

# Crystal Structure and Magnetic Properties of a Ce<sup>III</sup> – Cu<sup>II</sup> Heterodinuclear Complex

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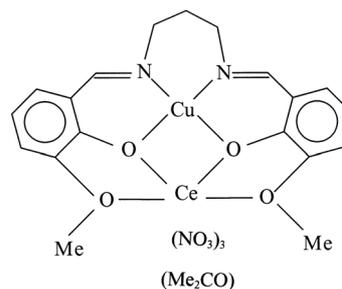
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Crystal structure and magnetic properties of a heterodinuclear complex, LCu(Me<sub>2</sub>CO)Ce(NO<sub>3</sub>)O<sub>3</sub> (L = (N,N'-propylene-bis(3-methoxysalicylideneimine))) are reported. (C<sub>19</sub>H<sub>22</sub>N<sub>2</sub>O<sub>4</sub>)Cu(C<sub>3</sub>H<sub>6</sub>O)Ce(NO<sub>3</sub>)<sub>3</sub>, monoclinic, space group *P*2<sub>1</sub>/*c*, with *a* = 9.8295(4), *b* = 19.049(3), *c* = 15.668(3) Å,  $\beta$  = 94.873(12)°, *V* = 2923.2(7) Å<sup>3</sup>, *Z* = 4. The central region of the complex is occupied by Cu<sup>II</sup> and Ce<sup>III</sup> ions which are bridged by two phenolato oxygen atoms of the ligand. The copper ion adopts a square-based 4+1 coordination made, the equatorial N<sub>2</sub>O<sub>2</sub> donors being afforded by the ligand while the axial position is occupied by an oxygen atom of the acetone molecule. The Ce<sup>III</sup> ion is deca-coordinated. In addition to the two phenolate oxygen atoms, the coordination sphere contains two oxygen atoms of the OMe side arms of L and six oxygen atoms from the three bidentate nitrate ions. The Ce...Cu separation is 3.601(2) Å and the dihedral angle between the CeO(2)Cu and CeO(3)Cu planes is 17.4(1)°. The magnetic susceptibility of the complex was measured over the range 5 – 350 K. The magnetic properties of the investigated compound are dominated by the crystal field effect on the Ce<sup>III</sup> site, masking the magnetic interaction between the paramagnetic centers.

**Key words:** Copper, Cerium, Crystal Structure, Heterodinuclear Complex, Magnetic Properties

## Introduction

In past two decades or so, a large number of heteropolymetallic compounds have been described. Molecular coordination compounds of lanthanide ions attract a growing interest in material science due to modeling of novel probes of biological interest [1] or in the preparation of new catalyst [2]. A special emphasis has been brought to the magnetic properties. In the field of molecular magnetism, their high magnetic moment together with their magnetic anisotropy are of particular interest. Coupled polynuclear systems containing 3*d* elements have been extensively investigated [3] but only relatively few hetero- binuclear and trinuclear complexes derived from Schiff's base reagents, that contain both 3*d* metal ions and either 4*f* or 5*f* ions have been reported [4]. In attempt to gain more information on the properties of lanthanide polynuclear complexes, we have now studied and investigated 3*d* – 4*f* complexes. In this paper, we present the synthesis and magnetic properties of the LCu(Me<sub>2</sub>CO)Ce(NO<sub>3</sub>)O<sub>3</sub> [L = (N,N'-propylene-bis(3-methoxysalicylideneimine))] complex.



## Experimental Section

### Preparation

The ligand was prepared by reaction of 1,3-diaminopropane (1 mmol) with 3-methoxysalicylaldehyde (2 mmol) in hot ethanol (100 ml). The yellow compound precipitated from solution on cooling. For the preparation of the monomeric copper(II) complex, LCu, to a hot ethanol solution (50 ml) of the ligand (1 mmol) a hot ethanol solution (10 ml) of copper(II) acetate monohydrate (1 mmol) was added dropwise. The mixture was stirred and then cooled to room temperature to give a purple precipitate which was collected by suction filtration and washed with cold ethanol and finally dried in air. For the preparation of the Cu-Ce complex,

Table 1. Crystallographic data.

