

## Crystal and Molecular Structure of a Copper(II)–Glycinehydroxamic Acid Complex

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### Abstract

Crystals of *trans*-bis(glycinehydroxamato)copper(II) dihydrate ( $\text{CuC}_4\text{H}_{10}\text{N}_4\text{O}_4 \cdot 2\text{H}_2\text{O}$ ) were obtained by mixing concentrated solutions of copper(II) perchlorate and glycinehydroxamic acid ( $\text{H}_2\text{NCH}_2\text{-CONHOH}$ ) in a 1:2 molar ratio and adjusting the pH to about 8. X-ray crystallographic data show the crystals to be orthorhombic: *Pbca*,  $a = 5.052(3)$ ,  $b = 11.152(2)$ ,  $c = 17.876(2)$  Å,  $V = 1007$  Å<sup>3</sup>,  $Z = 4$ . The copper ion lies on an inversion center, in which it is octahedrally coordinated by four nitrogens and two oxygens from neighboring molecules. IR spectra of the complex confirm these crystallographic results. The ESR powder and dilute solution spectra are characteristic of axial symmetry with respectively  $g_{\parallel} = 2.198$ ,  $g_{\perp} = 2.083$  and  $g_{\parallel} = 2.196$ ,  $g_{\perp} = 2.055$  and  $A_{\parallel}^{\text{Cu}} = 202$  gauss,  $A_{\perp}^{\text{Cu}} = 30.2$  gauss and  $A_{\parallel}^{\text{N}} = 15$  gauss.

### Introduction

The coordination chemistry of transition metal hydroxamates has received considerable attention recently [1–5] due to their important role in biological systems [6, 7] and potential usefulness in both human and veterinary medicine [8, 9].

Hydroxamic acids are important as analytical reagents [10] and naturally occurring compounds containing the  $-\text{CON}(\text{OH})-$  group can act as growth factors, cell division agents, tumor inhibitors, antibiotics and antibiotic antagonists [6].

A range of hydroxamic acids has been investigated as sequestering agents for the treatment of iron overload [8] and some ferric monohydroxamates, such as ferric glycinehydroxamato, are proposed as a source of iron in animal therapy for iron deficiency [9].

Solution equilibria of glycinehydroxamic acid ( $\text{HL} = \text{H}_2\text{NCH}_2\text{CONHOH}$ ) with iron(III) [9], nickel(II) [11] and copper(II) [3] ions were studied and the stability constants determined by potentiometric methods.

In the solid state, the X-ray crystal structure of square-planar *trans*-bis(glycinehydroxamato)nickel(II) [12] was found to be the first example of coordination of a transition metal by a hydroxamic acid via the nitrogen atom of the NHOH group. Recently, the structure of another square-planar nickel(II) complex with this ligand, a monosodium salt formed in basic medium, was reported [13]. The coordination of the central atom is again by the nitrogen atom of the hydroxamate group, but it has a *cis* configuration and three water molecules are present.

We now report the crystal structure of the copper(II) complex of glycinehydroxamic acid formed in neutral medium, in which the metal is also coordinated via the N atom of the (NHOH) group. In this case, however, the metal ion has a distorted octahedral structure, in which the nitrogens of amino groups and the oxygen of carbonyl groups in adjacent molecules complete the coordination around the copper ion [14].

Also, the hydrogen-bonding system in the copper complex is more complex due to the presence of two water molecules. Besides intermolecular hydrogen bonds, adjacent ligand molecules are held together by metal–carbonyl interactions, an aspect which is not observed in the structures of the nickel complexes.

### Experimental

#### Complex Preparation

The species distribution [3] for the copper(II)–HL system shows that  $\text{CuL}_2$  reaches almost 100% of total copper content at pH 8 for a metal–ligand ratio of 1:2, being the predominant species in the pH range 7–9. Using this metal–ligand relation, the solid complex was isolated as violet crystals from aqueous solution.

*trans*-Bis(glycinehydroxamato)copper(II) dihydrate preparation was carried out by adding 0.370 g (0.1 mmol) of copper(II) perchlorate hexahydrate dissolved in a minimum amount of water to an aqueous solution of HL prepared by dissolving

0.18 g (0.2 mmol) of HL in acidic medium. The pH of the solution was adjusted to 8 by adding sodium hydroxide. The solution was left at room temperature and after 12 h bright violet crystals were separated and dried under vacuum over calcium chloride. Yield: 50%.

