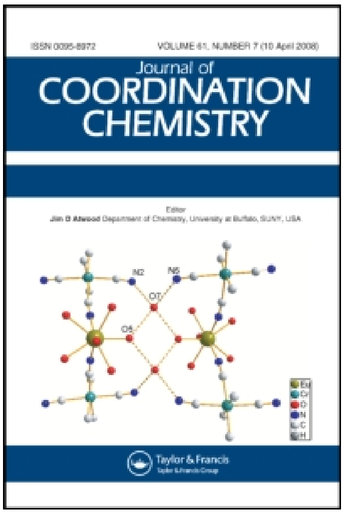

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STRUCTURES AND PROPERTIES OF COPPER(II) COMPLEXES WITH IMINODIACETATO AND IMIDAZOLE OR RELATED LIGANDS. I. CRYSTAL STRUCTURE OF AQUA(IMIDAZOLE) (IMINODIACETATO)COPPER(II) MONOHYDRATE AND (IMIDAZOLE)(*N*-CARBOXYMETHYL-D,L-THREONINATO)COPPER(II)

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STRUCTURES AND PROPERTIES OF COPPER(II) COMPLEXES WITH IMINODIACETATO AND IMIDAZOLE OR RELATED LIGANDS. I. CRYSTAL STRUCTURE OF AQUA(IMIDAZOLE) (IMINODIACETATO)COPPER(II) MONOHYDRATE AND (IMIDAZOLE)(*N*-CARBOXYMETHYL-D,L-THREONINATO)COPPER(II)

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The crystal structures of two mixed-ligand copper(II) complexes having iminodiacetate(2-) (IDA) or *N*-carboxymethyl-*D,L*-threoninato(2-) ion (CMT) as terdentate ligands and imidazole (ImH) as an *N*-heterocyclic ligand are reported. Both compounds crystallize in the orthorhombic system, space group *Pbca* with $Z = 8$. Aqua(imidazole)(iminodiacetato)copper(II) monohydrate (**I**,$R = 0.065$, $R_w = 0.075$) consists of H_2O molecules and $[Cu(IDA)(ImH)(H_2O)]$ complex units in a hydrogen bonding network. The structure of imidazole(*N*-carboxymethyl)-*D,L*-threoninatocopper(II) (**IV**, $R = 0.066$, R_ω 0.078) is built up of hydrogen bonded polynuclear chains. In both compounds the Cu(II) ion exhibits a flattened and distorted square-based pyramidal coordination, with a terdentate aminoacidate ion, IDA or CMT, and one ImH ligand at the base and H_2O (in **I**) or the oxygen atom of the OH side chain from one adjacent CMT ion (in **IV**) as the fifth apical ligand. The nearly coplanar conformation of the two five-membered chelate rings in **I** and **IV** is discussed in connection with the known structure of corresponding aquacomplexes (with H_2O instead of ImH) and the ability of terdentate aminoacids to give ternary Cu(II) complexes having two *N*-heterocyclic donors (2 ImH or one 2,2'-bipy) per Cu(II) atom.

KEYWORDS: imidazole, iminodiacetate, *N*-carboxymethyl-*D,L*-threoninate, copper(II), crystal structure

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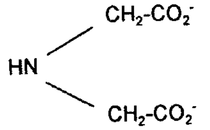
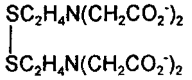
INTRODUCTION

Because of the presence of imidazole rings of histidine residues in copper-protein centres, low molecular weight, mixed-ligand copper complexes of aminoaci-dates, peptides or related chelating ligands and imidazole or closely related *N*-heterocyclic donors have broad bioinorganic interest.[1] In this context several reports of the structure and properties of mixed-ligand, copper (II) complexes with iminodiacetate(2-) ion $(IDA)^{2-}$[2-7] or *N,N,N',N'-tetrakis*(carboxymethyl)cystaminato(4-) ion $(TCC)^{4-}$[8-10] as chelating ligand and water[2,8] imidazole (ImH),[3,4,9] 2-or 5-methyl-ImH[5,10] and bipyridines (2,2'-bipy[6] or 4,4'-bipy[7]) have proved a source of a variety of structural correlations.