Sum formula	C <sub>22</sub> H <sub>26</sub> CeCuN <sub>5</sub> O <sub>14</sub>
f <sub>w</sub> (g·mol <sup>-1</sup> )	788.13
Space group	P2 <sub>1</sub> /c
a = 9.8295(4) Å	
b = 19.049(3)	β = 94.873(12)°
c = 15.668(3)	
Vol [Å <sup>3</sup> ]	2923.2(7)
Z	4
D <sub>calc</sub> (g·cm <sup>-3</sup> )	1.791
μ [cm <sup>-1</sup> ]	2.340
F(000)	1568
Index ranges	0 ≤ h ≤ 12, 0 ≤ k ≤ 23, -19 ≤ l ≤ 19
Reflections collected	5931
Independent reflections	4560 [R(int) = 0.029]
Data / restraints / parameters	4310 / 0 / 389
Goodness-of-fit on F <sup>2</sup>	1.130
Final R indices [I > 2σ (I)]	R = 0.0408, wR = 0.1015
Final R indices for all data	R = 0.0640, wR = 0.1459
Largest diff. peak and hole	1.530 and -0.378 e · Å <sup>-3</sup>

an acetone solution (10 ml) of Ce(NO<sub>3</sub>)<sub>3</sub>·H<sub>2</sub>O (1 mmol) was added to a suspension of the copper(II) complex, LCu (1 mmol), in acetone (40 ml). Soon, the suspension became clear and red crystals began to precipitate, which were collected by suction filtration and washed with cold acetone and finally dried in air. C<sub>22</sub>H<sub>26</sub>N<sub>5</sub>O<sub>14</sub>CuCe (788.13): calcd. C 33.5, H 3.3, N 8.9, Cu 8.1, Ce 17.8; found: C 34.3, H 3.3, N 8.9, Cu 8.3, Ce 18.1.

#### X-ray structure determination

X-ray data collection was carried out on an Enraf-Nonius CAD-4 diffractometer [5] using a single crystal with dimension 0.10 × 0.15 × 0.25 mm<sup>3</sup> with a graphite monochromatized Mo-K<sub>α</sub> radiation (λ = 0.71073 Å). Experimental conditions are summarized in Table 1. Precise unit cell dimensions were determined by least-squares refinement on the setting angles of 25 reflections (2.10° ≤ θ ≤ 11.20°) carefully centered on the diffractometer. The standard reflections were measured every 7200 s and the orientation of the crystal was checked after every 600 reflections. Data reduction and corrections for absorption and decomposition were achieved using the Nonius Diffractometer Control Software [5]. The structure was solved by SHELXS-97 [6] and refined with SHELXL-97 [7]. All nonhydrogen atoms were treated anisotropically. The positions of the H atoms bonded to C atoms were calculated (C-H distance 0.96 Å), and refined using a riding model, and H atom displacement parameters were restricted to be 1.2 U<sub>eq</sub> of the parent atom. The final positional parameters are presented in Table 2. Selected bond lengths and angles are summarized in Table 3. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge

Table 2. Atomic coordinates and equivalent isotropic displacement parameters. All atoms lie on the Wyckoff position 4e.