#### X-ray Crystallography

A single crystal with approximate dimensions  $0.300 \times 0.125 \times 0.100$  mm was used for crystal data determination and intensity data collection using an Enraf-Nonius CAD-4 automated diffractometer, room temperature,  $\theta < 25.0^\circ$ ,  $\theta-2\theta$  scan mode, graphite monochromated Mo K $\alpha$  radiation Lp and absorption corrections applied. 1912 reflections were collected of which 787 were unique and 558 considered observed ( $I > 3\sigma(I)$ )  $R_i = 0.0465$ . The structure was solved by Patterson and difference Fourier methods. The atomic parameters, except for the hydrogens, were refined by a full-matrix least-squares method by minimization of  $\sum w(K[F_o] - [F_c])^2$ , where  $w = 1.813/(\sigma^2(F_o) + 0.0008 F_o^2)$  for observed and  $w = 0$  for unobserved reflections, until all atomic parameter shifts were smaller than their standard deviations. The final  $R$  factors were:  $R_{obs} = 0.0480$ , weighted  $R_w = 0.0481$ . Anisotropic temperature factors were assigned to all non-hydrogen atoms and isotropic temperature factors, assumed to be 3.9, to all hydrogens. Neutral complex atomic scattering factors were taken from International Tables for X-ray Crystallography. All computer calculations were performed using SHELX-79, except data reduction for which the Enraf-Nonius structure determination package was used.

#### IR Spectroscopy

Infrared spectra were recorded in the 4000–200  $\text{cm}^{-1}$  range with a 283B Perkin-Elmer spectrophotometer. Samples were prepared as KBr pellets and nujol mulls. The deuterated ligand and its copper(II) and nickel(II) complexes were prepared by recrystallization from heavy water.

#### ESR Spectroscopy

ESR spectra were measured at X-band (9.5 GHz) in a Varian E-9 series spectrometer. The powder spectrum was measured at room temperature and the solution spectrum at  $-150^\circ\text{C}$ . Amplitude modulation was 1.0 gauss, microwave power 10 mW and the field scan range was 1.0 K gauss centered at 3200 gauss. The  $g$ -values were obtained using a standard DPPH sample ( $g = 2.0036$ ).

## Results and Discussion

#### X-ray Crystallography

Table I gives the atomic positional and equivalent temperature parameters for all non-hydrogen atoms.

TABLE I. Fractional Atomic Coordinates and Equivalent Isotropic Temperature Factors with Estimated Standard Deviations in Parentheses

Atom	$x/a$	$y/b$	$z/c$	$B_{iso}$
Cu	0.5000(0)	0.0000(0)	0.5000(0)	2.08(5)
C(1)	0.195(2)	-0.006(1)	0.3642(5)	2.5(3)
C(2)	0.074(2)	-0.0923(9)	0.4178(6)	1.8(3)
N(1)	0.388(2)	0.0735(8)	0.4020(5)	2.3(3)
N(2)	0.213(2)	-0.1072(7)	0.4772(5)	2.0(3)
O(1)	-0.146(1)	-0.1401(7)	0.4021(5)	3.5(3)
O(2)	0.087(1)	-0.1858(6)	0.5300(4)	2.5(2)
OW	-0.229(2)	-0.2815(7)	0.2812(5)	3.9(3)

TABLE II. Intramolecular Bond Distances (Å) and Angles ( $^\circ$ ) with Standard Deviations in Parentheses

Atoms A–B–C	Bonds (Å)		Angles ( $^\circ$ )
	A–B	B–C	
N(2)–Cu–N(1)	1.923(8)	2.015(9)	81.7(3)
C(1)–N(1)–Cu	1.480(14)	2.015(9)	109.7(6)
C(2)–N(2)–Cu	1.285(13)	1.923(8)	120.5(7)
O(2)–N(2)–Cu	1.436(11)	1.923(8)	125.1(6)
O(2)–N(2)–C(2)	1.436(11)	1.285(13)	112.3(7)
C(2)–C(1)–N(1)	1.489(15)	1.480(14)	111.4(8)
C(1)–C(2)–N(2)	1.489(15)	1.285(13)	112.9(8)
O(1)–C(2)–N(2)	1.263(11)	1.285(13)	127.7(1.0)
O(1)–C(2)–C(1)	1.263(11)	1.489(15)	119.4(9)
HO(2)–O(2)–N(2)	0.771(7)	1.436(11)	95.5(7)
HOW–OW–H'OW	0.975(8)	1.085(8)	112.8(7)
HN(1)–N(1)–Cu	0.975(9)	2.015(9)	130.8(7)
HN(1)–N(1)–C(1)	0.975(9)	1.480(14)	110.2(8)
H'N(1)–N(1)–Cu	0.861(8)	2.015(9)	101.2(8)
H'N(1)–N(1)–C(1)	0.861(8)	1.480(14)	115.2(9)
H'N(1)–N(1)–HN(1)	0.861(8)	0.975(9)	86.2(7)
HC(1)–C(1)–N(1)	1.081(10)	1.480(14)	138.3(1.2)
HC(1)–C(1)–C(2)	1.081(10)	1.489(15)	94.0(8)
H'C(1)–C(1)–N(1)	1.066(11)	1.480(14)	75.2(8)
H'C(1)–C(1)–C(2)	1.066(11)	1.489(15)	173.5(1.0)
H'C(1)–C(1)–HC(1)	1.066(11)	1.081(10)	80.5(7)
N(1)–Cu–N'(1)	2.015(9)	2.015(9)	180.0 <sup>a</sup>
N(2)–Cu–N'(2)	1.923(9)	1.923(8)	180.0 <sup>a</sup>

