

# Crystal Structure and Magnetic Property of Heteronuclear Copper-Lanthanum Carboxylate Complex

WU, Bin(吴斌) LU, Wei-Min\*(陆维敏) ZHENG, Xiao-Ming(郑小明)

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

The title complex,  $[\text{CuLaL}_5(\text{phen})(\text{C}_2\text{H}_5\text{OH})]_2$  (where L =  $\alpha$ -methylacrylate; phen = 1,10-phenanthroline), has been prepared and its structure has been determined by X-ray diffraction analysis. The complex crystallizes in triclinic system with space group  $P\bar{1}$ . Crystal data:  $a = 1.2725(3)$  nm,  $b = 1.4421(4)$  nm,  $c = 1.2109(2)$  nm,  $\alpha = 109.48(2)^\circ$ ,  $\beta = 115.26(2)^\circ$ ,  $\gamma = 66.42(2)^\circ$ . The complex is a discrete tetranuclear CuLaLaCu molecule bridged by  $\alpha$ -methylacrylate groups. Magnetic property of the complex was also measured and discussed.

**Keywords** copper, lanthanum, heteronuclear, crystal structure, magnetic property

## Introduction

Since the reports of heteronuclear CuLn and NiLn complexes (Ln = lanthanide) by Chisari<sup>1</sup> and Abid<sup>2</sup> in 1984, a number of heteronuclear complexes comprising transition metal ions and lanthanide ions have been studied owing to their electronic, electrochemical and magnetic properties arising from the metal-metal interaction.<sup>3-6</sup> The Cu and Ln are bridged by multigroup ligands in most of complexes<sup>7,8</sup> and the reported Ln<sub>2</sub>M<sub>2</sub> cluster cores are relatively rare.<sup>9,10</sup> In this paper the synthesis, crystal structure and magnetic property of the title complex are reported.

## Experimental

### *Synthesis and elemental analysis*

LaL<sub>3</sub>·2H<sub>2</sub>O (860 mg, 2.0 mmol; HL = CH<sub>2</sub>C(CH<sub>3</sub>)-

COOH) and Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (242 mg, 1.0 mmol) were dissolved into 20 mL of H<sub>2</sub>O and adjusted to pH 4.1 with HL (0.1 mmol/cm<sup>3</sup>). An ethanol solution of 1, 10-phenanthroline (200 mg, 1.0 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 in 60% yield.

C, H and N were analyzed using a Carlo-Erba 1110 elemental analyzer, and La and Cu were analyzed by titration with EDTA. Anal. calcd for C<sub>34</sub>H<sub>39</sub>N<sub>2</sub>O<sub>11</sub>CuLa: C 47.81, H 4.60, N 3.28, La 16.26, Cu 7.44; found C 47.69, H 4.64, N 3.27, La 16.20, Cu 7.39.

### *Infrared spectrum*

Infrared spectrum of the title complex was measured with a Nicolet AVATAAR FT-IR Model 560 spectrophotometer (4000—400 cm<sup>-1</sup>) in KBr pellets. IR spectra:  $\nu_{\text{as}}(\text{COO})$  1550,  $\nu_{\text{s}}(\text{COO})$  1419,  $\nu(\text{C}=\text{C})$  1648,  $\nu(\text{C}-\text{C}, \text{phen ring})$  1520,  $\nu(\text{C}-\text{H}, \text{out of phen ring bend})$  726 and 847 cm<sup>-1</sup>.

### *Crystal structure determination*

A prismatic crystal of the title complex with approximate dimensions 0.30 nm × 0.20 nm × 0.20 mm was mounted on a glass fiber. X-Ray intensity data were collected on a Rigaku AFC7R diffractometer up to a  $2\theta$  value of 55.0° with graphite-monochromatized Mo K $\alpha$  radiation ( $\lambda = 0.071069$  nm) by the  $\omega$ - $2\theta$  scan technique. A total of 7972 independent reflections was collected, of which

\* E-mail: cuihua@dial.zju.edu.cn

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5829 reflections were considered as observed and used for the structure determination. Usual  $L_p$  and adsorption corrections were applied.

