研究简报

镧 - 锌杂多核配合物的合成和晶体结构

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Synthesis and Crystal Structure of Heteronuclear La (Ⅲ) -Zn (Ⅱ) Complex

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A new heteronuclear complex, $[LaZnL_5(C_2H_5OH)(phen)]_2$ (HL = α-methylacrylic acid, phen = 1, 10-phenanthroline), was synthesized and characterized by elemental analysis, infrared absorption spectra (IR) and single crystal X-ray diffraction analysis. The complex crystallizes in space group $P\bar{1}$ with the cell dimensions $a = 12.614(3)$, $b = 14.485(4)$, $c = 12.148(2)$ Å, $\alpha = 109.68(2)$, $\beta = 115.65(1)$, $\gamma = 66.87(2)°$. The complex molecule is a discrete tetranuclear molecule bridging by α-methylacrylate groups.

Keywords: lanthanum zinc heteronuclear crystal structure

0 Introduction

Heteronuclear complexes have received much attention owing to their electronic, electrochemical and magnetic properties arising from the metal-metal interaction[1], mimicking of the active centers of some metalloenzymes, for example, copper-zinc superoxide dismutase[2], cytochrome oxidase[3], hydrogenase[4], etc. Until now many polynuclear complexes containing both rare earth and transition metal ions have been synthesized and studied, these transition metals contain Co[5], Ni[6], Cu[7], Fe[8], Mn[9] and Pd[10]. In contrast, the investigations for Ln-Zn system have rarely been reported[11]. Here, a new heteronuclear complex, $[LaZnL_5(C_2H_5OH)(phen)]_2$ (HL = α-methylacrylic acid, phen = 1, 10-phenanthroline), in which the La ion and Zn ion were bridged by α-methylacrylate are reported.

1 Experimental

1.1 Synthesis

$LaL_3 \cdot 2H_2O$ (2.0mmol; HL = $CH_2C(CH_3)COOH$; 860 mg) and $Zn(NO_3)_2 \cdot 6H_2O$ (300 mg, 1.0 mmol) were dissolved into 20mL aqueous and adjusted pH = 4.1 with HL (0.1mmol · L^{-1}), 5mL ethanol solution of 1, 10-phenanthroline (200mg, 1.0mmol) was added into the mixed solution with the stirring. After filtration, the filtrate was allowed to stand at room temper-

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ature and single crystals suitable for X-ray work were obtained after two weeks. Yield was about 60% according to calculation of 1, 10-phenanthroline.

1.2 Elemental Analysis

$[LaZnL_5(C_2H_5OH)(phen)]_2$: $C_{68}H_{78}O_{22}N_4La_2Zn_2$, calculated C 47.71, H 4.59, N 3.27%; found C 47.69, H 4.64, N 3.15%.

1.3 Infrared Spectra

Infrared spectra of the complex were recorded with a spectrophotometer (4000 ~ 400cm^{-1}) using a powered sample spread on a KBr plate. IR spectra: ν_{as}(COO) 1556, ν_s(COO) 1425, ν(C=C) 1649, ν(C-H, out of phen ring bend) 728 and 853cm^{-1}.

1.4 Crystal Structure Determination

X-ray intensity data were collected on a Rigaku AFC7R diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71069$Å) by the ω-2θ scan technique. Usual Lp and adsorption corrections were applied.

The structure was solved by the Patterson method followed by Fourier syntheses. Structure refinement was carried out by full-matrix least-squares procedures using the TEXSAN program package[12]. 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 $R = 0.031$ and $R_w = 0.039$, where $w = 1/\sigma^2(F)$. Atomic scattering factors were taken from International Tables for X-ray Crystallography[13]. Crystal data collection and refinement parameters are summarized in Table 1.

