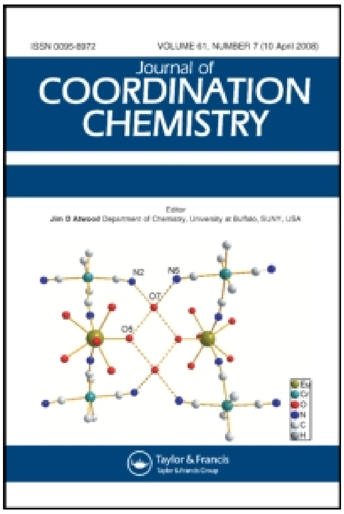
This article was downloaded by:
On: *23 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry

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

Note: Structure and Magnetic Properties of a Heteronuclear Cobalt-Cerium complex: $[CoCe(CH_2C(CH_3)COO)_5(phen)(C_2H_5OH)]_2$

Bin Wu[a]; Weimin Lu[a]; Xiaoming Zheng[a]
[a] Institute of Catalysis, Zhejiang University, Hangzhou, China

Online publication date: 15 September 2010

To cite this Article Wu, Bin , Lu, Weimin and Zheng, Xiaoming(2003) 'Note: Structure and Magnetic Properties of a Heteronuclear Cobalt-Cerium complex: $[CoCe(CH_2C(CH_3)COO)_5(phen)(C_2H_5OH)]_2$', Journal of Coordination Chemistry, 56: 1, 65 — 70

To link to this Article: DOI: 10.1080/0095897031000065368

URL: http://dx.doi.org/10.1080/0095897031000065368

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J. Coord. Chem., 2003, Vol. 56, No. 1, pp. 65–70

Taylor & Francis
Taylor & Francis Group

Downloaded At: 13:52 23 January 2011

Note

STRUCTURE AND MAGNETIC PROPERTIES OF A HETERONUCLEAR COBALT–CERIUM COMPLEX: $[CoCe(CH_2C(CH_3)COO)_5(PHEN)(C_2H_5OH)]_2$

BIN WU, WEIMIN LU* and XIAOMING ZHENG

Institute of Catalysis, Zhejiang University, Xixi Campus, Hangzhou 310028, China

(Received 7 June 2002; In final form 29 August 2002)

A novel heteronuclear complex, $[CoCe(CH_2C(CH_3)COO)_5(phen)(C_2H_5OH)]_2$ (where phen = 1,10-phenanthroline), has been prepared and its structure determined by X-ray diffraction methods. The complex crystallizes in the triclinic system with space group $P\bar{1}$, $a = 12.0982(8)$, $b = 12.6068(9)$, $c = 14.4492(10)$ Å, $\alpha = 67.388(1)$, $\beta = 70.816(1)$, $\gamma = 64.480(1)°$. The structure was refined to $R = 0.045$ for 5987 observed reflections ($I > 2\sigma(I)$). The complex is a discrete tetranuclear molecule bridged by α-methylacrylato groups. Magnetic properties of the complex were also measured and are discussed.

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

INTRODUCTION

The study of heterometallic complexes containing *d*-transition metals and rare-earth(III) cations connected by bridging ligands is being actively pursued. The nature of attendant magnetic exchange interactions is not only of theoretical interest [1–9], but is also relevant to the possible use of rare-earth orthoferrites and related materials as magnetic bubble devices [10]. Yttrium and rare-earth copper oxides exhibit superconductivity with relatively high Tc values [11]. In most polynuclear compounds, *d*-transition metal ions and Ln ions are bridged by multi-group ligands [12,13]. It may be noted, however, that structural studies of heterometallic Co–Ln complexes bridged by carboxylate groups are scarce, although a few other heteronuclear CoLn complexes have been reported [14,15]. The synthesis, crystal structure and magnetic properties of the title complex are reported in this article as part of our studies of heteronuclear complexes of rare earths and transition metals bridged by α-unsaturated carboxyl groups.