IDA^{2-} ion



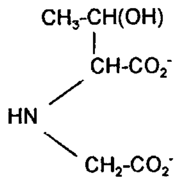
$$\begin{array}{l} SC_2H_4N(CH_2CO_2^-)_2 \\ | \\ SC_2H_4N(CH_2CO_2^-)_2 \end{array}$$

TCC^{4-} ion

For IDA-Cu(II) complexes,[2-7] the following correlations are claimed. The first incoming *N*-heterocyclic donor atom exhibits a clear preference for the Cu(II) *trans*-coordination site with respect to the *N*-donor atom of IDA. The two five-membered Cu(IDA) chelate rings (sharing the Cu-N(IDA) bond) are nearly coplanar or nearly perpendicular as a function of the number of *N*-heterocyclic donors (one or two, respectively) linked to the same Cu(II) ion. Complexes with equimolar ratio for Cu:IDA:*N*-heterocyclic donor have the Cu-N(IDA) bond (<2.00(1)Å shorter than in $[Cu(IDA)(H_2O)_2]$. Steric reasons cause the coordination of one or two 4-methyl-ImH molecules to copper(II) in Cu(IDA)[5] or $Cu_2(TCC)$[10] as the 5MelmH "remote" isomer instead of the 4MeImH "adjacent" isomer.[5,10] Coordination of two *N*-heterocyclic donors per Cu(II) atom (two ImH or one 2,2'-bipy) imposes a nearly perpendicular configuration of the two five-membered chelate rings of the Cu(II) moiety.[4,6]

In order to test the scope of the above structural correlations we have carried out new studies with selected copper(II) complexes of *C*- and/or *N*-substituted H_2IDA acids and ImH or its *N*- and/or *C*-derivatives. Earlier reports[3,4] showed that the reaction of diaqua(iminodiacetato)copper(II)[2] with ImH can give two different compounds, **I** = $Cu(IDA)(ImH)\cdot 2H_2O$, with unresolved crystal structure, and **II** = $[Cu(IDA)(ImH)_2]_2\cdot 2H_2O$, with a dinuclear structure.[4] Recrystallization of **I** at room temperature from hot methanol yields **III** = $[Cu(IDA)(ImH)(CH_3OH)]\cdot 0.37H_2O$, an air (moisture) sensitive compound with known structure.[3] As a part of our research programme, we report the crystal structure of compound **I** (previously not obtained despite many attempts)[3] as well as that of compound **IV** = [Cu(CMT)(ImH)] with *N*-carboxymethyl-*D,L*-threoninate(2-) ion (CMT) as an example of a *C*-substituteds-IDA derivative.

The $Cu(II)$-H_2CMT system in solution and the crystal structure and properties of $[Cu(CMT)(H_2O)]$ were the subject of a recent paper.[11]



