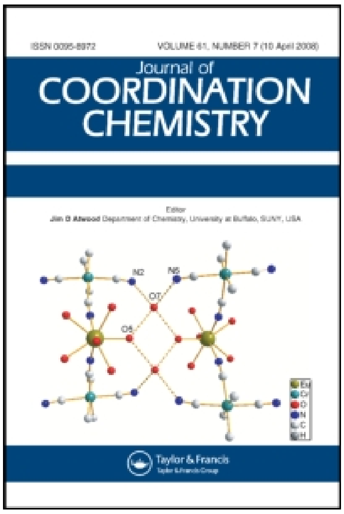

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Synthesis and crystal structure of d–f heteronuclear Gd(III)–Co(II) system

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A carboxylate-bridged Co(II)–Gd(III) complex, [(bipy)CoL$_3$Gd(NO$_3$)L$_3$Co(bipy)] (HL = α-methylacrylic acid, bipy = 2,2′-bipyridine), was prepared and characterized. Single crystal X-ray analysis reveals that the complex assumes a carboxylate-bridged CoGdCo unit. Magnetic measurements showed $\chi_m T$ decreases when the temperature is lowered.

Keywords: Gadolinium; Cobalt; Heteronuclear; Crystal structure; Magnetic properties

1. Introduction

A number of 3d and 4f heterometallic complexes have been studied [1–7] to understand the mechanism of the magnetic interaction between 3d and 4f centers, which are potential magnetic materials. In most polynuclear compounds the transition metal and Ln ions are bridged by multi-group ligands [8–11]. Here we report the synthesis and magnetic properties of trinuclear Co–Gd–Co complexes made with carboxylate ligands.

2. Experimental

GdL$_3$ was synthesized according to the literature [12]. All other chemicals were of reagent grade quality obtained from commercial sources and used without further purification.

2.1. *Physical measurements*

Elemental analyses were performed on a Cobra–Erba1110 instrument. IR spectra were recorded on a Nicolet 560 IR spectrophotometer. Magnetic data were measured using

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a Quantum Design model 6000 magnetometer over the temperature range 5–300 K at 10 kOe applied field. Diamagnetic corrections were made with Pascal's constants for all the constituent atoms [13].

2.2. *Synthesis*

$GdL_3 \cdot H_2O$ (860 mg, 2.0 mmol; $HL = CH_2C(CH_3)COOH$) and $Co(NO_3)_2 \cdot 6H_2O$ (435 mg, 1.5 mmol) were dissolved into 10 mL water and adjusted to pH = 4.1 with HL. Ethanol solution (3 mL) of 2,2′-bipyridine (235 mg, 1.5 mmol) was added into the mixed solution with stirring. After filtration, the filtrate was allowed to stand at room temperature and single crystals suitable for X-ray work were obtained after two weeks. Elemental analysis for $C_{44}H_{46}O_{15}N_5GdCo_2$, calculated: C, 45.56; H, 4.00; N, 6.04%. Found: C, 45.61; H, 3.94; N, 8.97%. IR(KBr, cm^{-1}): ν_{as}(COO) 1570, ν_s(COO) 1421, ν (C=C) 1645.

2.3. *X-ray crystallographic studies*

Crystallographic data were collected using a Rigaku R-AXIS RAPID area detector diffractometer. Absorption corrections were applied using multi-scan. The structure was solved by direct methods and refined for all data using SHELXL 97 [13]. Crystal data: $C_{44}H_{46}Co_2GdN_5O_{15}$, M = 1159.97, Triclinic, $a = 11.4226(7)$ Å, $b = 13.5183(7)$ Å, $c = 16.4069(9)$ Å, $\alpha = 103.457(3)°$, $\beta = 100.000(3)°$, $\gamma = 100.070(3)°$, space group $P\bar{1}$, $Z = 2$, $\mu = 2.152\ mm^{-1}$, 18319 reflections measured, 8318 unique ($R_{int} = 0.019$) which were used in all calculations. The final $wR(F^2)$ was 0.0496 (all data).

