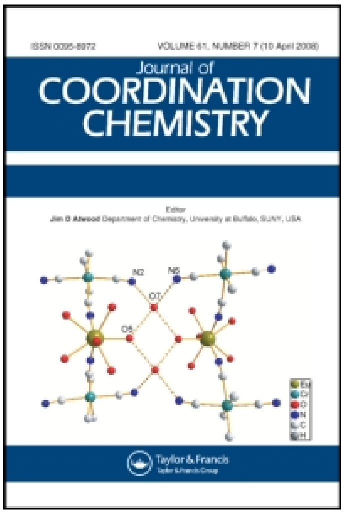

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Crystal, Molecular and Electronic Structures of Complexes of *N-(ortho*-Methyl)- And *N-(ortho*-Methoxy)-Phenyliminodiacetatocopper(II)

Yun-Ti Chen[a]; Heng-Qian Liu[a]; Jing-Jiang Liu[a]; Xian-He Bu[a]; Jin-Ling Wang[b]; Li-Juan Zhang[a]; Fang-Ming Miao[b]
[a] Department of Chemistry, Nankai University, Tianjin, PRC [b] Department of Chemistry, Tianjin Normal University, Tianjin, PRC

To cite this Article Chen, Yun-Ti , Liu, Heng-Qian , Liu, Jing-Jiang , Bu, Xian-He , Wang, Jin-Ling , Zhang, Li-Juan and Miao, Fang-Ming(1992) 'Crystal, Molecular and Electronic Structures of Complexes of *N-(ortho*-Methyl)- And *N-(ortho*-Methoxy)-Phenyliminodiacetatocopper(II)', Journal of Coordination Chemistry, 25: 1, 43 — 51
To link to this Article: DOI: 10.1080/00958979209407901
URL: http://dx.doi.org/10.1080/00958979209407901

J. Coord. Chem. 1992, Vol. 25, pp. 43–51
Reprints available directly from the publisher
Photocopying permitted by license only

CRYSTAL, MOLECULAR AND ELECTRONIC STRUCTURES OF COMPLEXES OF *N*-(*ortho*-METHYL)- AND *N*-(*ortho*-METHOXY)-PHENYLIMINODIACETATOCOPPER(II)

YUN-TI CHEN,[a]* HENG-QIAN LIU,[a] JING-JIANG LIU,[a] XIAN-HE BU,[a] JIN-LING WANG,[b] LI-JUAN ZHANG[b] and FANG-MING MIAO[b]

[a] *Department of Chemistry, Nankai University, Tianjin 300071, PRC.*
[b] *Department of Chemistry, Tianjin Normal University, Tianjin 300074, PRC.*

(Received November 30, 1990; in final form March 27, 1991)

The title compounds, $\{Cu[CH_3C_6H_4N(CH_2COO)_2]\}\cdot 2H_2O$ (I) and $\{Cu[CH_3OC_6H_4N(CH_2COO)_2]\}\cdot 2H_2O$ (II) have been prepared and crystal structures determined. The crystallographic data are as follows: (I) $Mr = 320.8$, monoclinic, $P2_1/c$, $a = 12.523(2)$, $b = 7.481(2)$, $c = 15.126(4)$ Å, $\beta = 111.85(2)°$, $V = 1314.9$ Å^3, $Z = 4$, $\lambda(CuK\alpha) = 1.5410$ Å, $F(000) = 660$, room temperature, $R = 0.052$ for 1952 observed reflections with $I > 3\sigma(I)$; (II) $Mr = 336.39$, monoclinic, $P2_1/c$, $a = 11.452(2)$, $b = 7.595(2)$, $c = 15.416(2)$ Å, $\beta = 101.60(1)°$, $V = 1313.4$ Å^3, $Z = 4$, $\lambda(MoK\alpha) = 0.7107$ Å, $F(000) = 692$, room temperature, $R = 0.052$ for 1091 observed reflections with $I > 3\sigma(I)$.