CMT^{2-} ion

EXPERIMENTAL

Synthesis

The title compounds **I** or **IV** can be obtained by reaction of purified samples of [Cu(IDA)$(H_2O)_2$]^2 or [Cu(CMT)(H_2O)],^{11} respectively, with ImH (Sigma; molar ratio 1:1 or 1:1.5, respectively) in water. Slow evaporation of the deep blue complex solutions gives the desired products. Both compounds need to be recrystallized from relatively concentrated solutions (>4%) in water to avoid disproportion to the corresponding aqua-chelate copper(II), which precipitates, and imidazole, which remains in solution. The parent aqua-complexes and the ImH-containing derivatives can be routinarily distinguished by means of their infrared spectra. Taking into account the above, the yield of both syntheses can reach 90%. Calcd. for **I** = $C_7H_{13}CuN_2O_6$: C, 28.13; H, 4.39; N, 14.04; Cu, 21.27%. Found: C, 28.54; H, 4.15; N, 14.07; Cu, 21.0 ± 1% (complexometry).[3] Calcd. for **IV** = $C_9H_{13}CuN_3O_5$: C, 35.24; H, 4.27; N, 13.70; Cu, 20.71%. Found: C, 35.06; H, 4.28; N, 13.74; Cu, 20.4 ± 1% (complexometry). Compounds **I** and **IV** can be also prepared by reaction of 2 mmol of *N*-carboxymethyl-amino acid (H_2IDA (Sigma) or H_2CMT,[11] respectively and 1mmol of $Cu_2CO_3(OH)_2$(Aldrich) in 100 cm^3 of hot H_2O (60°C) with stirring and under vacuum (to remove CO_2) followed by addition of ImH (1 or 1.5 mmol, respectively). Evaporation of these solutions gives **I** or **IV**. However, this strategy has the lowest yield because of the difficulty to ensure in practice the appropriate molar ratio in the ternary solution. The crude products obtained in such a way should be recrystallized two or more times to yield well shaped crystals of **I** or **IV**.

X-ray data collection, solution and refinement of the structures

Prismatic crystals of **I** and **IV** with appropriate dimensions were mounted on glass fibres and used for data collection on an Enraf-Nonius CAD4 diffractometer at room temperature (293K) with MoKα radiation. Cell constants and the orientation matrix for data collection were obtained by least-squares refinement of diffraction data from 25 reflections[12] in the range $5.7 < \theta < 13.0°$ for **I** and 4.5–11.5° for **IV**. For structure determination and refinement data were collected with the $\omega/2\theta$ scan technique and corrected for Lorentz and polarization effects. Two intensity control reflections monitored every two hours showed no loss of intensity. For **I** and **IV**, respectively, 4451 and 3442 reflections measured in the θ range 3–29° result in 649 and 721 independent observed data with $I>3\sigma(I)$. The structures were solved by direct methods[13] which gave the positions of all non-hydrogen atoms. Refinements were based on *F* by full-matrix least-squares procedures. An empirical absorbtion correction was made with the program DIFABS.[14] Anisotropic displacement parameters have been calculated for Cu and the N and O coordinating atoms and isotropic parameters for remaining non H-atoms. The positions of the hydrogen atoms were obtained by difference Fourier syntheses. Further refinements were made with the H atoms included in structure factor calculations with β_{iso} = 4.0 or 5.0 Å^2; positional parameters were not refined. A secondary extinction correction were applied[15] in the last cycle of refinements. A summary of crystal data and final agreement factors is given in Table 1. All calculations were carried out a DECMicro VAXII computer. Atomic scattering factors were taken from International Tables.[16] Molecular graphics were generated using SCHAKAL.[17]

Physical measurements

TG and DTA measurements, and IR, diffuse reflectance and ESR spectra of **IV** were obtained as described in refs. 6 and 11. Data for **I** were from ref. 3.

RESULTS AND DISCUSSION

Molecular and crystal structure of I

Positional parameters for **I** and **IV** are given in Table 2. Bond lengths and angles around the Cu(II) atom in both substances are listed in Table 3. Compound **I** consists of complex units of [Cu(IDA)(ImH)(H_2O)] and water molecules linked together in a hydrogen bonding network (Figures 1 and 2). The copper(II) ion exhibits a distorted square-based pyramidal coordination (type 4+1). The N(1), O(1) and O(3) atoms of the terdentate IDA ligand and the N(2) atom of ImH are at the folded base and the Cu(II) atom is displaced 0.149(2)Å from its mean plane towards the O(5) atom of the coordinated water molecule. The Cu-O(5) bond