3. Results and discussion

3.1. *Crystal structure*

Table 1 reports selected bond lengths and angles. The Gd–Co complex contains a neutral trinuclear CoGdCo molecule in an asymmetric unit (figure 1). Gadolinium is coordinated by six O atoms from six α-methylacryl groups and two O atoms from a nitrate. The coordination geometry about Gd atom is an irregular polyhedron. Each Co atom is five-coordinate with three O atoms from three α-methylacryl groups and two N atoms from a bipy. The coordination polyhedra of Co1 and Co2 are distorted pyramidal geometry. For Co1, N1, O1, O3 and O5 occupy the square base of the pyramid, while N2 occupies its apex; for Co2, N4, O11, O13 and O15 occupy the square base of the pyramid, while N5 occupies its apex. Gd and Co atoms are bridged by three carboxylate groups. The Gd ··· Co separations are not equal, Co1 ··· Gd is 3.863(1) Å and Co2 ··· Gd is 3.934(1) Å.

Neighboring bipy ligands are antiparallel with interplanar bipy-to-bipy distance of 3.49 Å for bipy ligand linked with Co1 and 3.40 Å for bipy ligand linked with Co2, indicating significant aromatic stacking interactions [15]. The aromatic stacking interactions are responsible for the supramolecular assemblies.

Table 1. Selected bond lengths (Å) and angles (°).

Gd–O(2)	2.3480(18)	Gd–O(4)	2.3509(18)
Gd–O(6)	2.3561(18)	Gd–O(7)	2.5244(18)
Gd–O(8)	2.5333(18)	Gd–O(10)	2.3103(19)
Gd–O(12)	2.3345(17)	Gd–O(14)	2.383(2)
Co(1)–O(1)	2.0089(19)	Co(1)–O(3)	2.0809(19)
Co(1)–O(5)	2.0339(19)	Co(1)–N(1)	2.131(2)
Co(1)–N(2)	2.083(2)	Co(2)–O(11)	2.015(4)
Co(2)–O(13)	1.9971(17)	Co(2)–O(15)	2.0507(18)
Co(2)–N(4)	2.149(2)	Co(2)–N(5)	2.0760(19)
O(1)–C(11)	1.251(3)	O(2)–C(11)	1.255(3)
O(2)–Gd–O(4)	91.22(7)	O(2)–Gd–O(6)	73.36(7)
O(2)–Gd–O(7)	73.54(7)	O(2)–Gd–O(8)	72.92(6)
O(2)–Gd–O(14)	144.02(7)	O(4)–Gd–O(6)	79.77(7)
O(4)–Gd–O(7)	72.43(6)	O(4)–Gd–O(8)	122.81(7)
O(4)–Gd–O(14)	88.13(9)	O(6)–Gd–O(14)	71.13(7)
O(6)–Gd–O(7)	135.76(7)	O(6)–Gd–O(8)	139.36(7)
O(7)–Gd–O(8)	50.41(7)	O(10)–Gd–O(2)	91.12(8)
O(10)–Gd–O(4)	165.15(6)	O(10)–Gd–O(6)	86.87(7)
O(10)–Gd–O(7)	122.23(7)	O(10)–Gd–O(8)	71.82(7)
O(10)–Gd–O(12)	90.74(8)	O(10)–Gd–O(14)	81.39(9)
O(12)–Gd–O(2)	142.17(7)	O(12)–Gd–O(4)	96.36(7)
O(12)–Gd–O(6)	144.46(7)	O(12)–Gd–O(7)	73.63(6)
O(12)–Gd–O(8)	71.85(7)	O(12)–Gd–O(14)	73.45(7)
O(14)–Gd–O(7)	139.28(8)	O(14)–Gd–O(8)	135.30(8)
O(1)–Co(1)–O(3)	96.22(8)	O(1)–Co(1)–O(5)	90.25(8)
O(5)–Co(1)–O(3)	161.00(8)	O(1)–Co(1)–N(1)	169.47(8)
O(1)–Co(1)–N(2)	94.43(8)	O(3)–Co(1)–N(1)	90.81(8)
O(5)–Co(1)–N(2)	101.79(8)	O(3)–Co(1)–N(2)	95.51(8)
O(5)–Co(1)–N(1)	85.53(8)	O(11)–Co(2)–N(4)	84.96(8)
O(11)–Co(2)–N(5)	97.60(8)	O(11)–Co(2)–O(15)	156.80(8)
O(13)–Co(2)–N(4)	172.99(7)	O(13)–Co(2)–N(5)	96.12(7)
O(13)–Co(2)–O(11)	95.53(8)	O(13)–Co(2)–O(15)	96.61(8)
O(15)–Co(2)–N(4)	85.38(8)	O(15)–Co(2)–N(5)	100.66(8)

