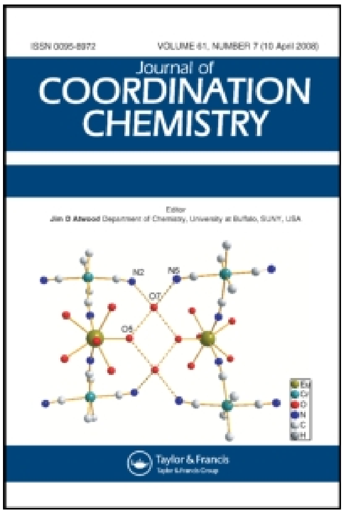

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Preparation and crystal structure of a heteronuclear yttrium and copper complex with *n*-carboxymethyl-*n*-(2-carboxyphenyl)glycine(h_3l): $[cuy(l)(h_2o)_6](clo_4)_2$

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PREPARATION AND CRYSTAL STRUCTURE OF A HETERONUCLEAR YTTRIUM AND COPPER COMPLEX WITH *N*-CARBOXYMETHYL-*N*-(2-CARBOXYPHENYL)GLYCINE(H_3L): $[CuY(L)(H_2O)_6](ClO_4)_2$

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The title complex $[CuY(L)(H_2O)_6](ClO_4)_2$ was synthesized in aqueous solution, where L^{3-} is *N*-carboxymethyl-*N*-(2-carboxyphenyl) glycine anion, and its crystal structure determined by single-crystal X-ray diffraction methods. Crystals are monoclinic, space group $P2_1/n$, with a = 17.514(2), b = 8.221(1), c = 17.874(2)Å, β = 112.170(10)°, V = 2383.3(5)Å^3, Z = 4; the final R value is 0.031. The complex has a two-dimensional network structure in which each yttrium is coordinated by three oxygen atoms from three L^{3-} ions and five oxygen atoms from water molecules forming a distorted square antiprism; the copper ion is coordinated by three carboxyl oxygen atoms and a nitrogen atom from the same L^{3-} ion and an oxygen atom of water molecule to form a distorted square pyramid.

Keywords: crystal structure; yttrium; copper; *N*-Carboxymethyl-*N*-(2-carboxyphenyl)glycine

INTRODUCTION

N-Carboxymethyl-*N*-(2-carboxyphenyl)glycine (H_3L) is an unusual glycine derivative. The crystal structures of lanthanide complexes with glycine have been investigated. [1-3] Studies of metal complexes with H_3L in aqueous solution

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have determined thermodynamic stability constants. Complexes of lanthanides with H_3L are more stable than those with glycine. [4-7] However, the crystal structures of lanthanide complexes with H_3L have not been reported. In this paper, a heteronuclear yttrium and copper complex with H_3L is reported, its crystal structure being determined by X-ray analysis.

EXPERIMENTAL

Preparation

The ligand (H_3L) was synthesized according to the literature. [8] The title complex was prepared by mixing $Y(ClO_4)_3$ (1.0 mmol) and $Cu(ClO_4)_2$ (0.5 mmol) in an aqueous solution of H_3L (0.5 mmol) at pH 2. Blue crystals were obtained by slow evaporation of the aqueous solution at room temperature (yield 70%). The composition was deduced from ICP and elemental analysis. Found (%): Y, 12.1; Cu, 8.65; N, 2.07; C, 18.61; H, 2.96. Calc. for $[CuY(L)(H_2O)_6](ClO_4)_2$: Y, 12.5; Cu, 8.95; N, 1.97; C, 18.60; H, 2.84; this formula is consistent with the results of diffraction analysis.

IR Spectra

IR spectra of the complex and ligand were obtained using KBr pellets at 295K using a Nicolet Magna IR 750 spectrophotometer. Compared with the free ligand, the ν_s(coo) band at 1410 cm^{-1} of the complex is shifted by 13 cm^{-1} to higher wave numbers; the ν_{as}(coo) band at 1556 cm^{-1} of the complex is shifted 17 cm^{-1} to lower wave numbers. This shows that the carboxyl groups of the ligand are coordinated with the metal ions. [9] A broad absorption band for ν(OH) at 3405 cm^{-1} indicates the presence of water molecules in the crystal.