---

*Corresponding author.

ISSN 0095-8972 print: ISSN 1029-0389 online © 2003 Taylor & Francis Ltd
DOI: 10.1080/0095897031000065368

EXPERIMENTAL

Synthesis

$CeL_3 \cdot 2H_2O$ (860 mg, 2.0 mmol, $HL = CH_2C(CH_3)COOH$) and $Co(NO_3)_2 \cdot 6H_2O$ (350 mg, 1.2 mmol) were dissolved in 20 cm^3 of water and adjusted to pH 4.1 with HL (0.1 M). An ethanol solution (5 cm^3) of 1,10-phenanthroline (240 mg, 1.2 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 two weeks. C, H and N were analyzed using a Carlo-Erba 1110 instrument. Calculated: C, 48.00; H, 4.62; N, 3.29 %; Found: C, 47.95; H, 4.61; N, 3.36 %. Infrared spectra of the title complex were recorded with a Nicolet AVATAAR FT-IR Model 560 spectrophotometer (4000–400 cm^{-1}) in KBr pellets. IR : ν_{as} (COO) 1549, ν_s (COO) 1422, ν (C=C) 1647, ν (C–C, phen ring) 1516, ν (C–H, out of phen ring bend) 730 and 861 cm^{-1}.

Crystal Structure Determination

X-ray intensity data were collected on a Bruker CCD-APEX diffractometer up to a 2θ value of 56.62° with graphite-monochromatized MoKα radiation ($\lambda = 0.71073$ Å) by the $\omega - 2\theta$ scan technique. A total of 8058 independent reflections was collected, of which 5987 reflections were considered as observed [$I > 2.0\sigma(I)$] and used for the structure determination. Usual Lp and absorption corrections were applied. The structure was solved by direct methods. All non-H atoms were refined anisotropically by full-matrix least-squares methods. Some H atoms were located from a difference Fourier map and refined isotropically; others were geometrically fixed and allowed to ride on the parent carbon atoms. All calculations were performed using the SHELXTL/PC program package [16]. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* [17].

Downloaded At: 13:52 23 January 2011

Crystal Data

$C_{68}H_{78}N_4O_{22}Co_2Ce_2$, triclinic, $P\bar{1}$, $a = 12.0982(8)$, $b = 12.6068(9)$, $c = 14.4492(10)$ Å, $\alpha = 67.388(1)$, $\beta = 70.816(1)$, $\gamma = 64.480(1)°$, $V = 1800.4(2)$ Å^3, $D_c = 1.569$ g cm^{-3}, $Z = 1$, $R = 0.045$, $R_w = 0.078$, $(\Delta/\sigma)_{max} = 0.001$, $(\Delta\rho)_{max} = 1.0$, $(\Delta\rho)_{min} = -0.90$ e Å^{-3}.

RESULTS AND DISCUSSION

General Characterization

Published infrared data for ligands and unsaturated carboxylates [18] were used to assign the IR spectrum of the complex. A comparison of the spectrum of $CH_2C(CH_3)COOH$ with that of its complex reveals considerable changes due to coordination. A peak assigned to C=O at 1710 cm^{-1} in $CH_2C(CH_3)COOH$ disappears. Carboxyl groups give rise to very strong IR absorptions, which can be used to distinguish between different coordination modes [19,20]. Carboxyl group stretching was observed at 1549 cm^{-1} [ν_{as} (COO)] and 1422 cm^{-1} [ν_s (COO)]. Separation (127 cm^{-1}) is similar with that (131 cm^{-1}) reported previously [21]. The observed data are considered indicative of chelating and bridging carboxylato groups, there being no spectral criterion for distinguishing between them.

Description of the Crystal Structure

Figure 1 illustrates a perspective view of the complex showing the atom numbering scheme. Final atomic coordinates and equivalent isotropic displacement parameters for all non-H attoms are presented in Table I. Selected bond distances and angles are listed in Table II.