The Cu atom is five coordinate (N(1), O(1), O(2), O(10) and O(20)) in (I) to form a distorted square pyramid in which O(20) is at the apical site. The Cu(1)–O(20) bond is much longer than the basal bond lengths. In (II), the Cu atom is six coordinate (N(1), O(1), O(2), O(10), O(20) and O(01)) in the form of an unsymmetrical and elongated tetragonal bipyramid, manifesting an obvious Jahn–Teller effect.

The results of EHMO calculations are very similar to those for the ligand field theory model. The total charge at Cu is approximately +2. The electron population numbers indicate that there is approximately one electron in the $d_x{}^2 - {}_y{}^2$ orbital, but approximately two electrons in the other orbitals. It can be ascertained that the ligand mainly provided the field, with few of its electrons being donated to the central atom.

Keywords: Crystal structure, Cu(II) iminodiacetates

INTRODUCTION

Iminodiacetic acid is a terdentate ligand. Its aromatic substituted derivatives are isomeric and can also form complexes.[1] Some show both multidentate and multifunctional properties.[2,3]

Obodovskaya and co-workers[4] confirmed that the aromatically substituted iminodiacetic acid is quite different from glycine;[5] it not only acted as a chelate, but also as a bridging group. The maximum coordination number is generally three, but the *N*-(*para*-hydroxyl)phenyl derivatives may be tetradentate.[4] To further investigate the effects of various substituents and isomers on structures, we have synthesized a series of copper(II)-*N*-(*ortho*, *meta* and *para*)-substituted phenyl iminodiacetates and now report the crystal and molecular structures of the complexes Cu(II)-*N*-(*o*-methyl)-phenyliminodiacetate ($\{Cu[CH_3C_6H_4N(CH_2COO)_2]\}\cdot 2H_2O$, (I) and Cu(II)-*N*-(*o*-methoxy)phenyliminodiacetate ($\{Cu[CH_3OC_6H_4N(CH_2COO)_2]\}\cdot 2H_2O$, (II).

* Author for correspondence.

EXPERIMENTAL

The ligands in (I) and (II) were prepared by the method of Hilya and Lezenko.[6] The compounds (I) and (II) were obtained by dissolving the corresponding ligands and copper perchlorate[7] in a minimum amount of 95% ethanol solution and sealing the solution under nitrogen gas at room temperature. Blue-green, transparent, prismatic crystals of (I) and (II) were obtained during the course of several days and were found suitable for X-ray analysis.

A crystal (approximately $0.1 \times 0.2 \times 0.4$ mm) was mounted on an Enraf-Nonius CAD-4 diffractometer for data collection with graphite-monochromated CuKα radiation at room temperature for compound (I). The crystal dimensions of compound (II) were $0.15 \times 0.2 \times 0.4$ mm (MoKα radiation). Unit cell dimensions were obtained by least-squares refinement using 25 reflections with $15.8° < 2\theta < 46.9°$ for (I) and $12.2° < 2\theta < 27.2°$ for (II). The intensities of reflections with $\theta < 75°$ for (I) and $\theta < 26°$ for (II) were measured in the $\omega/2\theta$ scan mode. Three check reflections monitored every 200 reflections showed no obvious loss of intensity during the course of data collection. Crystallographic data are given in Table I.

TABLE I
Crystallographic data for (I) and (II).

	I	II
Formula	$\{Cu[CH_3C_6H_4N(CH_2COO)_2]\}\cdot 2H_2O$	$\{Cu[CH_3OC_6H_4N(CH_2COO)_2]\}\cdot 2H_2O$
M_r	320.79	336.79
Space group	$P2_1/c$	$P2_1/c$
a (Å)	12.523(2)	11.452(2)
b (Å)	7.481(2)	7.595(2)
c (Å)	15.126(4)	15.416(2)
β (°)	111.85(2)	101.60(1)
V (Å^3)	1314.9	1313.4
Z	4	4
d(calcd) (g cm^{-3})	1.620	1.702
μ (cm^{-1})	26.16	17.60
F(000)	660	692
cryst. dimens. (mm)	$0.1 \times 0.2 \times 0.4$	$0.15 \times 0.2 \times 0.4$
radiation	CuKα	MoKα
Max. 2θ (deg)	150	52
total No. of reflcns.	2396	2843
No. of unique data $I > 3\sigma(I)$	1952	1091
$R(Fo)$	0.052	0.052
$R_w(Fo)$	0.061	0.039
w	1	1