Atom	x	y	z	U <sub>eq</sub>
Ce1	0.77882(6)	0.07401(3)	0.25309(3)	0.0554(2)
Cu1	0.70233(13)	0.24754(6)	0.17141(8)	0.0605(3)
N1	0.7502(11)	0.3424(5)	0.2161(7)	0.079(3)
N2	0.6001(10)	0.2803(5)	0.0656(6)	0.072(2)
N3	0.5052(12)	0.0872(6)	0.3181(8)	0.084(3)
N4	1.0486(10)	0.0456(5)	0.1850(7)	0.072(2)
N5	0.7677(11)	-0.0683(5)	0.3407(7)	0.075(2)
O1	0.9448(8)	0.1199(4)	0.3788(5)	0.070(2)
O2	0.8078(7)	0.2021(3)	0.2675(4)	0.061(2)
O3	0.6942(7)	0.1497(3)	0.1325(4)	0.061(2)
O4	0.7382(8)	0.0155(4)	0.1015(4)	0.067(2)
O5	0.5174(10)	0.0616(5)	0.2452(8)	0.097(3)
O6	0.6103(12)	0.1108(7)	0.3584(7)	0.117(4)
O7	0.3937(12)	0.0923(7)	0.3481(9)	0.121(4)
O8	0.9960(8)	0.0034(4)	0.2336(5)	0.077(2)
O9	0.9928(8)	0.1043(4)	0.1748(6)	0.081(2)
O10	1.1456(12)	0.0299(5)	0.1480(9)	0.125(4)
O11	0.7163(10)	-0.0588(4)	0.2665(6)	0.084(2)
O12	0.8111(12)	-0.0148(5)	0.3788(6)	0.104(3)
O13	0.7723(12)	-0.1256(5)	0.3745(7)	0.110(3)
O14	0.4760(9)	0.2455(5)	0.2450(6)	0.086(2)
C1	1.0529(16)	0.0788(6)	0.4226(10)	0.092(4)
C2	0.9371(10)	0.1890(6)	0.4013(6)	0.063(2)
C3	0.9922(13)	0.2181(7)	0.4777(7)	0.082(3)
C4	0.9816(13)	0.2882(7)	0.4935(9)	0.087(4)
C5	0.9241(12)	0.3309(6)	0.4327(9)	0.084(4)
C6	0.8656(11)	0.3054(6)	0.3529(7)	0.070(3)
C7	0.8662(9)	0.2323(5)	0.3387(6)	0.055(2)
C8	0.8101(12)	0.3539(6)	0.2893(9)	0.076(3)
C9	0.7071(28)	0.4085(8)	0.1691(14)	0.147(9)
C10	0.6589(30)	0.4031(10)	0.0840(16)	0.162(10)
C11	0.5510(18)	0.3540(8)	0.0561(10)	0.100(4)
C12	0.5706(12)	0.2417(6)	-0.0012(8)	0.075(3)
C13	0.5927(11)	0.1686(6)	-0.0115(6)	0.066(2)
C14	0.5550(13)	0.1393(7)	-0.0928(7)	0.079(3)
C15	0.5721(14)	0.0710(7)	-0.1081(7)	0.079(3)
C16	0.6347(11)	0.0273(6)	-0.0434(7)	0.069(2)
C17	0.6748(11)	0.0541(6)	0.0351(6)	0.062(2)
C18	0.6541(10)	0.1257(5)	0.0546(6)	0.060(2)
C19	0.7900(13)	-0.0523(6)	0.0793(8)	0.076(3)
C20	0.3586(12)	0.2299(6)	0.2260(8)	0.075(3)
C21	0.3191(15)	0.1939(8)	0.1431(10)	0.102(4)
C22	0.2463(16)	0.2465(10)	0.2818(13)	0.115(5)

Crystallographic Data Centre as supplementary publication no. CCDC 205953 [8].

#### Susceptibility measurements

Magnetic susceptibility data were collected on a powdered sample of the compound with use of a SQUID-based sample magnetometer on a QUANTUM Design Model MPMS instrument in the temperature range 5–350 K. Diamagnetic corrections of the molar magnetic susceptibility of the compound were applied using Pascal's constant [9]. The applied field was 10 KOe.