Table 1 Crystal data for I = [Cu(IDA)(ImH)(H_2O)]·H_2O and IV = [Cu(CMT)(ImH)].*

	I	IV
Crystal size	0.10 × 0.10 × 0.25 mm	0.10 × 0.20 × 0.10 mm
Chemical formula	$C_7H_{13}CuN_3O_6$	$C_9H_{13}CuN_3O_5$
Formula weight	298.74	306.76
Crystal System	Orthorhombic	Orthorhombic
Space group	*Pbca*	*Pbca*
Unit cell dimensions	a = 11.5411(1) b = 17.982(3) c = 10.509(1) V = 2180.8(7)Å^3	a = 18.512(2) b = 12.224(1) c = 10.213(1)Å V = 2311.2(8)Å^3
Z	8	8
$d_{calc.}$	1.820 g.cm^{-3}	1.764 g.cm^{-3}
$F(000)$	1224	1256
$\mu_{MoK\alpha}$	20.274 cm^{-1}	15.260 cm^{-1}
R	0.065	0.066
R_w	0.075	0.078
w	$1/\sigma^2(F)$	$1/\sigma^2(F)$

* Further details of the structure determination and full list of thermal parameters, H atom positions and observed and calculated structure factors for both compounds are available from the authors.

Table 2 Positional parameters for non-H atoms in **I** and **IV** with e.s.d.s in parentheses.

Compound I

Atom	*x*	*y*	*z*	*B*(Å^2)
Cu	0.0148(2)	0.1397(1)	0.1595(2)	1.70(3)
O1	-0.107(1)	0.0663(7)	0.109(1)	1.9(2)
O2	-0.166(1)	0.0027(8)	-0.059(1)	2.7(3)*
O3	0.164(1)	0.1941(7)	0.161(1)	2.6(3)
O4	0.295(1)	0.2433(8)	0.037(1)	3.6(3)*
O5	-0.105(1)	0.2437(8)	0.204(1)	2.9(3)
O6	0.224(1)	-0.0382(8)	0.301(1)	3.1(3)*
N1	0.015(1)	0.1656(7)	-0.026(1)	1.9(3)
N2	0.014(1)	0.1115(7)	0.338(2)	1.8(2)
N3	-0.055(1)	0.0834(8)	0.527(1)	2.2(3)*
C1	-0.108(2)	0.055(1)	-0.008(2)	1.8(3)*
C2	-0.040(2)	0.102(1)	-0.098(2)	2.2(4)*
C3	0.137(2)	0.816(1)	0.062(2)	2.7(4)*
C4	0.201(1)	0.212(1)	0.050(2)	1.6(3)*
C5	-0.075(2)	0.085(1)	0.399(2)	2.0(4)*
C6	0.060(2)	0.103(1)	0.544(2)	3.4(4)*
C7	0.100(2)	0.123(1)	0.436(2)	2.0(4)*

Compound IV

Atom	*x*	*y*	*z*	*B*(Å^2)
Cu	0.3243(1)	0.1519(2)	0.0514(2)	1.65(3)
O1	0.3587(6)	0.029(1)	-0.053(1)	2.5(3)
O2	0.3222(7)	-0.1341(9)	-0.112(1)	2.3(2)*
O3	0.2741(5)	0.2688(9)	0.141(1)	1.6(2)
O4	0.1629(6)	0.318(1)	0.198(1)	2.0(2)*
O5	0.1944(5)	-0.0265(9)	-0.266(1)	1.5(2)*
N1	0.2279(7)	0.112(1)	-0.025(1)	1.3(3)
N2	0.4195(7)	0.202(1)	0.109(1)	1.7(3)
N3	0.5343(8)	0.200(1)	0.147(2)	2.6(3)*
C1	0.3107(8)	-0.042(1)	-0.075(1)	1.4(3)*
C2	0.2326(8)	-0.011(1)	-0.038(2)	1.3(3)*
C3	0.174(1)	0.155(2)	0.071(2)	2.6(3)*
C4	0.2058(8)	0.257(2)	0.142(2)	1.5(3)*
C5	0.178(1)	-0.061(1)	-0.137(1)	1.4(3)*
C6	0.099(1)	-0.034(2)	-0.100(2)	3.4(5)*
C7	0.4810(9)	0.151(2)	0.075(2)	2.6(3)*

* Atoms refined isotropically.