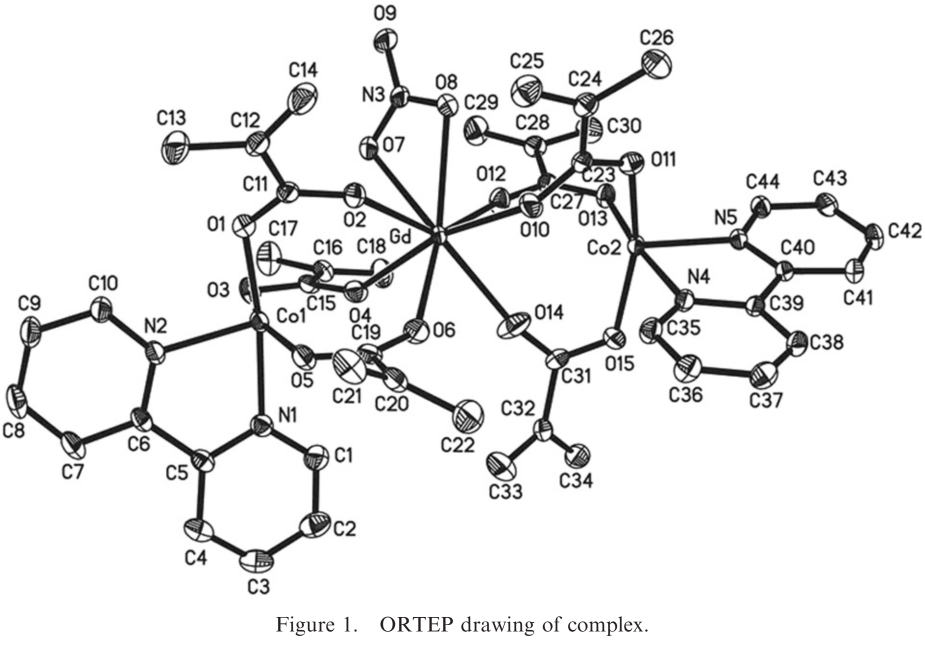

Figure 1. ORTEP drawing of complex.