The complex crystallizes in the $P\bar{1}$ space group triclinic with one molecule in the unit cell. The structure consists of a centrosymmetic tetranuclear molecule. Co is coordinated by three oxygen atoms from three carboxyl groups and two nitrogen atoms from a 1,10-phenanthroline molecule. The coordination polyhedron is a slightly distorted pyramid. N1, O2, O3 and O6 occupy sites which define the square base of the pyramid, while N2 occupies its apex. Co is threefold bridged to Ce ion by μ_2-carboxylate groups, giving rise a dinuclear subunit with a Co$\cdots$Ce distance of 3.971 Å. A pair of centrosymmetrically related Ce ions in adjacent dinuclear CoCe subunits are linked together by a pair of μ_2-carboxylate groups with an intramolecular Ce$\cdots$Ce separation of 4.537 Å, resulting in the formation of a tetranuclear complex. Except for five atoms from five μ_2-carboxylate groups, the coordination sphere of each Ce ion is completed by one ethanol ligand and two atoms from a chelating carboxyl group to give eight-coordination. The coordination sphere around Ce forms an irregular polyhedron.

Magnetic Properties

Magnetic measurements were carried out with a Quantum Design model 6000 magnetometer using a DC field of 10 000 Oe. Temperature dependencies of magnetic susceptibilities were examined in the temperature range 5–300 K. Plots of $\chi_m T$ and