The structure was solved by the Patterson method followed by Fourier syntheses. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation.<sup>11</sup> Structure refinement was carried out by full-matrix least-squares procedures. H atoms were located in a difference Fourier map, and coordinates and thermal parameters were fixed during structure refinement. Anisotropic refinement including all the non-H atoms converged to agreement factors  $R = 0.032$  and  $R_w = 0.038$ , where  $w = 1/\sigma^2(F)$ . Atomic scattering factors were taken from international tables for X-ray crystallography. In the complex the enclosed  $C_2H_5OH$  coordinated molecule is disordered, and the occupation factors of C(33) and C(33') are 50% and 50%, respectively. Crystal parameters and refinement results are summarized in Table 1.

#### Magnetic property measurement

Magnetic measurements were carried out with a Quantum Design model 6000 magnetometer using a dc field of 1000 Oe. The molar magnetic susceptibilities were corrected for the diamagnetic contribution.

## Results and discussion

#### General characterization

The carboxyl groups give rise to very strong IR absorptions,<sup>12</sup> which can be used to distinguish between the

different coordination modes of the ligands (*i. e.* ionic, monodentate or bidentate) by comparison of the band separation with that of the corresponding sodium compound.<sup>13</sup> Separation ( $131\text{ cm}^{-1}$ ) between  $\nu_{as}(\text{COO})$  and  $\nu_s(\text{COO})$ , which is smaller than the value of  $146\text{ cm}^{-1}$  for the sodium salt, is indicative of bidentate coordination. However, spectroscopic technique could not correctly identify bridging bidentate and chelating bidentate.

#### Description of the crystal structure

Final atomic coordinates and equivalent temperature factors for non-hydrogen atoms are given in Table 2. Selected bond distances and angles are listed in Table 3. Fig. 1 shows ORTEP diagrams of the molecular structure.

X-Ray analysis revealed that the complex consists of a discrete tetranuclear  $\text{CuLaLaCu}$  molecule as coordination of phen ligands to Cu ions prevents the formation of net structure. The complex crystallizes in triclinic system with space group  $P\bar{1}$  in which symmetric center places between two La atoms. The Cu and La ions are bridged by three carboxylate groups with di- $\mu$ -mode. The La and La\* ions are linked by two carboxylate groups with the same mode. Each lanthanum metal center is coordinated by eight O atoms from five bridging bidentate, one chelating bidentate carboxyl groups and one ethanol molecule. The coordination sphere around La is a distorted square antiprism. Each Cu ion is five-coordinated by three O atoms from three bridging carboxyl groups and two N atoms from a phen group. The coordination polyhedron of Cu ion is a slightly distorted pyramid. The N(1), O(1), O(5) and O(3) atoms form the square face of pyramid. The N(2) atom occupies the vertex of the pyramid.

Table 1 Crystallographic data for the title complex

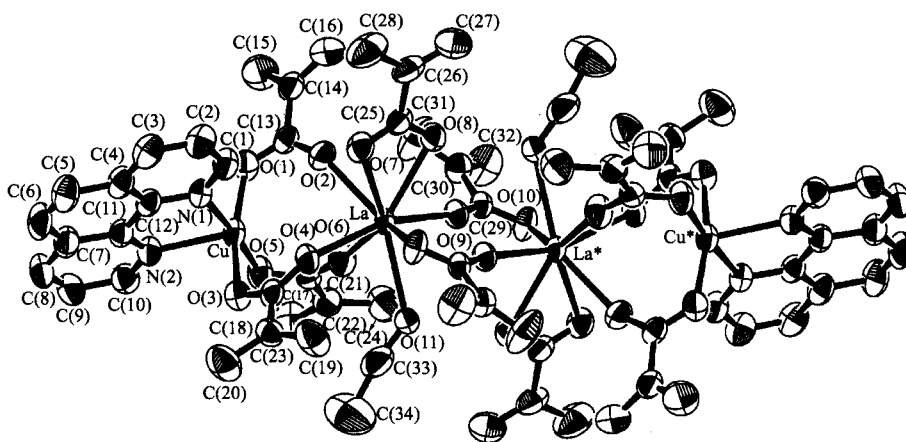
Chemical formula	$C_{34}H_{39}N_2O_{11}CuLa$	$Z$	2
Crystal system	triclinic	$\theta_{max}(\text{°})$	27.5
Space group	$P\bar{1}$	$T(\text{K})$	293
$a(\text{nm})$	1.2725(3)	Total reflections	7927
$b(\text{nm})$	1.4421(4)	Unique reflections	7552
$c(\text{nm})$	1.2109(2)	Reflections with $I > 3.0\sigma(I)$	5829
$\alpha(\text{°})$	109.48(2)	$R$ values	$R = 0.032, R_w = 0.038$
$\beta(\text{°})$	115.26(2)	Maximum shift ( $\Delta/\sigma$ )	0.02
$\gamma(\text{°})$	66.42(2)	Goodness-of-fit	1.30
$V(\text{nm}^3)$	1.8060(9)	Residual ( $e \times 10^3 \text{ nm}^{-3}$ )	0.58 to -0.52
$D_c(\text{g} \cdot \text{cm}^{-3})$	1.571		