<sup>a</sup>Not refined due to symmetry relation.

The copper ion lies on an inversion center and is octahedrally coordinated by four nitrogens of the amino and hydroxamate groups and two oxygens of carbonyl groups from neighboring molecules. These nitrogens and the copper ion are coplanar, with very similar N–Cu distances of 1.923(8) and 2.015(9) Å, while the oxygens are axial, with larger Cu–O distances of 2.950(8) Å. The carbonyl oxygens are *trans* relative to copper. All important interatomic distances and angles are given in Table II. The Cu–N distances are similar to the ones found in the litera-

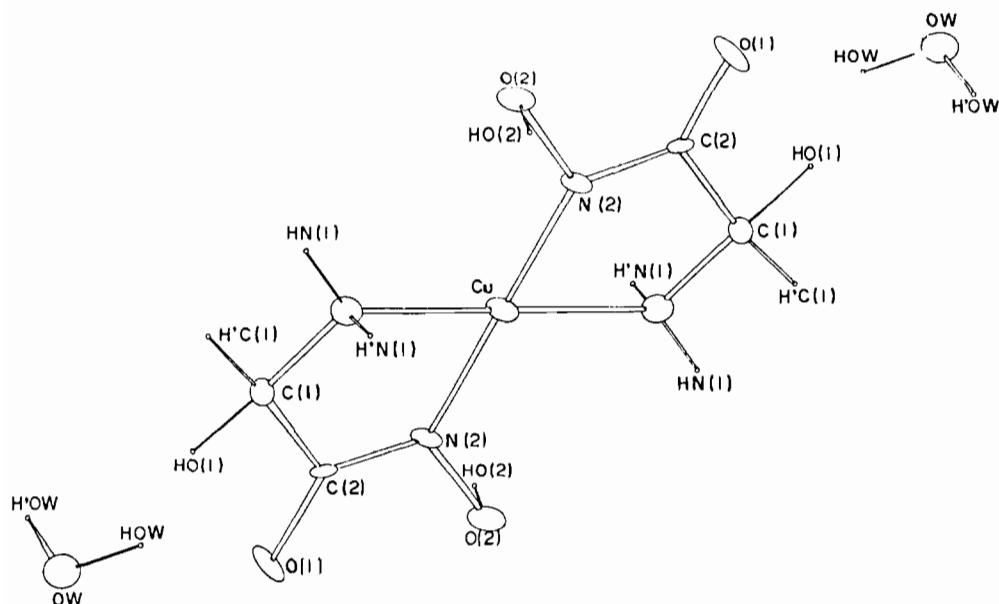


Fig. 1. Molecular structure of *trans*-bis(glycinehydroxamato)copper(II) dihydrate.