Downloaded At: 13:52 23 January 2011

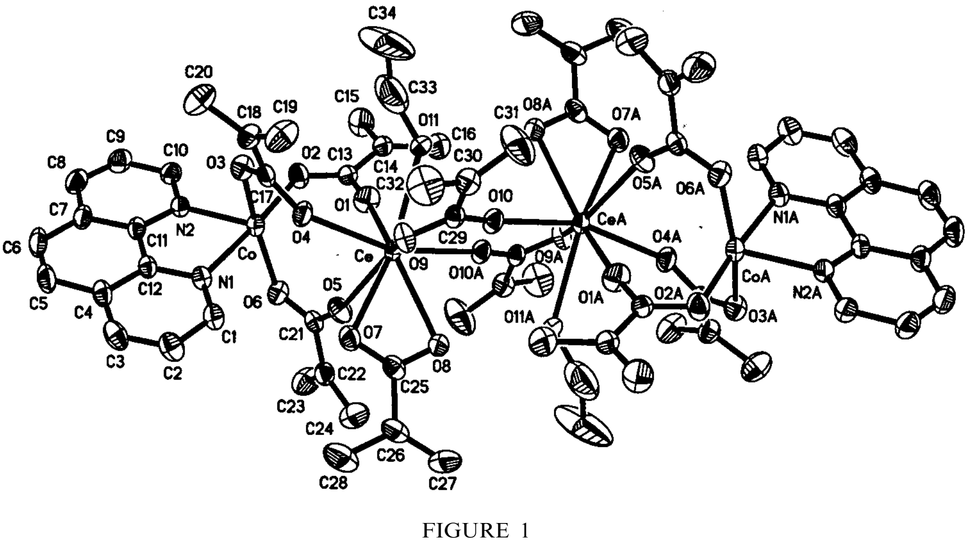


FIGURE 1

TABLE I Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for the complex

Atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}
Ce	4245(1)	5739(1)	1375(1)	36(1)
Co	2223(1)	8390(1)	2722(1)	42(1)
O(1)	2875(3)	7867(3)	849(3)	64(1)
O(2)	1790(3)	9525(3)	1356(2)	57(1)
O(3)	3943(3)	8523(3)	2402(2)	54(1)
O(4)	4812(3)	6626(3)	2263(2)	53(1)
O(5)	2233(3)	6069(3)	2611(2)	60(1)
O(6)	853(3)	7687(3)	3110(2)	54(1)
O(7)	4417(3)	4096(3)	3111(2)	54(1)
O(8)	4098(3)	3634(3)	1929(2)	54(1)
O(9)	6513(3)	4462(3)	1434(2)	54(1)
O(10)	6398(3)	4388(2)	−11(2)	49(1)
O(11)	5497(3)	6932(3)	−155(2)	55(1)
N(1)	2643(3)	7296(3)	4222(3)	46(1)
N(2)	1519(3)	9717(3)	3498(3)	41(1)
C(1)	3145(4)	6097(4)	4582(3)	52(1)
C(2)	3449(4)	5543(5)	5547(4)	62(1)
C(3)	3238(4)	6230(5)	6154(4)	63(1)
C(4)	2694(4)	7510(5)	5804(3)	52(1)
C(5)	2408(5)	8331(5)	6380(4)	66(2)
C(6)	1833(5)	9538(5)	6024(4)	68(2)
C(7)	1490(4)	10066(5)	5045(4)	53(1)
C(8)	877(4)	11320(5)	4621(4)	65(1)
C(9)	606(4)	11735(5)	3680(4)	64(1)
C(10)	955(4)	10905(4)	3129(4)	52(1)
C(11)	1795(4)	9301(4)	4436(3)	43(1)
C(12)	2394(4)	8007(4)	4828(3)	42(1)
C(13)	2197(4)	8969(4)	684(3)	43(1)
C(14)	1825(4)	9667(4)	−314(3)	50(1)
C(15)	1063(5)	10876(5)	−474(4)	79(2)
C(16)	2264(6)	9043(5)	−1077(4)	87(2)
C(17)	4879(4)	7583(4)	2296(3)	45(1)
C(18)	6128(4)	7597(4)	2229(4)	53(1)
C(19)	7167(5)	6700(5)	1946(4)	83(2)
C(20)	6152(5)	8604(5)	2458(5)	85(2)
C(21)	1169(4)	6647(4)	3001(3)	43(1)
C(22)	199(4)	6063(5)	3414(3)	53(1)
C(23)	−1002(5)	6736(5)	3653(4)	85(2)
C(24)	603(5)	4763(5)	3567(5)	97(2)
C(25)	4229(4)	3371(4)	2841(4)	49(1)
C(26)	4135(4)	2190(5)	3585(4)	59(1)
C(27)	4040(6)	1357(5)	3274(5)	103(2)
C(28)	4153(5)	1988(5)	4631(4)	95(2)
C(29)	7028(4)	4284(3)	584(3)	40(1)
C(30)	8403(4)	3990(4)	247(4)	51(1)
C(31)	8915(5)	4094(6)	−764(5)	110(2)
C(32)	9103(5)	3664(6)	992(5)	98(2)
C(33)	5652(8)	8074(8)	−397(5)	142(3)
C(34)	6720(10)	8393(12)	−765(6)	287(9)

$1/\chi_m$ *versus* T are presented in Fig. 2 with χ_m being the molar magnetic susceptibility corrected for diamagnetic contributions and T being the temperature.

Values of $\chi_m T$ decrease as temperature decreases from $6.10\,\text{emu K mol}^{-1}$ at 295 K to $3.72\,\text{emu K mol}^{-1}$ at 5 K. Plots of $1/\chi_m$ *versus* T follows the Curie–Weiss law with a Curie constant $C = 6.26\,\text{emu K mol}^{-1}$ and Weiss constant $\theta = -9.52\,\text{K}$, indicating an antiferromagnetic interaction. However, it is difficult to discern the nature of