Data reduction gave 2396, for (I), and 2843, for (II), independent reflections, of which 1952, for (I), and 1091, for (II), with $I > 3\sigma(I)$, were used for structure refinement. Maximum counting time for each reflection was 60 s. All reflections were corrected for Lorentz and polarization effects.

The Cu atom position was determined by the Patterson methods, and the remaining non-hydrogen atoms were located by Fourier syntheses. The structures were refined with anisotropic temperature factors for non-H atoms in both compounds. The H atoms were located from a difference Fourier map calculated at $R = 0.052$ for (I) and $R = 0.073$ for (II). No attempt was made to include the hydrogen atoms in the refinement for (I); the hydrogen positions in compound (II) were refined with isotropic thermal parameters. The final discrepancy factors are R = 0.052, $R_w = 0.061$ for (I) and R = 0.052, $R_w = 0.039$ for (II). The highest peaks in the final difference map were 0.976 and 0.543 e^{-3} Å for (I) and (II), respectively. Lists of observed and calculated structures and anisotropic thermal parameters for the non-hydrogen atoms in (I) and (II) can be obtained from the Editor on request.

RESULTS AND DISCUSSION

Independent atomic coordinates and equivalent isotropic thermal parameters for (I) and (II) are given in Tables II and III, respectively. Selected bond lengths, hydrogen bond lengths and angles for both compounds are listed in Tables IV and V, respectively. Parameters for EHMO calculations are listed in Table VI. Perspective drawings of molecules (I) and (II), respectively, are shown in Figures 1 and 2, with the atomic numbering scheme. In (I), the coordination polyhedron around Cu is a tetragonal pyramid with the Cu(1) atom at the centre of the basal plane and O(20) at the apical site. The maximum deviation of the atoms from the mean basal plane is 0.13 Å(Cu). The four equatorial bond lengths Cu(1)–N(1), Cu(1)–O(1), Cu(1)–O(2) and Cu(1)–O(10) are 2.047, 1.909, 1.926 and 1.934 Å, respectively, compatible with corresponding normal coordination bond lengths.[8] The Cu(1)–O(20) distance is 2.303 Å, much longer than the basal bond lengths.

TABLE II
Atomic coordinates and equivalent isotropic thermal parameters for (I).

Atom	x/a	y/b	z/c	B(eq)*
Cu(1)	0.34606(7)	0.35622(9)	0.33292(4)	2.70(1)
O(1)	0.3360(3)	0.5384(5)	0.4179(2)	3.52(8)
O(2)	0.3391(3)	0.1991(5)	0.2300(2)	3.07(7)
O(3)	0.3543(4)	0.8288(5)	0.4387(2)	4.4(1)
O(4)	0.3641(3)	0.2157(5)	0.0934(2)	3.90(8)
O(10)	0.3599(4)	0.1715(5)	0.4261(2)	3.89(8)
O(20)	0.5423(3)	0.3759(5)	0.3752(2)	3.43(8)
N(1)	0.2869(3)	0.5501(5)	0.2307(2)	2.22(8)
C(1)	0.3416(4)	0.6943(7)	0.3884(3)	2.9(1)
C(2)	0.3357(5)	0.7163(7)	0.2856(3)	2.8(1)
C(3)	0.3468(4)	0.2882(7)	0.1604(3)	2.5(1)
C(4)	0.3420(4)	0.4915(7)	0.1623(3)	2.65(9)
C(11)	0.1621(4)	0.5539(8)	0.1870(3)	3.1(1)
C(12)	0.1026(5)	0.6785(9)	0.1167(4)	4.2(1)
C(13)	−0.0193(6)	0.672(1)	0.0791(5)	5.7(2)
C(14)	−0.0769(6)	0.545(1)	0.1104(5)	6.8(2)
C(15)	−0.0183(6)	0.421(1)	0.1797(5)	6.4(2)
C(16)	0.1013(5)	0.425(1)	0.2178(4)	4.5(1)
C(10)	0.1572(7)	0.822(1)	0.0788(5)	5.8(2)