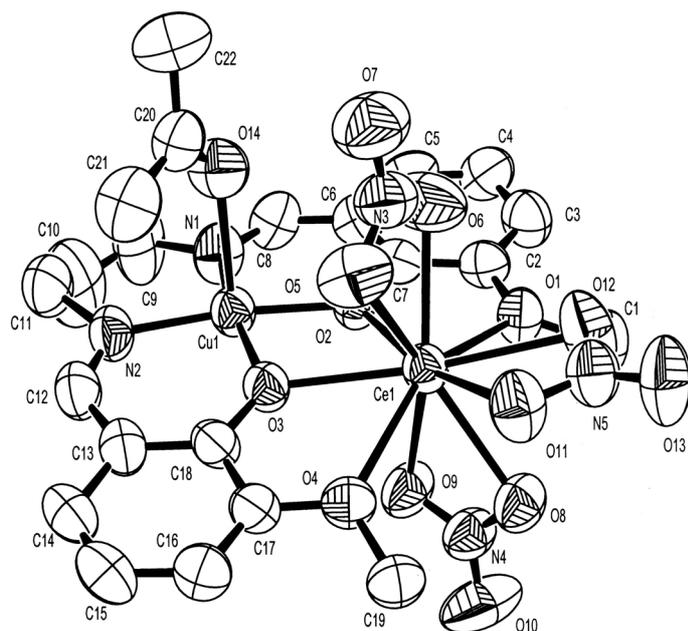


Fig. 1. View of the molecule (numbering of atoms corresponds to Table 2). Displacement ellipsoids are plotted at the 50% probability level and H atoms have been omitted for clarity.

Table 3. Selected bond lengths [Å] and angles [°].

Ce1 – O1	2.600(7)	Ce1 – O3	2.464(6)
Ce1 – O2	2.464(7)	Ce1 – O4	2.623(7)
Ce1 – O5	2.573(9)	Ce1 – O6	2.534(10)
Ce1 – O8	2.564(8)	Ce1 – O9	2.588(8)
Ce1 – O11	2.617(8)	Ce1 – O12	2.595(8)
Ce1 – N3	2.966(11)	Ce1 – N4	2.991(9)
Cu1 – O2	1.956(7)	Cu1 – O3	1.960(7)
Cu1 – N2	1.966(9)	Cu1 – N1	1.981(9)
Ce1 – O2 – Cu1	108.5(1)	Ce1 – O3 – Cu1	108.4(1)
O2 – Ce1 – O1	62.5(2)	O3 – Ce1 – O2	61.3(2)
O3 – Ce1 – O1	122.2(2)	N3 – Ce1 – N4	174.3(3)
O2 – Cu1 – O3	79.8(3)	N2 – Cu1 – N1	95.6(4)
O2 – Cu1 – N2	171.5(3)	O3 – Cu1 – N2	92.0(3)
O2 – Cu1 – N1	92.1(3)	O3 – Cu1 – N1	168.4(4)

## Results and Discussion

The unit cell contains four discrete Cu(Me<sub>2</sub>CO)Ce(NO<sub>3</sub>)O<sub>3</sub> entities. The ORTEP view [10] of the molecular structure is shown in Fig. 1. The central region is occupied by Cu<sup>II</sup> and Ce<sup>III</sup> ions which are bridged by two phenolato oxygen atoms of the ligand. The intramolecular Ce···Cu distance is 3.601(2) Å. This value is comparable with the values previously reported [11–14] for polynuclear Cu/Ce complexes from 3.288(2) to 3.607(1) Å. The dihedral angle between the CeO(2)Cu and CeO(3)Cu planes is 17.4(1)°.

The Cu<sup>II</sup> ion adopts a square-based 4+1 coordination mode, the equatorial N<sub>2</sub>O<sub>2</sub> donors being af-

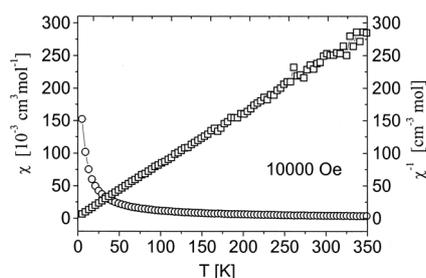


Fig. 2. Molar susceptibility and inverse susceptibility *versus* temperature.