Table 1 Crystal Data, Data Collection and Refinement Parameters for the La-Zn Complex

chemical formula	$C_{68}H_{78}N_4O_{22}La_2Zn_2$
crystal system	triclinic
space group	$P\bar{1}$
a/Å	12.614(3)
b/Å	14.485(4)
c/Å	12.148(2)
α/(°)	109.68(2)
β/(°)	115.65(1)
γ/(°)	66.87(2)
V/Å^3	1802.4(8)
D_c/(g · cm^{-3})	1.577
Z	1
F(000)	864.00
$2\theta_{max}$/(°)	55.0
T/K	293
total reflections	8663
unique reflections	8285
reflections with $I > 3.0\sigma(I)$	6758
No. of variables	451
R values	$R = 0.031$, $R_w = 0.039$
maximum shift (Δ/σ)	0.07
goodness-of-fit	1.33
residual max in final difference map/(e · Å^{-3})	0.53 to −0.62

2 Results and Discussion

2.1 Crystal Structure

Selected bond distances and angles are listed Table 2 for the complex. Fig. 1 shows ORTEP diagram

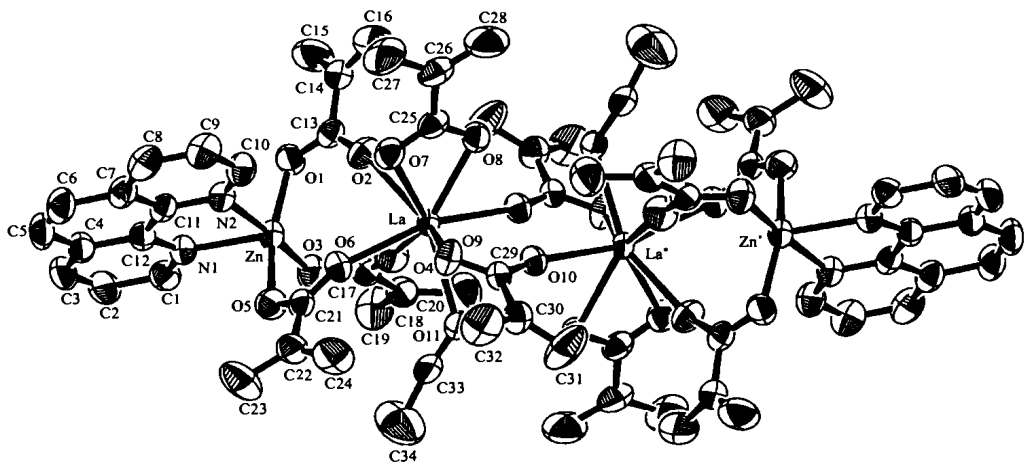

Fig. 1 Molecular structure and atom-numbering scheme for La-Zn complex. displacement ellipsoids are shown at the 30% probability level and H atoms have been omitted for clarity