Crystal Structure Measurement

A blue crystal of the complex with dimensions 0.57 × 0.46 × 0.37 mm was mounted in a thin-walled capillary for the structure determination. Intensity data were collected on a Siemens P4 diffractometer with MoKα radiation in the ω-scan mode. Lattice parameters were obtained from a least-squares refinement of 40 reflections in the range $6.99° \leq 2\theta \leq 38.81°$ and 4632 independent reflections were collected, of which 2967 reflections with $F > 4\sigma(F)$ were used to refine the structure.

Empirical absorption corrections were applied using the XPRED program. [10] All calculations were performed in the Siemens SHELXTL/PC system. The

TABLE I Crystal data for $[CuY(L)(H_2O)_6](ClO_4)_2$.

Empirical formula	$C_{11}H_{20}Cl_2CuNO_{20}Y$
Molecular weight	709.63
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	17.514(2)
b (Å)	8.221(1)
c (Å)	17.874(2)
β (°)	112.17(1)
V (Å^3)	2383.3(5)
Z	4
Dc (g/cm^3)	1.978
Absorption coefficient (mm^{-1})	3.633
F(000)	1420
λ(MoKα) (Å)	0.71073
Scan type	ω
2θ range (°)	3-52
Scan speed (deg min^{-1})	7
Range h; k; l	0-12; 0-10; −22-20
Reflections collected	5142
Independent reflections	4632 [R(int) = 0.0235]
Observed reflections	2967 [$F > 4.0\sigma(F)$)]
Absorption correction	Semi-empirical
Hydrogen atoms	Difference Fourier
Number of parameters refined	406
Final R	0.031
R_w	0.071

structure was determined by direct methods and difference-Fourier syntheses and then refined by full-matrix least-squares to $R = \Sigma|F_o| - |F_c|/\Sigma|F_o| = 0.031$ and $R_w = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2} = 0.071$. Crystal data, detail of data collection and refinement are listed in Table I. Non-hydrogen atomic parameters are given in Table II. Tables of H atom positions thermal parameter and observed and calculated structure factors are available from the authors.

RESULTS AND DISCUSSION

The molecular structure of the title complex and the coordination polyhedra are shown in Figures 1 and 2, respectively. Bondlengths and angles are given in Tables III and IV. In the complex, each Y^{3+} ion is coordinated by three carboxyl oxygen {O(2), O(4B), O(6A)} atoms from the different three L^{3-} ions and five oxygen {O(12), O(13), O(14), O(15), O(16)} atoms of water molecules. The eight coordinating oxygen atoms form a distorted square antiprism (Figure 2 and Table V). The O(6A), O(14), O(12), and O(15) atoms lie approximately in a

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for non-hydrogen atoms.

Atom	*x/a*	*y/b*	*z/c*	*U(eq)**
Y	4585(1)	−839(1)	1695(1)	21(1)
Cu	7153(1)	3914(1)	3355(1)	24(1)
Cl(1)	8397(1)	10100(2)	4511(1)	39(1)
Cl(2)	3567(1)	3812(2)	3134(1)	49(1)
O(1)	6206(3)	2555(5)	2797(2)	34(1)
O(2)	5275(3)	749(5)	2786(3)	44(1)
O(3)	6501(3)	6231(5)	2798(3)	38(1)
O(4)	5327(3)	7420(5)	2704(3)	42(1)
O(5)	8185(2)	4703(5)	4162(2)	31(1)
O(6)	8706(3)	5779(5)	5379(2)	40(1)
O(7)	7651(4)	3636(7)	2552(3)	46(1)
O(8)	7927(4)	10990(7)	3817(3)	82(2)
O(9)	8990(5)	11182(10)	5035(4)	114(3)
O(10)	7944(4)	9494(8)	4940(4)	91(2)
O(11)	8850(5)	8888(8)	4323(4)	111(3)
O(12)	3718(3)	−455(7)	2416(3)	53(1)
O(13)	5128(4)	−2740(7)	1029(3)	57(1)
O(14)	4008(4)	1870(6)	1356(3)	53(1)
O(15)	3686(3)	−3143(6)	1520(3)	53(1)
O(16)	5556(3)	578(6)	1346(3)	51(1)
O(17)	2986(5)	2913(20)	3116(9)	318(11)
O(18)	3284(12)	5228(13)	2891(7)	293(10)
O(19)	4112(6)	3813(19)	3884(7)	226(7)
O(20)	3990(8)	3595(21)	2713(10)	308(10)
N	6647(3)	4563(5)	4161(3)	23(1)
C(1)	5846(4)	1684(7)	3160(3)	30(1)
C(2)	6098(4)	1777(7)	4054(3)	29(1)
C(3)	5918(5)	398(9)	4412(5)	44(2)
C(4)	6165(6)	277(11)	5241(5)	62(3)
C(5)	6613(6)	1528(10)	5724(4)	61(2)
C(6)	6770(5)	2934(9)	5374(4)	43(2)
C(7)	6508(3)	3070(7)	4545(3)	24(1)
C(8)	5857(4)	5415(8)	3707(4)	27(1)
C(9)	5910(4)	6450(7)	3013(3)	28(1)
C(10)	7246(4)	5719(8)	4711(4)	28(1)
C(11)	8119(4)	5353(7)	4769(3)	26(1)

*Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

plane (plane 1); the O(2), O(4B), O(13) and O(16) atoms make up plane 2. Distances between the Y^{3+} ion and two planes are 1.318 Å and 1.202 Å, respectively. The dihedral angle between the two planes is 1.4°. Copper is coordinated by three carboxyl oxygen {O(1), O(3), and O(5)} atoms and a nitrogen (N) atom all from the same L^{3-} ion and an oxygen atom {O(7)} of a water molecule, forming a distorted square pyramid coordination polyhedron

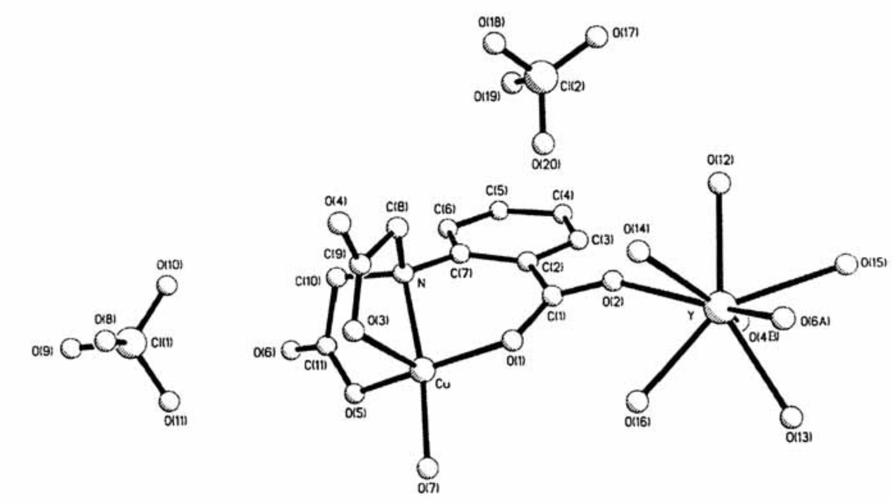

FIGURE 1 Crystal structure of $[CuY(L)(H_2O)_6](ClO_4)_2$ showing atom labelling scheme.

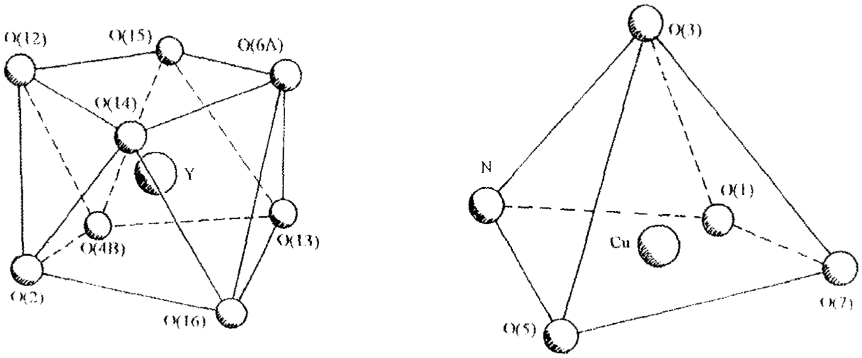

FIGURE 2 Coordination polyhedra of Y^{3+} and Cu^{2+} in $[CuY(L)(H_2O)_6](ClO_4)_2$.

(Figure 2 and Table V). N, O(1), O(7), O(5) atoms and Cu^{2+} ion lie in the basal plane (plane 3) of the square pyramid.

Each Y^{3+} ion is connected with three Cu^{2+} ions through three carboxyl groups, and each Cu^{2+} ion is also connected with three Y^{3+} ions by three carboxyl bridges. The three Cu^{2+} ions, three Y^{3+} ions and six carboxyl bridges (three atoms each) form a large ring. Three such rings are connected two-dimensionally by the metal centres to form a planar structure. Cu^{2+} and Y^{3+} ions are located at the intersection of three rings. Between the layers lie perchlorate anions and these

TABLE III Selected bond lengths (Å).