(2.37(1)Å) is typically elongated. The deviations from the basal plane of the N donors towards O(5) and Cu(II) atoms and of O(1) and O(3) atoms in the opposite sense are nearly equivalent (mean dev. = 0.12(1)Å). A closely related Cu(II) coordination, but less distorted, has been reported for [Cu(IDA)(5MelmH)].[5] In compound **I** the trigonal distortion of the square pyramidal stereochemistry[18] as obtained from the angles θ = N(1)-Cu-N(2) and ρ = O(1)-Cu-O(3) is $\tau = 100(\theta - \rho)/60 = 30.2\%$ (20.7% in the 5MelmH derivative).[5]

In addition, the Cu-N(2) bond distance falls in the range (1.93(1)–1.98(2)Å of a variety of related compounds (see refs. 2–11 and references therein). In this compound the strictly planar ImH ligand forms a dihedral angle of 19° with the mean basal plane, between the corresponding values for **III** = [Cu(IDA)(ImH)(CH_3OH)]·0.37H_2O(36.8°)[3] and [Cu(IDA)(5MelmH)]·H_2O (7°).[5] Another

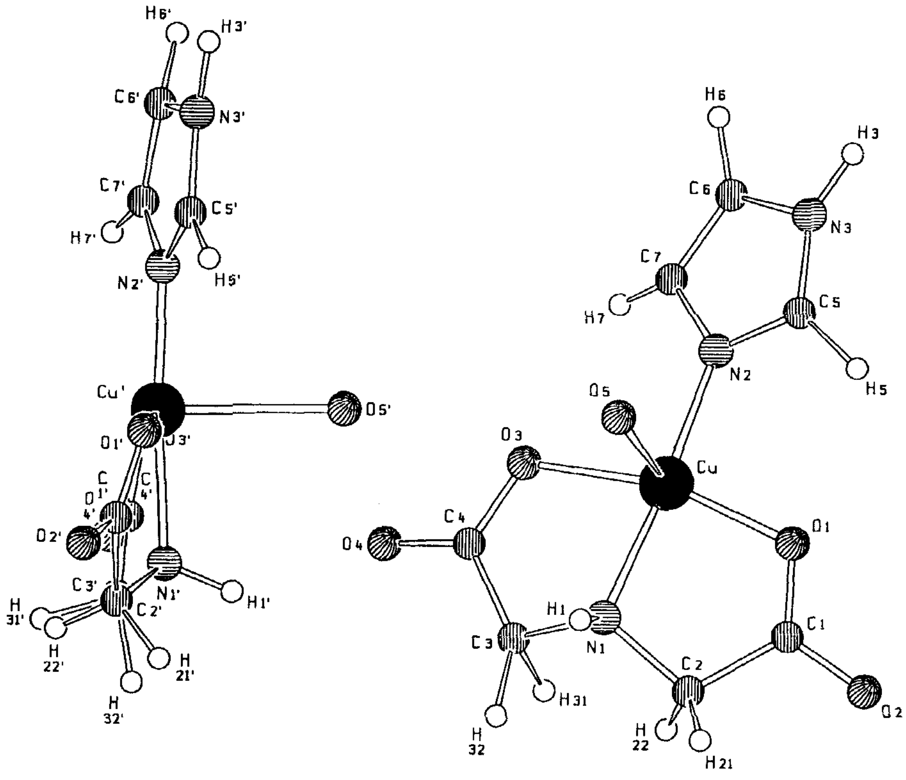


Figure 1 Structure of two complex units of **I** showing the short Cu-Cu^i distance (6.051(3) Å). Symmetry code i = *x*, -*y*, -*z* for atoms with primes.

structural feature in common for these three complexes is the nearly coplanar conformation of the two chelate ring in the Cu(IDA) moiety. The dihedral angle between the ring mean planes (ϕ) is larger in **I** (25.1°) than in **III** (15.5°)[2] or in [Cu(IDA)(5MeImH)]·H_2O (13.6°).[5] In the crystal packing, the N-H groups of the ligands play a donor roll in hydrogen bonds: (IDA)N(1)-H(1)-O(4^{ii})(3.02(3)Å, 146°, symmetry code ii = x - 0.5, 0.5 - y, $-z$) and (ImH) N(3)-H(3)-O(6^{iii}) (2.79(2) Å, 142(1)°, symmetry code iii = $-x$, $-y$, 1 - z). Other interatomic distances strongly suggest the implication of both hydrogen atoms of the water molecules (not located in the structure) in hydrogen bonds with oxygen atoms of neighbouring IDA ligands.