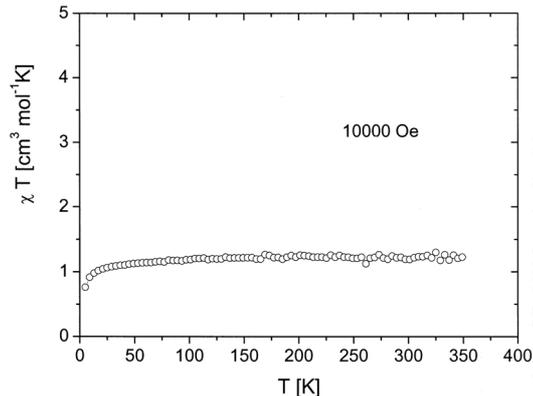


Fig. 3. Plot of  $\chi T$  *versus* temperature.

forded by the ligand while the axial position is occupied by an oxygen atom of the acetone molecule.

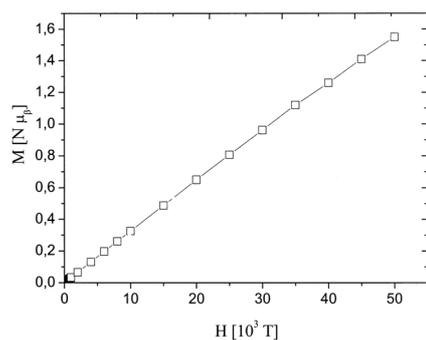


Fig. 4. The magnetization *versus* field.

The Cu<sup>II</sup> centre is 0.078 Å above the mean equatorial N<sub>2</sub>O<sub>2</sub> coordination plane. The Ce<sup>III</sup> ion is deca-coordinated. In addition to the two phenolate oxygen atoms, the coordination sphere contains two oxygen atoms of the OMe side arms of L and six oxygen atoms of the three bidentate nitrate ions. The range of the Ce-O bond lengths is rather large (from 1.956(7) to 2.617(8) Å) with significant differences between the phenolic, methoxy, and nitrate oxygen atoms. The shortest Ce-O bonds (1.956(7) Å) are related to the phenolic oxygen atoms while the largest bonds (2.617(8) Å) involve the methoxy oxygen atoms. The intermolecular distance between paramagnetic centers of neighbouring molecules is larger than 6 Å; the molecules can be considered as being magnetically isolated.

The magnetic susceptibilities and inverse susceptibility are shown as a function of temperature in Fig. 2. The major difficulties in analyzing the magnetic properties of the Ce<sup>III</sup> – Cu<sup>II</sup> couples arise from the fact that the ground state of the Ce<sup>III</sup> ion has a first-order angular momentum which prevents the use of a spin-