Y-O(2)	2.277(4)	Y-O(16)	2.333(5)
Y-O(4)B	2.284(4)	Cu-O(1)	1.934(4)
Y-O(6)A	2.274(4)	Cu-O(3)	2.251(4)
Y-O(12)	2.354(5)	Cu-O(5)	1.950(4)
Y-O(13)	2.371(5)	Cu-O(7)	1.954(5)
Y-O(14)	2.426(5)	Cu-N	2.028(4)
Y-O(15)	2.407(5)		

TABLE IV Selected bond angles (°)[†]

O(2)-Y-O(4)B	74.0(2)	O(12)-Y-O(14)	73.7(2)
O(2)-Y-O(6)A	143.7(2)	O(12)-Y-O(15)	69.6(2)
O(2)-Y-O(12)	72.4(2)	O(12)-Y-O(16)	140.0(2)
O(2)-Y-O(13)	128.6(2)	O(13)-Y-O(14)	133.5(2)
O(2)-Y-O(14)	74.0(2)	O(13)-Y-O(15)	77.4(2)
O(2)-Y-O(15)	132.2(2)	O(13)-Y-O(16)	73.9(2)
O(2)-Y-O(16)	74.8(2)	O(14)-Y-O(15)	120.0(2)
O(4)B-Y-O(6)A	142.3(2)	O(14)-Y-O(16)	75.6(2)
O(4)B-Y-O(12)	86.8(2)	O(15)-Y-O(16)	149.9(2)
O(4)B-Y-O(13)	76.5(2)	O(1)-Cu-O(3)	93.9(2)
O(4)B-Y-O(14)	146.3(2)	O(1)-Cu-O(5)	161.5(2)
O(4)B-Y-O(15)	76.1(2)	O(1)-Cu-O(7)	95.0(2)
O(4)B-Y-O(16)	105.6(2)	O(1)-Cu-N	89.9(2)
O(6)-Y-O(12)	103.8(2)	O(3)-Cu-O(5)	102.7(2)
O(6)-Y-O(13)	74.8(2)	O(3)-Cu-O(7)	93.8(2)
O(6)A-Y-O(14)	70.5(2)	O(3)-Cu-N	78.8(2)
O(6)A-Y-O(15)	74.2(2)	O(5)-Cu-O(7)	92.1(2)
O(6)A-Y-O(16)	89.4(2)	O(5)-Cu-N	85.3(2)
O(12)-Y-O(13)	145.8(2)	O(7)-Cu-N	171.4(2)

[†] Symmetry operation: A = $x - 1/2$, $-y + 1/2$, $z - 1/2$; B = x, $y - 1$, z; C = x, $y + 1$, z; D = $x + 1/2$, $-y + 1/2$, $z + 1/2$.

TABLE V Least-squares equations of planes containing coplanar atoms.

Plane 1	Equation	16.061 X − 1.031 Y + 0.080 Z = 6.1464				
Atoms		O(12)	O(14)	O(15)	O(6A)	Y
P*[¶] (Å)		−0.1080	0.1082	0.1096	−0.1099	1.3175
Plane 2	Equation	15.926 X − 0.947 Y + 0.486 Z = 8.6649				
Atoms		O(2)	O(13)	O(16)	O(4B)	Y
P*[¶] (Å)		−0.2000	−0.1894	0.1945	0.1949	−1.2016
Plane 3	Equation	−3.521 X + 7.123 Y − 6.211 Z = −1.8953				
Atoms		O(1)	O(5)	O(7)	N	Cu
P*[¶] (Å)		−0.2071	−0.2208	0.2069	0.2210	0.0813

[¶] P* is the distance of the atom from the plane.

form strong H-bonds which hold the layers together. The structure is analogous to the graphite structure.

Comparing the structure of the title complex $[CuY(L)(H_2O)_6](ClO_4)_2$ with the glycine complex $[CuY(Gly)_5(H_2O)_2](ClO_4)_5 \cdot H_2O$, [3] we note some differences: the glycine complex is a one dimensional chain complex of infinite length; the average bond length Y-O (COO) in former is shorter, (Y-O(H_3L) = 2.278 Å, Y-O(Gly) = 2.304 Å). The results indicate that the coordination ability of the H_3L ligand is stronger than glycine.

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