* $B(eq) = 4/3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

TABLE III
Atomic coordinates and equivalent isotropic thermal parameters for (II).

Atom	x/a	y/b	z/c	$B(eq)$
Cu(1)	0.1569(1)	0.3572(1)	0.39701(7)	1.89(2)
O(1)	0.1463(5)	0.2130(8)	0.2919(4)	2.2(1)
O(2)	0.1720(5)	0.5403(8)	0.4857(4)	2.1(1)
O(3)	0.1334(5)	0.2353(9)	0.1473(4)	2.6(1)
O(4)	0.1730(7)	0.8286(9)	0.5007(4)	4.4(2)
O(10)	0.1317(6)	0.1699(8)	0.4790(4)	3.2(1)
O(20)	−0.0580(5)	0.3846(9)	0.3558(4)	2.8(1)
O(01)	0.3625(6)	0.3104(8)	0.4191(5)	3.1(2)
N(1)	0.2108(6)	0.5523(9)	0.3320(4)	1.4(1)
C(1)	0.1463(7)	0.300(1)	0.2218(5)	1.9(2)
C(2)	0.1545(8)	0.501(1)	0.2289(6)	2.3(2)
C(3)	0.1699(8)	0.694(1)	0.4549(6)	2.3(2)
C(4)	0.1602(8)	0.714(1)	0.3543(6)	2.2(2)
C(11)	0.3404(8)	0.571(1)	0.3339(6)	2.2(2)
C(12)	0.4146(8)	0.444(1)	0.3837(6)	2.3(2)
C(13)	0.5387(9)	0.459(2)	0.3943(7)	3.7(3)
C(14)	0.5865(9)	0.601(2)	0.3563(7)	4.2(3)
C(15)	0.5137(9)	0.726(2)	0.3062(7)	4.4(3)
C(16)	0.3889(8)	0.711(1)	0.2950(7)	3.0(2)
C(01)	0.431(1)	0.155(2)	0.4505(8)	4.9(3)

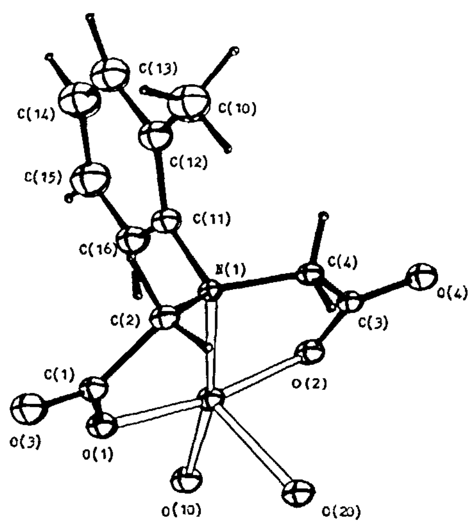

FIGURE 1 Perspective drawing of (I)

