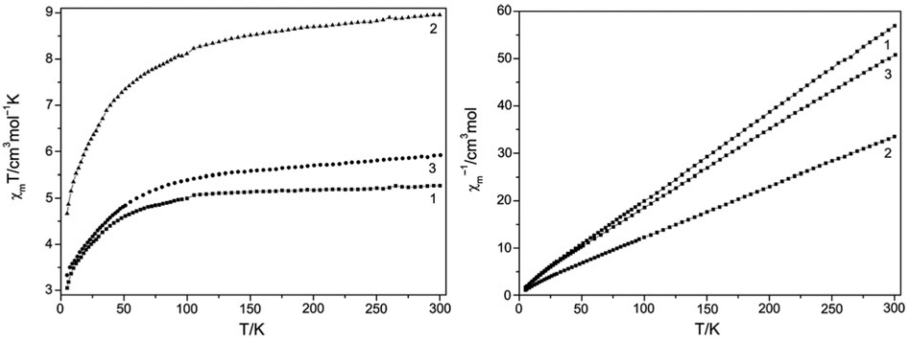

Figure 3. Plots of $\chi_M T$ and $1/\chi_M$ *vs.* $T$ for **1**, **2** and **3**.

complexes arise from electronic spins and spin-orbit coupling of Co(II), Sm(III) and Nd(III) ions, respectively. Magnetic properties of **1**, **2** and **3** at room temperature basically exhibit the magnetic behavior of each metal ion, although magnetic behavior is generally complicated in heteronuclear complexes. When the temperature lowers, the $\chi_M T$ values of **2** and **3** decrease slowly, reaching 4.67 and $3.33\,\mathrm{cm^3\,K\,mol^{-1}}$ at 5 K, respectively. The plot of **3** is between **1** and **2** rather than over **2**, because the direction of orbit magnetic moment is reversed to that of spin magnetic moment for Sm(III) [28]. Complexes **1**, **2** and **3** have analogous magnetic behavior with a weak antiferromagnetic interaction between metal centers.

## 4. Conclusion

Four Ln–Co (Ln = La, Nd, Sm and Gd) tetranuclear complexes are synthesized, Co–Ln (Ln from La to Gd) and are isostructural. Magnetic studies indicate that the interactions between Co(II) and Ln(III) (Ln from La to Sm) in the complexes are antiferromagnetic; at room temperature they are basically the magnetic behavior of each metal ion. Further studies for lanthanide and transition metal complexes are in progress in order to fully understand the 3d-4f interaction.

## Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 673660, 624630, 189348 and 191287 for **1**, **2**, **3** and **4**, respectively. Copies may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: t44-01223-336033; Email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

## Acknowledgements

The authors would like to thank the Key Laboratory of Zhejiang University for collecting X-ray data and the Education Committee of Zhejiang Province, China with funds.

## References

[1] H.Z. Kou, B.C. Zhou, R.J. Wang. *Inorg. Chem.*, **42**, 7658 (2003).
[2] H.H. Zhao, N. Lopez, A. Prosvirin, H.T. Chifotides, K.R. Dunbar. *Dalton. Trans.*, 878 (2007).
[3] A. Figuerola, J. Ribas, X. Solans, M.F. Bardía, M. Maestro, C. Diaz. *Eur. J. Inorg. Chem.*, 1846 (2006).
[4] S. Osa, T. Kido, N. Matsumoto, N. Re, A. Pochaba, J. Mrozinski. *J. Am. Chem. Soc.*, **126**, 420 (2004).
[5] F. Pointillart, K. Bernot, R. Sessoli, D. Gatteschi. *Chem. Eur. J.*, **13**, 1602 (2007).
[6] O. Kahn. *Molecular Magnetism*, VCH, Weinheim, Germany (1993).
[7] M. Murugesu, A. Mishra, W. Wernsdorfer, K.A. Abboud, G. Christou. *Polyhedron*, **25**, 613 (2006).

[8] M. Ferbinteanu, T. Kajiwara, K.Y. Choi, H. Nojiri, A. Nakamoto, N. Kojima, F. Cimpoesu, Y. Fujimura, S. Takaishi, M. Yamashita. *J. Am. Chem. Soc.*, **128**, 9008 (2006).

[9] B. Zhao, P. Cheng, Y. Dai, C. Cheng, D.Z. Liao, S.P. Yan, Z.H. Jiang, G.L. Wang. *Angew. Chem., Int. Ed.*, **42**, 934 (2003).

[10] C. Aronica, G. Pilet, G. Chastanet, W. Wernsdorfer, J.F. Jacquot, D. Luneau. *Angew. Chem., Int. Ed.*, **45**, 4659 (2006).

[11] A.C. Rizzi, R. Calvo, R. Baggio, M.T. Garland, O. Pena, M. Perec. *Inorg. Chem.*, **41**, 5609 (2002).

[12] F. Mori, T. Nyui, T. Ishida, T. Nogami, K.Y. Choi, H. Nojiri. *J. Am. Chem. Soc.*, **128**, 1440 (2006).

[13] J.P. Costes, F. Dahan, W. Wernsdorfer. *Inorg. Chem.*, **45**, 5 (2006).

[14] Y.P. Ren, L.S. Long, B.W. Mao, Y.Z. Yuan, R.B. Huang, L.S. Zheng. *Angew. Chem., Int. Ed.*, **42**, 532 (2003).

[15] T.K. Prasad, M.V. Rajasekharan, J.P. Costes. *Angew. Chem., Int. Ed.*, **46**, 1 (2007).

[16] F. He, M.L. Tong, X.M. Chen. *Inorg. Chem.*, **44**, 8285 (2005).

[17] W.M. Lu, Z.P. Shao, J.B. Hu, X.Y. Lao, J.M. Gu. *J. Coord. Chem.*, **40**, 145 (1996).

[18] G.M. Sheldrick. *SHELXTL 6.10. Bruker AXS*, Madison, WI, USA (2000).

[19] *International Tables for X-ray Crystallography*, Vol. χ, Kynoch Press, Birmingham (1974).

[20] W.M. Lu, Z.P. Shao, J.P. Hu, X.Y. Luo, J.M. Gu. *J. Coord. Chem.*, **40**, 145 (1996).

[21] G.B. Deacon, R.J. Phillips. *Coord. Chem. Rev.*, **33**, 227 (1980).

[22] B. Wu, W.M. Lu, X.M. Zheng. *J. Coord. Chem.*, **56**, 65 (2003).

[23] B. Wu, W.M. Lu, X.M. Zheng. *J. Coord. Chem.*, **55**, 497 (2002).

[24] B. Wu, W.M. Lu, X.M. Zheng. *Trans. Met. Chem.*, **28**, 323 (2003).

[25] Y. Zhu, W.M. Lu, F. Chen. *Acta Cryst.*, **E60**, m963 (2004).

[26] B. Wu, W.M. Lu, F.F. Wu, X.M. Zheng. *J. Coord. Chem.*, **57**, 805 (2004).

[27] Y. Zhu, W.M. Lu, M. Ma, F. Chen. *Acta Cryst.*, **E61**, m1610 (2005).

[28] J.H. Van Vleck. *The Theory of Electric and Magnetic Susceptibilities*, The Clarendon Press, Oxford (1932).