**Table 2** Fractional coordinates and equivalent isotropic displacement parameters ( $\text{nm}^2$ ) for non-hydrogen atoms

Atom	$x/a$	$y/b$	$z/c$	$U_{\text{eq}}$
La	0.07143(2)	0.13523(2)	0.07273(2)	0.000368
Cu	0.33086(4)	0.27381(4)	0.27399(5)	0.000444
O(1)	0.2670(3)	0.3086(2)	0.4103(3)	0.000549
O(2)	0.1032(3)	0.2614(2)	0.2762(3)	0.000572
O(3)	0.3533(3)	0.2354(2)	0.1079(3)	0.000544
O(4)	0.1646(3)	0.2255(2)	0.0209(3)	0.000514
O(5)	0.4361(3)	0.1397(2)	0.3134(3)	0.000569
O(6)	0.2825(3)	0.0741(2)	0.2108(3)	0.000627
O(7)	-0.0949(3)	0.3152(2)	0.0596(3)	0.000568
O(8)	-0.1390(3)	0.1954(2)	0.0913(3)	0.000567
O(9)	0.0583(2)	-0.0039(2)	0.1365(2)	0.000461
O(10)	0.0534(3)	-0.1477(2)	0.1556(3)	0.000543
O(11)	0.1954(3)	-0.0189(2)	-0.0562(3)	0.000568
N(1)	0.2348(3)	0.4181(3)	0.2384(3)	0.000467
N(2)	0.4785(3)	0.3477(3)	0.3508(3)	0.000492
C(1)	0.1150(4)	0.4529(3)	0.1879(4)	0.000550
C(2)	0.0548(4)	0.5505(4)	0.1560(5)	0.000641
C(3)	0.1227(5)	0.6124(3)	0.1751(4)	0.000636
C(4)	0.2495(5)	0.5776(3)	0.2295(4)	0.000575
C(5)	0.3264(5)	0.6377(4)	0.2555(5)	0.000702
C(6)	0.4469(6)	0.6036(4)	0.3135(5)	0.000749
C(7)	0.5047(5)	0.5047(4)	0.3489(4)	0.000595
C(8)	0.6309(5)	0.4645(4)	0.4112(5)	0.000719
C(9)	0.6757(4)	0.3689(4)	0.4383(5)	0.000679
C(10)	0.5958(4)	0.3120(4)	0.4059(4)	0.000594
C(11)	0.4324(4)	0.4420(3)	0.3210(4)	0.000469
C(12)	0.3025(4)	0.4793(3)	0.2607(4)	0.000456
C(13)	0.1641(4)	0.2996(3)	0.3828(4)	0.000464
C(14)	0.1078(4)	0.3400(3)	0.4824(4)	0.000559
C(15)	0.1802(6)	0.3600(5)	0.6026(5)	0.000883
C(16)	-0.0198(6)	0.3581(5)	0.4479(6)	0.000946
C(17)	0.2604(4)	0.2263(3)	0.0144(4)	0.000465
C(18)	0.2641(4)	0.2182(4)	-0.1099(4)	0.000551
C(19)	0.1757(5)	0.1864(5)	-0.2156(5)	0.000867
C(20)	0.3611(6)	0.2416(5)	-0.1117(5)	0.000883
C(21)	0.3907(4)	0.0673(3)	0.2785(4)	0.000451
C(22)	0.4705(4)	-0.0315(3)	0.3217(4)	0.000542
C(23)	0.5886(5)	-0.0390(4)	0.3956(5)	0.000779
C(24)	0.4155(5)	-0.1123(4)	0.2856(6)	0.000841
C(25)	-0.1653(4)	0.2869(3)	0.0784(4)	0.000488
C(26)	-0.2850(4)	0.3614(4)	0.0890(4)	0.000646
C(27)	-0.3658(5)	0.3279(5)	0.0980(7)	0.001068
C(28)	-0.3061(5)	0.4666(5)	0.0874(6)	0.001017
C(29)	0.0699(3)	-0.0620(3)	0.2026(3)	0.000393
C(30)	0.0989(4)	-0.0244(3)	0.3410(4)	0.000516
C(31)	0.0901(7)	0.0778(5)	0.3895(5)	0.001055
C(32)	0.1295(6)	-0.0970(5)	0.4137(5)	0.000888
C(33)	0.303(1)	-0.0394(8)	-0.064(1)	0.000793
C(33')	0.295(2)	-0.084(1)	-0.199(2)	0.00144(6)
C(34)	0.4072(8)	-0.0653(6)	-0.110(1)	0.001518