The geometrical effect of five-membered ring formation on the Cu coordination polyhedron can be shown by the fact that the intra-ring bond angles O(1)–Cu(1)–N(1) and O(2)–Cu(1)–N(1) (84.7° and 85.8°) are both much less than the inter-ring bond angles O(1)–Cu(1)–O(10) and O(2)–Cu(1)–O(10) (91.7° and 96.8°). As a terdentate ligand, two five-membered rings with a Cu–N bond in common are formed by coordinating to the Cu atom. The dihedral angle between the two best fit ring planes is 16.4°, with the same fold as in potassium *cis*-bis(iminodiacetato)chromate(III) trihydrate[9] and sodium *trans*-bis(*N*-isopropyliminodiacetato)chromate(III) dihydrate.[10] The value 112.5° for the Cu(1)–N(1)–C(11) (phenyl) angle reflects the plane of the phenyl group nearly being normal to the basal plane of the tetragonal pyramid of the coordination polyhedron around the Cu(1) atom, while the phenyl plane is so twisted around the N(1)–C(11) bond as to make the methyl group, attached to the phenyl ring in the *ortho* position, as far as possible from the Cu coordination environment. This can be shown by the torsion angle values C(2)–N(1)–C(11)–C(12) 63.7° and C(4)–N(1)–C(11)–C(12) −68.7°.

TABLE IV
Selected bond lengths (Å), hydrogen bond lengths (Å) and bond angles (°) for (**I**).

Bond lengths			
Cu(1)–O(1)	1.909(3)	Cu(1)–O(2)	1.926(3)
Cu(1)–O(10)	1.934(3)	Cu(1)–N(1)	2.047(3)
Cu(1)–O(20)	2.303(3)	O(1)–C(1)	1.259(5)
O(2)–C(3)	1.280(5)	O(3)–C(1)	1.235(5)
O(4)–C(3)	1.238(5)	C(1)–C(2)	1.539(5)
C(3)–C(4)	1.522(6)	N(1)–C(2)	1.493(5)
N(1)–C(4)	1.506(5)	N(1)–C(11)	1.453(5)
C(11)–C(12)	1.402(6)	C(12)–C(13)	1.418(7)
C(13)–C(14)	1.379(10)	C(14)–C(15)	1.390(10)
C(15)–C(16)	1.391(8)	C(11)–C(16)	1.409(7)
C(12)–C(10)	1.496(8)		
O(10)- - -O(3)	2.574		
O(10)- - -O(4)$^{i'}$	2.649		
O(20)- - -O(4)$^{i''}$	2.765		
Bond angles			
O(1)–Cu(1)–O(2)	170.1(1)	O(1)–Cu(1)–N(1)	84.7(1)
O(1)–Cu(1)–O(10)	91.7(1)	O(1)–Cu(1)–O(20)	95.7(2)
O(2)–Cu(1)–N(1)	85.8(1)	O(2)–Cu(1)–O(10)	96.8(1)
O(2)–Cu(1)–O(20)	89.2(2)	N(1)–Cu(1)–O(10)	164.9(2)
N(1)–Cu(1)–O(20)	102.3(2)	O(10)–Cu(1)–O(20)	92.6(2)
O(1)–C(1)–O(3)	123.2(4)	O(2)–C(3)–O(4)	122.4(4)
O(1)–C(1)–C(2)	118.0(3)	O(2)–C(3)–C(4)	119.2(4)
O(3)–C(1)–C(2)	118.8(4)	O(4)–C(3)–C(4)	118.2(4)
N(1)–C(2)–C(1)	109.2(3)	N(1)–C(4)–C(3)	109.6(3)
C(2)–N(1)–C(4)	115.3(3)	Cu(1)–N(1)–C(11)	112.5(3)
Cu(1)–N(1)–C(2)	102.2(2)	Cu(1)–N(1)–C(4)	100.5(2)
C(2)–N(1)–C(11)	112.6(3)	C(4)–N(1)–C(11)	112.6(3)
N(1)–C(11)–C(12)	122.4(4)	N(1)–C(11)–C(16)	117.3(4)
C(11)–C(12)–C(13)	118.1(5)	C(12)–C(13)–C(14)	120.5(6)
C(13)–C(14)–C(15)	121.6(6)	C(14)–C(15)–C(16)	118.8(6)
C(11)–C(16)–C(15)	120.7(6)	C(12)–C(11)–C(16)	120.3(5)
C(11)–C(12)–C(10)	125.3(5)	C(13)–C(12)–C(10)	116.6(5)

* Symmetry codes are i′ : x, $1/2 - y$, $1/2 + z$; i″: $-x$, $1/2 + y$, $1/2 - z$.