Table 2　Selected Bond Distances(Å) and Bond Angles(°) for the La-Zn Complex

bond distances					
La-O(2)	2.499(3)	La-O(4)	2.478(3)	La-O(6)	2.427(2)
La-O(7)	2.612(3)	La-O(8)	2.546(3)	La-O(9)	2.562(3)
La-O(10)	2.459(2)	La-O(11)	2.605(3)	Zn-O(1)	2.025(3)
Zn-O(3)	2.029(3)	Zn-O(5)	2.051(3)	Zn-N(1)	2.110(3)
Zn-N(2)	2.201(3)	O(1)-C(13)	1.259(4)	O(2)-C(13)	1.249(4)
O(3)-C(17)	1.258(4)	O(4)-C(17)	1.246(4)	O(5)-C(21)	1.256(4)
O(6)-C(21)	1.254(4)	O(7)-C(25)	1.247(5)	O(8)-C(25)	1.271(4)
O(9)-C(29)	1.243(4)	O(10)-C(29)	1.267(4)	O(11)-C(33)	1.33(1)
bond angles					
O(2)-La-O(4)	70.09(9)	O(2)-La-O(6)	84.99(9)	O(2)-La-O(7)	67.13(9)
O(2)-La-O(8)	79.53(9)	O(2)-La-O(9)	135.45(9)	O(2)-La-O(10)	100.34(9)
O(2)-La-O(11)	140.76(9)	O(4)-La-O(6)	79.59(9)	O(4)-La-O(7)	133.19(9)
O(4)-La-O(8)	136.4(1)	O(4)-La-O(9)	140.6(1)	O(4)-La-O(10)	82.26(9)
O(4)-La-O(11)	71.55(9)	O(6)-La-O(7)	78.67(9)	O(6)-La-O(8)	128.85(9)
O(6)-La-O(9)	75.08(9)	O(6)-La-O(10)	158.05(8)	O(6)-La-O(11)	80.33(8)
O(7)-La-O(8)	50.36(8)	O(7)-La-O(9)	70.05(9)	O(7)-La-O(10)	123.09(8)
O(7)-La-O(11)	142.60(9)	O(8)-La-O(9)	82.76(9)	O(8)-La-O(10)	73.09(8)
O(8)-La-O(11)	136.76(8)	O(9)-La-O(10)	113.00(8)	O(9)-La-O(11)	74.82(9)
O(10)-La-O(11)	82.29(8)	O(1)-Zn-O(3)	93.9(1)	O(1)-Zn-O(5)	161.4(1)
O(1)-Zn-N(1)	105.7(1)	O(1)-Zn-N(2)	88.1(1)	O(3)-Zn-O(5)	93.6(1)
O(3)-Zn-N(1)	98.1(1)	O(3)-Zn-N(2)	175.6(1)	O(5)-Zn-N(1)	90.1(1)
O(5)-Zn-N(2)	85.8(1)	N(1)-Zn-N(2)	77.6(1)		

of the molecular structures with the numbering scheme for the complex.

As shown in Fig. 1, the La-Zn complex consists of a discrete tetranuclear ZnLaLaZn molecule. The complex crystallizes in triclinic system with space group $P\bar{1}$. Zn and La ions are bridged by three carboxylate groups with di-μ-model. La ion and La* ion are linked by two carboxylate groups with the same model. 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 Zn 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 Zn ion is a slightly distorted pyramid. The N2, O1, O5, O3 atoms form the square face of pyramid. The N1 atom occupies the peak of pyramid.

As the same with most case, the carboxyl groups in the title complex serve as chelating or bridging bidentate ligands. The average bond lengths of $La\text{-}O_{chelating}$ and $Ln\text{-}O_{bridging}$ are 2.579 and 2.485Å, respectively. The former is longer than the later because there is ring strain in four-membered (La, O7, C25, O8). The distances of three Zn-O bonds are similar at 2.025(3), 2.029(3) and 2.051(3) Å, respectively, and the average bond lengths of Zn-N are 2.156Å. The separation of La···La* in the complex is 4.4997(7) Å which is nearly the same with that (4.0456Å) in the complex of $[La(CH_2C(CH_3)COO)_3(phen)(HL)]_2$[14] in which there are four bridging carboxylate groups between La ions. The neighboring La···Zn separation is 4.0102(8) Å and exceeds the sum of corresponding ionic radii.

2.2　IR Spectra

The carboxyl groups give rise to very strong IR absorptions, which can be used to distinguish between the different coordination modes of the ligands (i.e. ionic, monodentate or bidentate)[15]. The stretching vibration of the carboxyl group was observed at 1556cm^{-1} [ν_{asym}(COO)] and 1425cm^{-1} [ν_{sym}(COO)] in the complex. Separation(131cm^{-1}) between ν_{asym}(COO) and ν_{sym}(COO) which are smaller than the value of 146cm^{-1} for the sodium salt is indicative of bidentate coordination. However, spectroscopic technique could not correctly identify bridging bidentate

and chelating bidentate.

3 Supplementary Material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 155111 for the complex; Copies of this 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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