**Table 3** Selected bond distances (nm) and bond angles ( $^{\circ}$ ) for the complex

La—O(2)	0.2508(3)	La—O(4)	0.2431(3)
La—O(6)	0.2459(3)	La—O(7)	0.2614(3)
La—O(8)	0.2550(3)	La—O(9)	0.2462(3)
La—O(10)	0.2561(3)	La—O(11)	0.2617(3)
Cu—O(1)	0.1977(3)	Cu—O(3)	0.2013(3)
Cu—O(5)	0.1939(3)	Cu—N(1)	0.2030(3)
Cu—N(2)	0.2232(3)	O(1)—C(13)	0.1255(5)
O(2)—C(13)	0.1258(5)	O(3)—C(17)	0.1257(5)
O(4)—C(17)	0.1260(5)	O(5)—C(21)	0.1257(5)
O(6)—C(21)	0.1249(5)	O(7)—C(25)	0.1245(5)
O(8)—C(25)	0.1272(5)	O(9)—C(29)	0.1269(4)
O(10)—C(29)	0.1238(4)	C(14)—C(15)	0.1356(7)
C(18)—C(19)	0.1381(7)	C(22)—C(23)	0.1362(6)
C(26)—C(27)	0.1353(8)	C(30)—C(31)	0.1370(7)
O(2)-La-O(4)	84.8(1)	O(2)-La-O(6)	71.0(1)
O(2)-La-O(7)	66.9(1)	O(2)-La-O(8)	79.5(1)
O(2)-La-O(9)	99.7(1)	O(2)-La-O(10)	135.45(9)
O(2)-La-O(11)	140.7(1)	O(4)-La-O(6)	81.1(1)
O(4)-La-O(7)	78.9(1)	O(4)-La-O(8)	129.2(1)
O(4)-La-O(9)	157.38(9)	O(4)-La-O(10)	75.51(9)
O(4)-La-O(11)	79.61(9)	O(6)-La-O(7)	134.5(1)
O(6)-La-O(8)	135.5(1)	O(6)-La-O(9)	79.6(1)
O(6)-La-O(10)	141.2(1)	O(6)-La-O(11)	71.1(1)
O(7)-La-O(8)	50.48(9)	O(7)-La-O(9)	123.36(9)
O(7)-La-O(10)	70.2(1)	O(7)-La-O(11)	142.3(1)
O(8)-La-O(9)	73.35(9)	O(8)-La-O(10)	82.8(1)
O(8)-La-O(11)	137.14(9)	O(9)-La-O(10)	113.74(9)
O(9)-La-O(11)	83.13(9)	O(10)-La-O(11)	74.6(1)
O(1)-Cu-O(3)	165.4(1)	O(1)-Cu-O(5)	92.5(1)
O(1)-Cu-N(1)	89.4(1)	O(1)-Cu-N(2)	105.4(1)
O(3)-Cu-O(5)	92.1(1)	O(3)-Cu-N(1)	87.3(1)
O(3)-Cu-N(2)	87.9(1)	O(5)-Cu-N(1)	174.7(1)
O(5)-Cu-N(2)	96.2(1)	N(1)-Cu-N(2)	78.5(1)

**Fig. 1** Molecular structure and atom-numbering scheme for the title complex (displacement ellipsoids are shown at the 40% probability level. H atoms and C(33') atom are omitted for clarity).