TABLE V
Selected bond lengths (Å), hydrogen bond lengths (Å) and bond angles (°) for (**II**).

Bond lengths			
Cu(1)-O(1)	1.937(4)	Cu(1)-O(2)	1.932(4)
Cu(1)-O(10)	1.962(4)	Cu(1)-N(1)	2.049(5)
Cu(1)-O(20)	2.424(4)	Cu(1)-O(01)	2.337(5)
O(1)-C(1)	1.265(7)	O(2)-C(3)	1.256(7)
O(3)-C(1)	1.229(7)	O(4)-C(3)	1.240(7)
C(1)-C(2)	1.536(9)	C(3)-C(4)	1.538(8)
N(1)-C(2)	1.498(8)	N(1)-C(4)	1.485(8)
N(1)-C(11)	1.462(7)	C(11)-C(12)	1.402(9)
C(12)-C(13)	1.399(9)	C(13)-C(14)	1.395(11)
C(14)-C(15)	1.388(11)	C(15)-C(16)	1.407(10)
C(11)-C(16)	1.389(9)	C(12)-C(01)	1.348(7)
O(01)-C(01)	1.447(9)		
O(10)- - -O(4)	2.644		
O(10)- - -O(3)$^{i'}$	2.689		
O(20)- - -O(3)$^{i''}$	2.798		
Bond angles			
O(1)-Cu(1)-O(2)	168.2(2)	O(1)-Cu(1)-N(1)	85.0(2)
O(1)-Cu(1)-O(10)	97.8(2)	O(1)-Cu(1)-O(20)	86.5(3)
O(1)-Cu(1)-O(01)	85.9(3)	O(2)-Cu(1)-N(1)	83.4(2)
O(2)-Cu(1)-O(10)	94.0(2)	O(2)-Cu(1)-O(20)	93.8(3)
O(2)-Cu(1)-O(01)	93.5(3)	N(1)-Cu(1)-O(10)	170.9(2)
N(1)-Cu(1)-O(20)	101.3(3)	N(1)-Cu(1)-O(01)	77.5(3)
O(10)-Cu(1)-O(20)	87.6(3)	O(10)-Cu(1)-O(01)	94.0(3)
O(20)-Cu(1)-O(01)	172.4(3)	Cu(1)-N(1)-C(11)	114.3(4)
Cu(1)-N(1)-C(2)	103.5(4)	Cu(1)-N(1)-C(4)	103.0(3)
O(1)-C(1)-O(3)	124.7(5)	O(2)-C(3)-O(4)	123.7(6)
O(1)-C(1)-C(2)	118.0(3)	O(2)-C(3)-C(4)	117.7(6)
O(3)-C(1)-C(2)	117.2(6)	O(4)-C(3)-C(4)	118.6(6)
N(1)-C(2)-C(1)	109.5(5)	N(1)-C(4)-C(3)	107.6(6)
C(2)-N(1)-C(4)	114.4(5)	C(2)-N(1)-C(11)	111.8(5)
C(4)-N(1)-C(11)	109.4(5)	N(1)-C(11)-C(12)	119.2(5)
N(1)-C(11)-C(16)	120.1(6)	C(12)-C(11)-C(16)	120.7(6)
C(11)-C(12)-C(13)	119.8(7)	C(12)-C(13)-C(14)	119.1(7)
C(13)-C(14)-C(15)	121.5(8)	C(14)-C(15)-C(16)	119.2(9)
C(11)-C(16)-C(15)	119.7(7)	C(11)-C(12)-C(01)	118.0(5)
C(13)-C(12)-O(01)	122.1(6)	C(12)-O(01)-C(01)	119.8(6)

* Symmetry codes for the primed atoms are as for Table IV.