only Hamiltonian for isotropic exchange [15,16]. The joint effects of the crystal field and orbital contribution can result in an anisotropy of the magnetic susceptibility and exchange interaction. Informative magnetic susceptibility measurements have been performed for the investigated compound. As a general trend, for the complexes of the paramagnetic Ln<sup>III</sup> ions of the first half of the series the  $\chi T$  *versus* T curves are characterized by a continuous decrease as the temperature is lowered (Fig. 3). Kahn *et al.* [17] concluded that for the  $4f^1 - 4f^6$  configuration of Ln<sup>III</sup>, angular and spin momenta are antiparallel in  $^{2S+1}L_J$  free-ion ground state ( $\mathbf{J} = \mathbf{L} - \mathbf{S}$ ). A parallel alignment of the Cu<sup>II</sup> and Ln<sup>III</sup> spin momenta would lead to an antiparallel alignment of the angular momenta, that is to an overall antiferromagnetic interaction. Conversely, for the  $4f^8 - 4f^{13}$  configurations ( $\mathbf{J} = \mathbf{L} + \mathbf{S}$ ), a parallel alignment of the Cu<sup>II</sup> and Ln<sup>III</sup> spin momenta would result in an overall ferromagnetic interaction. Recently, an experimental approach has been developed to determine the nature of the magnetic interaction in Ln<sup>III</sup> – Cu<sup>II</sup> [4, 18]. It consists of comparing the magnetic properties of two series of isostructural compounds, one composed of Ln<sup>III</sup> – M pairs and the other of Ln<sup>III</sup> – M' pairs, M being a paramagnetic and M' a diamagnetic  $3d$  ion. This method was applied to infinite [18] and finite compounds [4]. Concerning the finite compounds, ferromagnetic interactions were observed for Ln = Gd, Tb, Dy, Ho and Er, and antiferromagnetic interactions observed for Ln = Ce, Nd, Sm, Tm and Yb. We measured also the variation of the magnetization ( $M$ ) at 5 K as a function of the field ( $H$ ) up to 50 KOe. The field dependence of the magnetization at 5 K (Fig. 4) shows that saturation is not completely reached in the maximum field available (50 KOe).

- [1] J.-C. Bünzli, G.R. Choppin, Lanthanide in life, chemical and earth sciences. Theory and practice, Elsevier Science Publishers, London, NY (1989).
- [2] A. Roigk, R. Hettich, H. Schneider, *Inorg. Chem.* **37**, 751 (1998).
- [3] O. Kahn, *Inorg. Chim. Acta* **62**, 3 (1982).
- [4] J.-P. Costes, F. Dahan, A. Dupuis, J.-P. Laurent, *Chem. Eur. J.* **4**, 9 (1998).
- [5] Enraf-Nonius diffractometer control software, Release 5.1., Enraf-Nonius, Delft, Netherlands (1993).
- [6] G.M. Sheldrick, SHELXS-97, Program for the solution of crystal structures, University of Göttingen, Germany (1997).
- [7] G.M. Sheldrick, SHELXL-97, Program for the refinement of crystal structures, University of Göttingen, Germany (1997).
- [8] Further information may be obtained from: Cambridge Crystallographic Data Center (CCDC), 12 Union Road, Cambridge CB21EZ, UK, by quoting the depository number CCDC 205953. E-mail: deposit@ccdc.cam.ac.uk.
- [9] A. Weiss, H. Witte, *Magnetochemie*, Verlag Chemie, Weinheim (1973).
- [10] L.J. Farrugia, ORTEPIII. *J. Appl. Crystallogr.* **30**, 565 (1997).

- [11] D. W. Harrison, J.-C. Bünzli, *Inorg. Chim. Acta* **109**, 185 (1985).
- [12] J.-P. Costes, F. Dahan, A. Dupuis, *Inorg. Chem.* **39**, 5994 (2000).
- [13] J.-P. Costes, F. Dahan, A. Dupuis, J.-P. Laurent, *New J. Chem.* 1525 (1998).
- [14] M. L. Kahn, T.M. Rajendiran, Y. Jeannin, C. Mathonière, O. Kahn, *C.R. Acad. Sci. Paris, Séries IIc* **3**, 131 (2000).
- [15] A. Furrer, H. U. Güdel, E. R. Krausz, H. Blank, *Phys. Rev. Lett.* **64**, 68 (1990), and references therein.
- [16] H. Lueken, P. Hannibal, K. Handrick, *J. Chem. Phys.* **143**, 151 (1990), and references therein.
- [17] M. Andruh, I. Ramade, E. Codjovi, O. Guillou, O. Kahn, J.C. Trombe, *J. Am. Chem. Soc.* **115**, 1822 (1993).
- [18] M. L. Kahn, C. Mathonière, O. Kahn, *Inorg. Chem.* **38**, 3692 (1999).