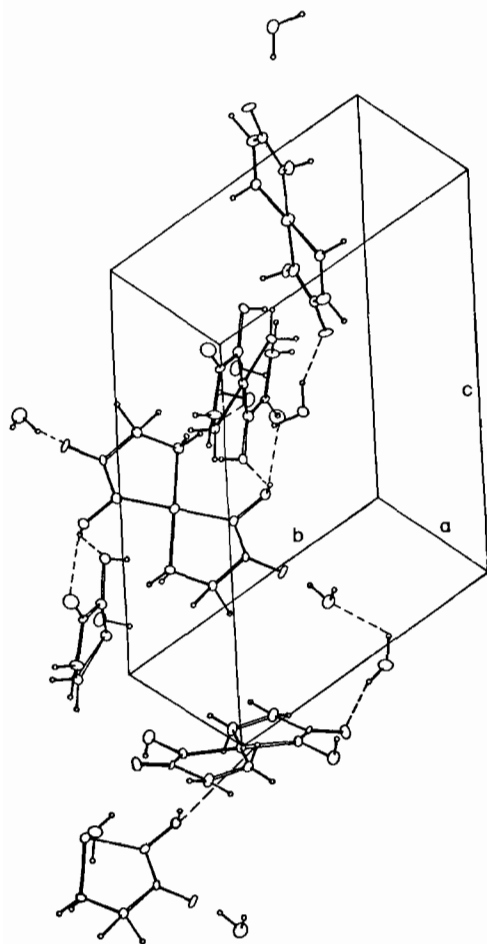


Fig. 2. Hydrogen bonds (indicated by fine dashed lines) in the crystal packing.

ture [15]. The short C(2)–N(2) interatomic distance is indicative of partial double bond character due to the interaction with the carbonyl group. This result is very close to those already reported for the structure of bis(glycinehydroxamato)nickel(II) [12]. All the other distances show no unexpected features. The coordination around Cu(II) is shown in Fig. 1 with atomic numbering.

The molecular crystal packing is very dense and formed by strips of the complex, in which the molecules are interlinked by hydrogen bonds between water oxygen as donor and carbonyl oxygen as receptor. These strips are then interconnected via the Cu(II) and carbonyl oxygen interaction and the hydrogen bonds shown in Table III. The crystal packing is presented in Fig. 2, where the hydrogen bonds are indicated by dotted lines.

#### IR Spectroscopy

The infrared absorption spectra of the complex were analysed by comparison with those of the free ligand and nickel(II) complex and with those of copper(II) complexes of amino acids [16, 17].

The strong broad absorptions at 3000–3200  $\text{cm}^{-1}$  in the IR spectra of free glycinehydroxamic acid shift to lower frequencies upon deuteration and are assigned to NH and OH stretching vibrations [18] of hydroxamic acids and  $\text{NH}_2$  stretching vibrations of the amino group [22].

In the copper(II) complex spectra we observed strong broad absorption at 3120 and 3220  $\text{cm}^{-1}$  which shifts to lower frequencies in the deuterated compound and can be assigned to NH stretching vibrations. They are similar to observed bands in copper(II) amino acid complexes [16, 17], which

TABLE III. Hydrogen-bond Distances (Å) and Angles with Estimated Standard Deviations in Parentheses<sup>a</sup>

Atoms A–H···B	Bonds (Å)			Angles (°)
	A–H	H···B	A···B	
N(1)–H···Ow <sup>i</sup>	0.975(9)	2.228(8)	3.201(12)	177.9(5)
O(2)–H···O(1) <sup>ii</sup>	0.771(7)	2.130(8)	2.658(10)	126.0(5)
O(2)–H···O(2) <sup>ii</sup>	0.771(7)	2.424(6)	3.095(9)	146.2(5)
N(1)–H···O(2) <sup>iii</sup>	0.861(8)	2.345(6)	2.986(10)	129.4(6)
OW–H···O(1)	0.975(9)	1.811(8)	2.708(11)	151.5(5)
OW–H'···Ow <sup>iv</sup>	1.085(8)	2.164(8)	2.761(11)	112.1(5)

<sup>a</sup>Symmetry codes: (i)  $0.5 - x, 0.5 + y, z$ ; (ii)  $0.5 + x, -0.5 - y, 1 - z$ ; (iii)  $-x, -y, 1 - z$ ; (iv)  $0.5 + x, y, 0.5 - z$ .

confirms the coordination through the amino group as found by the crystallographic method.

The deuterated compounds show bands at  $1608 \text{ cm}^{-1}$  (free ligand) and  $1590 \text{ cm}^{-1}$  (copper complex), which are assigned to the carbonyl stretching frequency, corresponding to a shift of  $\Delta\nu = 18 \text{ cm}^{-1}$ . This shift, not observed in the nickel complex, is less intense than observed shifts for metal-hydroxamates coordinated through the carbonyl oxygen [11, 19, 20]. This may be due to the longer C–O distances giving weaker metal-interaction with carbonyl oxygen and to the presence of the intermolecular hydrogen bonds.

Infrared spectra of the ligand and copper complex show important changes in the  $700\text{--}950 \text{ cm}^{-1}$  region. The strong sharp bands at  $830$  and  $938 \text{ cm}^{-1}$  and the medium bands at  $725$  and  $775 \text{ cm}^{-1}$  in the ligand spectrum disappear in the spectra of the complex, indicating coordination by the deprotonated hydroxamate group in agreement with the crystallographic determination.