Downloaded At: 13:52 23 January 2011

TABLE II Selected bond distance (Å) and angles (°) for the complex

Ce–O(1)	2.439(3)	Ce–O(4)	2.391(3)
Ce–O(5)	2.476(3)	Ce–O(7)	2.570(3)
Ce–O(8)	2.529(3)	Ce–O(9)	2.524(3)
Ce–O(10A)	2.423(3)	Ce–O(11)	2.578(3)
Co–O(2)	2.020(3)	Co–O(3)	2.045(3)
Co–O(6)	2.030(3)	Co–N(1)	2.163(3)
Co–N(2)	2.090(3)		
O(1)–Ce–O(4)	80.05(11)	O(1)–Ce–O(5)	70.27(11)
O(1)–Ce–O(7)	133.50(10)	O(1)–Ce–O(8)	137.31(10)
O(1)–Ce–O(9)	141.02(10)	O(1)–Ce–O(10A)	81.70(10)
O(1)–Ce–O(11)	71.60(11)	O(4)–Ce–O(5)	86.24(10)
O(4)–Ce–O(7)	78.32(10)	O(4)–Ce–O(8)	128.84(10)
O(4)–Ce–O(9)	76.03(10)	O(4)–Ce–O(10A)	157.85(10)
O(4)–Ce–O(11)	80.74(10)	O(5)–Ce–O(7)	67.68(10)
O(5)–Ce–O(8)	80.16(10)	O(5)–Ce–O(9)	136.92(10)
O(5)–Ce–O(10A)	99.31(10)	O(5)–Ce–O(11)	141.26(11)
O(7)–Ce–O(8)	50.85(9)	O(7)–Ce–O(9)	70.40(9)
O(7)–Ce–O(10A)	123.67(9)	O(7)–Ce–O(11)	142.45(10)
O(8)–Ce–O(9)	81.20(10)	O(8)–Ce–O(10A)	73.31(9)
O(8)–Ce–O(11)	135.27(9)	O(9)–Ce–O(10A)	111.87(9)
O(9)–Ce–O(11)	74.49(10)	O(10A)–Ce–O(11)	81.67(10)
O(2)–Co–O(3)	94.81(12)	O(2)–Co–O(6)	95.19(12)
O(2)–Co–N(1)	175.67(13)	O(2)–Co–N(2)	97.76(13)
O(3)–Co–O(6)	161.77(13)	O(3)–Co–N(1)	84.59(12)
O(3)–Co–N(2)	88.66(12)	O(6)–Co–N(1)	86.55(12)
O(6)–Co–N(2)	105.02(12)	N(2)–Co–N(1)	77.94(13)

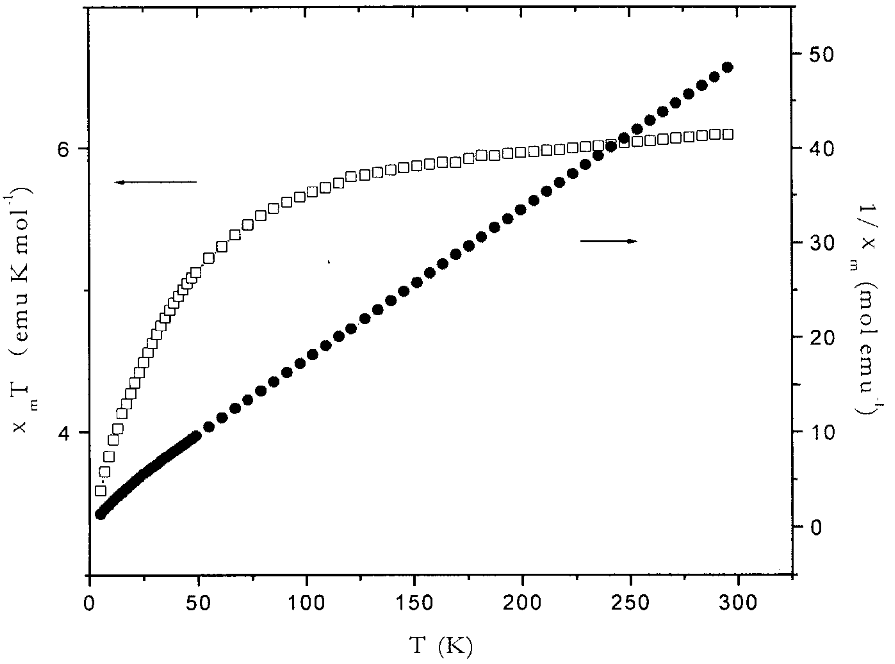


FIGURE 2 Plots of $\chi_m T$ and $1/\chi_m$ *versus* T for the complex.