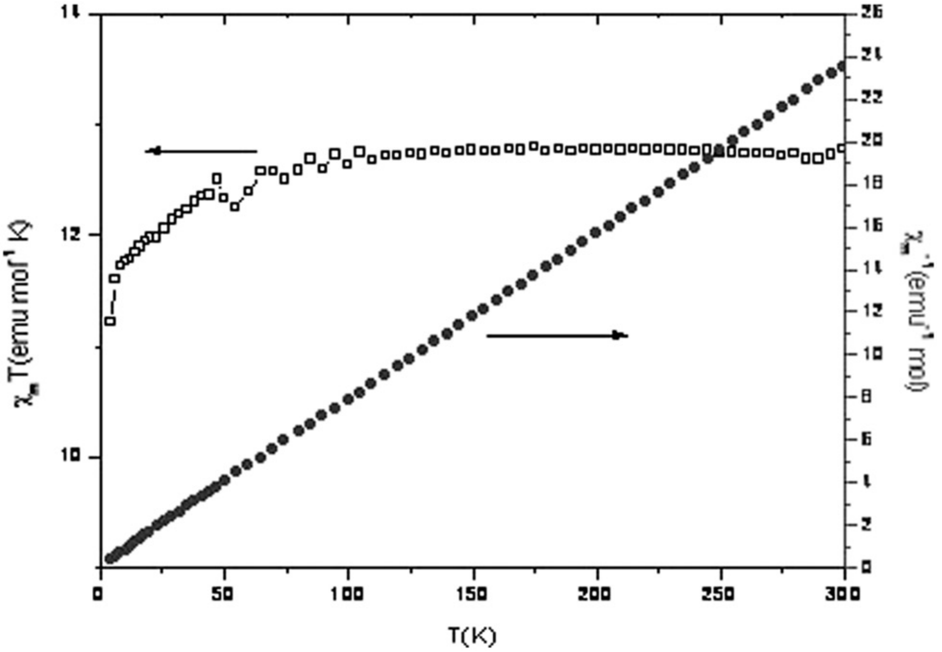

Figure 2. Plots of χ_mT and $1/\chi_m$ *vs.* T for complex.

3.2. *Magnetic properties*

The value of χ_mT decreases as the temperature is lowered from 12.77 emu K mol^{-1} at 300 K to 11.21 emu K mol^{-1} at 5 K. Plots of $1/\chi_m$ *versus* T follow the Curie–Weiss law with Weiss constant $\theta = -1.15$ K. Orbital contribution of the cobalt ions could decrease χ_mT in figure 2 or anti-ferromagnetic behavior; more detailed experiments are needed to better understand the Co–Gd interaction.

Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 238393. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44 1223 336033; Email: deposit@ccdc.cam.ac.uk].

Acknowledgements

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References

[1] C. Faser, B. Bosnich. *Inorg. Chem.*, **33**, 338 (1994).
[2] C. Benelli, D. Gatteschi. *Chem. Rev.*, **102**, 2369 (2002).
[3] J.P. Costes, F. Dahan, A. Dupuis. *Inorg. Chem.*, **39**, 165 (2000).
[4] X.M. Chen, S.M.J. Aubin, Y.L. Wu, Y.S. Yang, T.C.W. Mak, D.N. Hendrickson. *J. Am. Chem. Soc.*, **115**, 9600 (1995).
[5] B.Q. Ma, S. Gao, O. Bai, H.L. Sun, G.X. Xu. *Dalton Trans.*, 1003 (2000).
[6] B. Du, E.A. Meyers, S.G. Shore. *Inorg. Chem.*, **39**, 4639 (2000).
[7] J.J. Zhang, T.L. Sheng, S.Q. Xia, G. Leibeling, F. Meyer, S.M. Hu, R.B. Fu, S.C. Xiang, X.T. Wu. *Inorg. Chem.*, **43**, 5472 (2004).
[8] J.P. Costes, F. Dahan, J. García-Tojal. *Chem. Eur. J.*, **8**, 5430 (2002).
[9] J.P. Costes, F. Dahan, A. Dupuis, J.P. Laurent. *New J. Chem.*, **22**, 1525 (1998).
[10] J.P. Costes, F. Dahan, A. Dupuis, J.P. Laurent. *Inorg. Chem.*, **36**, 4284 (1997).
[11] G. Novitchi, S. Shova, A. Caneschi, J.P. Costes, M. Gdaniec, N. Stanica. *Dalton Trans.*, 1194 (2004).
[12] W.M. Lu, J.B. Hu, N. Dong, W.G. Chen, J.M. Gu. *Acta Cryst.*, **C51**, 1568 (1995).
[13] P.W. Selwood. *Magnetochemistry*, Interscience Publishers, New York (1956).
[14] G.M. Sheldrick. *SHELXL-97, Program for Crystal Structure Refinement*, University of Göttingen, Germany (1997).
[15] M. Munakata, L.P. Wu, M. Yamamoto, T. Kuroda-Sowa, M. Maekawa. *J. Am. Chem. Soc.*, **118**, 3117 (1996).