### ESR Spectroscopy

The ESR powder and dilute solution spectra are shown in Figs. 3 and 4. They are characteristic of axial symmetry with respectively  $g_{\parallel} = 2.198$ ,  $g_{\perp} = 2.083$  and  $g_{\parallel} = 2.196$ ,  $g_{\perp} = 2.055$  and  $A_{\parallel}^{\text{Cu}} = 202$  gauss and  $A_{\parallel}^{\text{N}} = 15$  gauss. In the powder spectrum copper hyperfine structure as well as nitrogen superhyperfine structure were not observed due to the considerable linewidth which is certainly due to the spin–spin interaction of copper ions which are quite close in the concentrated sample. In the dilute solution spectrum the copper and nitrogen hyperfine structures are well observed. The four large peaks are attributed to the  $3/2$  copper nuclear spin interaction, and the nine small peaks superimposed on the third large peak correspond to the four nitrogen ligands. This spectrum indicates clearly a square coordination of nitrogens with the copper ion in solution. Comparison of the dilute solution spectrum with the powder spectrum shows that the same coordination scheme prevails in the solid state. The

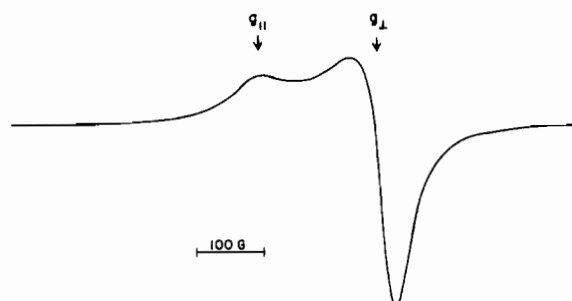


Fig. 3. ESR powder spectrum at room temperature. The powder was obtained through trituration of several single crystals.

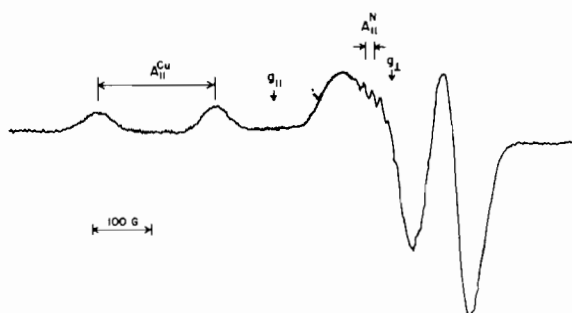


Fig. 4. ESR dilute solution spectrum at  $-150 \text{ }^{\circ}\text{C}$ . Several single crystals (3–4 mg) were dissolved in double distilled water (5 ml).

room temperature solution spectrum [3] allows determination of  $A_{\perp}^{\text{Cu}}$  from the relation  $A_0 = (A_{\parallel} + 2A_{\perp})/3$ , where  $A_0$  is the isotropic copper hyperfine splitting ( $A_0 = 87.5$  gauss). The electronic spectrum for the solution shows a broad band at  $545 \text{ nm}$  with a shoulder at  $580.5 \text{ nm}$  [3]. If the ground state of the complex is a  $d_{xy}$ , assuming the nitrogen ligands are in the  $xy$  plane, then the ESR data allow determination of the orbital reduction factors  $\gamma_{\parallel}$  and  $\gamma_{\perp}$  from the expressions

$$g_{\parallel} = 2.0023 - \gamma_{\parallel} \frac{8\lambda}{E_{xy} - E_{x^2-y^2}}$$

$$g_{\perp} = 2.0023 - \gamma_{\perp} \frac{2\lambda}{E_{xy} - E_{xz, yz}}$$

where  $\lambda$  is the free ion spin orbit constant, equal to  $-828 \text{ cm}^{-1}$  for copper. We obtained  $\gamma_{\parallel} = 0.53$  and  $\gamma_{\perp} = 0.58$ , suggesting a significant degree of covalency. Comparison of our results with data for monohydroxamic acids [23] shows that the metal ion is more tightly bound in our complex ( $g_{\parallel} = 2.198$  as compared to 2.250) and the degree of covalency is greater. This is consistent with the shift in the optical bands in our case to smaller wavelengths (545 nm and 580 nm as compared to 600 nm). All these results corroborate and are complementary to the crystallographic findings.

### Supplementary Material

Hydrogen atomic parameters and anisotropic thermal parameters have been deposited at the Cambridge Crystallographic Data Center, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K. Lists of observed and calculated structure factors can be obtained from the Editor-in-Chief.

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