Downloaded At: 13:52 23 January 2011

Co–Ce interaction because in the complex two different interactions may occur Co–Ce and Ce–Ce. Magnetic behaviour corresponds not only to Co–Ce interactions but also to overall properties of the molecule. Therefore, more detailed experiments are necessary to understand the details of the Co–Ce interaction.

Supplementary Material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 186184. Copies may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

References

[1] M. Andruk, I. Ramade, E. Codjovi, O. Guillou, O. Kahn and J.C. Trombe, *J. Am. Chem. Soc.* **115**, 1882 (1993).
[2] R. Georges, O. Kahn and O. Guillou, *Phys. Rev. B.* **49**, 3235 (1994).
[3] M. Andruh, F. Bakalbassis, O. Kahn, J.C. Trombe and P. Porcher, *Inorg. Chem.* **32**, 1616 (1993).
[4] C. Beaelli, A. Caneschi, D. Gatteschi, O. Guillou and L. Pardi, *J. Magn. Magn. Mater.* **83**, 522 (1990).
[5] C. Beaelli, A. Caneschi, D. Gatteschi, O. Guillou and L. Pardi, *Inorg. Chem.* **29**, 1750 (1990).
[6] X.M. Chen, M.S.J. Aubin, Y.L. Wu, Y.S. Yang, T.C.W. Mak and D.N. Hendrickson, *J. Am. Chem. Soc.* **117**, 9600 (1995).
[7] K.K. Abid and D.E. Fenton, *Inorg. Chim. Acta* **94**, 73 (1984).
[8] C. Benelli, A.J. Blake, P.E.Y. Milne, J.M. Rawson and R.E.P. Winpenny, *Chem-Eur. J.* **1**, 614 (1995).
[9] B. Yan, S.X. Wang and Z.D. Chen, *J. Coord. Chem.* **55**, 573 (2002).
[10] R. Blunt, *Chem. Br.* **19**, 740 (1983).
[11] D.L. Nelson, M.S. Wittingham and T.F. George, Chemistry of High-Temperature Superconductors, Eds.: ACS Symposium Series 351, (American Chemical Society, Washington, DC 1987).
[12] J.P. Costes, F. Dahan, A. Dupuis and J.P. Laurent, *Inorg. Chem.* **39**, 169 (2000).
[13] R. Baggio, M.T. Garland, Y. Moreno, O. Pena, M. Perec and E. Spodine, *J.C.S., Dalton Trans.* 2061 (2000).
[14] B.Q. Ma, S. Gao, O. Bai, H.L. Sun and G.X. Xu, *J.C.S., Dalton Trans.* 1003 (2000).
[15] Y. Cui, G. Chen, J. Ren, Y.T. Qian and J.S. Huang, *Inorg. Chem.* **39**, 4165 (2000).
[16] G.M. Sheldrick, SHELXTL 6.10. (Bruker AXS, Madison, WI, USA, 2000).
[17] International Tables for X-ray Crystallography, (Kynoch Press, Birmingham, 1974), Vol. IV.
[18] W.M. Lu, Z.P. Shao, J.P. Hu, X.Y. Luo and J.M. Gu, *J. Coord. Chem.* **40**, 145 (1996).
[19] Y.Q. Lu, W.M. Lu, B. Wu and L.N. Wang, *J. Coord. Chem.* **53**, 15 (2001).
[20] G.B. Deacon and R.J. Phillips, *Coord. Chem. Rev.* **33**, 227 (1980).
[21] B. Wu, W.M. Lu and X.M. Zheng, *J. Coord. Chem.* **55**, 497 (2002).

Downloaded At: 13:52 23 January 2011