In (**II**), the existence of the *ortho* methoxyl group in the phenyl ring of the ligand makes the Cu coordination environment significantly different from that found in (**I**); here the ligand molecule acts as a tetradentate. Two oxygen atoms from two water molecules results in an octahedral coordination polyhedron (Fig. 2). As expected with Jahn–Teller distortion[11] of six-coordinate Cu complexes, the octahedral coordination around Cu(1) is elongated along the O(01)-Cu(1)-O(20) direction; Cu(1)-O(01) and Cu(1)-O(20) are 2.337 and 2.424 Å, respectively, and the other four bonds, Cu(1)-O(1), Cu(1)-O(2), Cu(1)-O(10) and Cu(1)-N(1), in the basal plane of the octahedron are 1.937, 1.932, 1.962 and 2.049 Å. This is very similar to the case of copper(II)-*N*-(*para*-hydroxylphenyl)iminodiacetate.[4] As opposed to (I), the ligand makes three chelate rings with the Cu atom; the third forms through the coordination of the O(01) atom (methoxy group) to the Cu(1) atom. Other structural features of (II) are somewhat similar to those of (I).

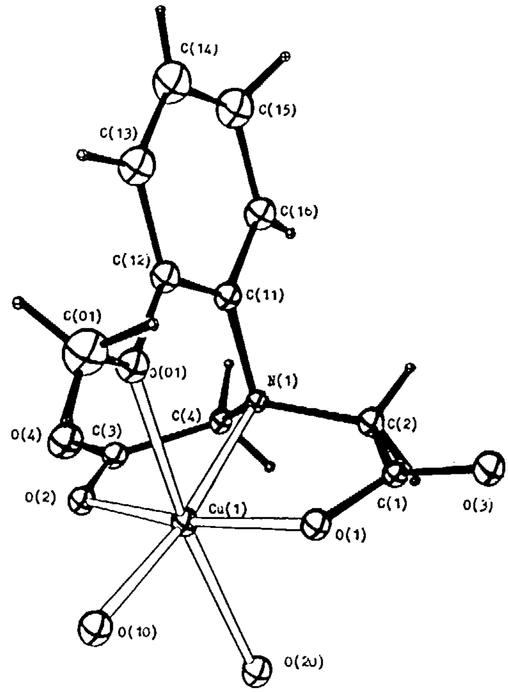

FIGURE 2 Perspective drawing of (II)

TABLE VI
Parameters for the EHMO calculations.

Atom	Cu	O	N	C	H
Principal quantum number (n)	4	2	2	2	1
ξ_{ns}, ξ_{np}	1.950	2.275	1.950	1.625	1.300
H_{ns} (ev)	−7.750	−32.300	−26.000	−21.400	−13.600
H_{np} (ev)	−3.950	−14.800	−13.400	−11.400	
$\xi^1_{(n-1)d}$	5.950				
$\xi^2_{(n-1)d}$	2.100				
C_{1d}	0.5770				
C_{2d}	0.6168				
$H_{(n-1)d}$ (ev)	−10.600				

In both (I) and (II), each of the two oxygen atoms from the water molecules forms intermolecular hydrogen bonds with the oxygen atoms of the carboxyl groups (see Tables IV and V). These indicate that the molecules in (I) and (II) are held together by intermolecular hydrogen bonding in the crystal packing.