The carboxyl groups in the title complex serve as chelating or bridging bidentate ligands. The average bond lengths of La—O<sub>chelating</sub> and Ln—O<sub>bridging</sub> are 0.2582 and 0.2484 nm, respectively. The former is longer than the later because there is ring strain in four-membered ring [La, O(7), C(25), O(8)]. The bond length of La—O<sub>ethanol</sub> is 0.2617 nm and is significantly longer than that of any other La—O. The distances of three Cu—O bonds are similar at 0.1977(3), 0.2013(3) and 0.1939(3) nm, respectively, and the average bond length of Cu—N is 0.2131 nm. It is noteworthy that the bond lengths of C—O in three bridging carboxyl groups between Cu and La are not obviously different (from 0.1248 to 0.1260 nm), indicating the delocalization of  $\pi$ -electronic density of carbonyl groups occurs in the carboxyl groups (COO<sup>-</sup>). The separation (0.44695 nm) of La $\cdots$ La\* (symmetric atom of La; symmetric code:  $-x, -y, -z$ ) in the complex is significantly longer than that (0.40456 nm) in [La(CH<sub>2</sub>C(CH<sub>3</sub>)COO)<sub>3</sub>(phen)(HL)]<sub>2</sub><sup>14</sup> in which there are four bridging carboxylate groups between La ions. The separation of Cu $\cdots$ La in the complex is 0.39994 nm, exceeds the sum of the two ionic radius.

### Magnetic properties

The temperature dependences of magnetic susceptibilities for the complex was examined in the temperature range of 5–250 K. The plot of  $\chi_m T$  and  $1/\chi_m$  versus  $T$  for the complex is presented in Fig. 2.

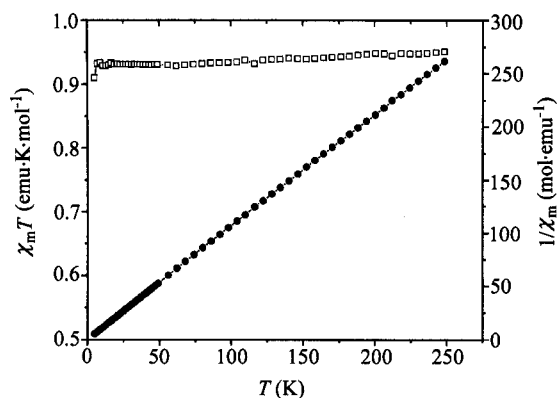


Fig. 2 Plot of  $\chi_m T$  and  $1/\chi_m$  vs.  $T$  for title complex.

The results show that  $\chi_m T$  decreases very slowly from 250 K down to 5 K ( $\chi_m T = 0.91$ – $0.95$  emu·K·mol<sup>-1</sup>). This high temperature value corresponds to that expected for two non-interacting  $S = 1/2$  spins belonging

to the copper(II) ions and no contribution is expected from two lanthanum ions. The value of  $\chi_m T = 0.95$  emu·K·mol<sup>-1</sup> allows us to calculate a magnetic moment of  $1.95 \mu_B$  per copper atom. The plot of  $1/\chi_m$  vs.  $T$  highly follows the Curie-Weiss law with the Weiss constant  $\theta = -0.82$  K, indicating a weak anti-ferromagnetic interaction. Since the closest interatomic Cu $\cdots$ Cu distance is greater than 0.7 nm, the possibility of an exchange between the copper centers is little, and weak anti-ferromagnetic interaction should be attributed to weak lattice interactions.

### Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 154806 for the title complex. Copies of the information 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).

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