EHMO calculations without charge iteration have been performed for (I) and (II), using the ICON8 program.[12] The results are very similar to those for the model ligand field theory.[13] The total charge of the Cu atom is +2.11 a.u. for (I) and +2.29 a.u. for (II), but with very few electrons in s and p orbitals; even though the total population number for the s orbital is largest, it has a value of only 0.12 for (I) and of 0.13 for (II). The electron population numbers for the $d_{x^2-y^2}$, d_{z^2}, d_{xy}, d_{xz} and d_{yz} orbitals are 0.94, 1.97, 1.95, 1.97 and 1.98 for (I) and 0.96, 1.93. 1.95, 1.99 and 1.84 for (II), respectively, which means that the nine d electrons of the Cu atom are essentially all in d orbitals with one electron in the $d_{x^2-y^2}$ orbital. In agreement with this model, the charges on the oxygen atoms of the two carboxyl groups are −1.28, −1.27 a.u. for the coordinated oxygen atoms and −1.28, −1.30 a.u. for the uncoordinated two oxygen atoms, respectively, in (I) and −1.26, −1.29 a.u. and −1.30, −1.30 a.u., respectively, in (II). The difference between the coordinated and the uncoordinated C–O bond lengths is only 0.02–0.03 Å (see Table V). The electron distribution in $d_{x^2-y^2}$ orbital of the Cu atom is one less than that in each of the other d orbitals leads to the observed Jahn–Teller effect. Deficiency of electrons on the x and y axes may decrease the repulsion of the central atom and the ligands on the x and y axes, thus leads to the formation of the six-coordinate compound with four shorter bonds in the xy plane and two longer bonds in the z axis direction in (II), and the formation of the five-coordinate compound with four shorter bonds in the xy plane and one longer bond in the z axis direction in (I), respectively. As the molecular orbital model is delocalized, the nine d electrons on Cu are partitioned in many orbitals. Taken as an example, the singly occupied molecular orbital (SOMO) is not a pure d orbital, but a delocalized orbital in which d forms the main part, as follows.

$$\Psi_{somo}=0.85\,d_{x^2-y^2}(\mathrm{Cu})+0.13p_x\ (\mathrm{O}_1)-0.12p_x\ (\mathrm{O}_2)+0.12p_y\ (\mathrm{O}_{10})-0.21p_y\ (\mathrm{N}_1)$$

Since the largest overlap population of the d orbitals of Cu with the ligand orbitals is only 0.0057 for (II), the nine d electrons are regarded as being essentially nonbonding. The SOMO energy for (II) (−9.910 e.v.) is higher than that of the d orbital of Cu (−10.600 e.v.), similar to the ligand field model. Therefore, it could be concluded that the ligand mainly provides the field, with very few of its electrons being coordinated to the central atom.

ACKNOWLEDGEMENTS

We gratefully acknowledge financial support for this work from the Doctoral Foundation of the National Education Commission of China.

REFERENCES

1. V.Ya. Temkina, N.M. Dyatlova, M.N. Rusina, O.Yu. Lavrova, B.V. Zhadanov and R.P. Lastovskii, *Khimicheskie reaktivy i preparaty*, **30**, 118 (1967).
2. L.M. Shkol'nikova and M.A. Porai-Koshits, *Itogi nauki i tekhniki, Kristallokhimiya*, 117 (1982).
3. L.M. Shkol'nikova and E.A. Shugam, *Itogi nauki i tekhniki, Kristallokhimiya*, 169 (1977).
4. A.E. Obodovskaya, L.M. Shkol'nikova and N.M. Dyatlova, *Koordinatsionnaya Khimiya*, **10**, 161 (1984).
5. Miao Fang-Ming, Wang Jin-Ling, Hao Jin-Ku, Chen Yun-Ti and Liu Heng-Qian, *Acta Inorganica Chimica Sinica*, **5**, 41 (1989).

6. V.P. Khilya and G.A. Lezenko, *Zhurnal Organicheskii Khimii*, **6**, 2048 (1970).
7. Chen Yun-Ti and Liu Heng-Qian, *Acta Chimica Sinica*, **43**, 884 (1985).
8. A.F. Wells, "Structural Inorganic Chemistry", Fourth Edition, (Oxford University Press, Oxford, 1975), p. 1125.
9. D. Mootz and H. Wunderlich, *Acta Cryst.*, **B36**, 445 (1980).
10. D. Mootz and H. Wunderlich, *Acta Cryst.*, **B36**, 721 (1980).
11. F. Basolo and R.C. Johnson, *Coordination Chemistry*, 149 (1962).
12. J. Howell, A. Rossi, D. Wallace, K. Haraki and R. Hoffmann, *QCPE*, **10**, 34 (1977).
13. H.L. Schläfer and G. Gliemann, "Basic Principles of Ligand Field Theory", (Wiley-Interscience, London, 1969).