Prior to knowledge of the structure of **I**, we remarked upon the low "diagnostic" value of several of its physical properties.[25] For example, TG-DTA data for water loss (-2H_2O, 373–418K, endo-effect at 400K) could correspond to two uncoordinated or weakly coordinated H_2O molecules as well as to one molecule of each of these types.[2] The third possibility is now confirmed. The electronic spectrum (v_{max} = 14,180 cm^{-1}) and the "reverse" ESR spectrum of **I** ($g_{\parallel}$ = 2.06, $g_{\perp}$ = 2.18 g 0.01) could be attributed to several distorted coordination structures.[18] Indeed a freshly prepared, polycrystalline sample of **III** also gives a "reverse" type ESR spectrum with $g_{\parallel}$ = 2.07 and $g_{\perp}$ = 2.19[19] corresponding with its elongated octahedral structure.[3]

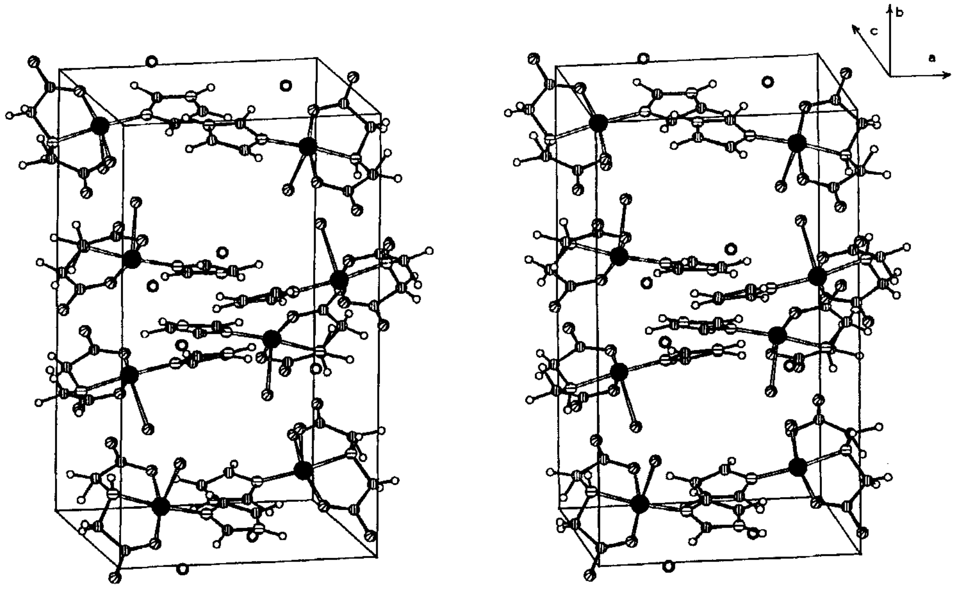


Figure 2 Stereo view of the cell of **I**.

The misalignment of the local molecular axes in **I** is apparent from Figures 1 and 2, but the suggested distorted octahedral structure[2,5] (as for compound **III** but with water instead of coordinated methanol) is now rejected in view of its square pyramidal coordination (Figure 1). With the necessary caution we can compare ν_{max} values for **I** and [Cu(IDA)(5MeImH)]·H_2O (14,750 cm^{-1})[5] with closely related five-coordinated Cu(II) complexes.

Crystal structure and properties of IV = [Cu(CMT)(ImH)]

Positional parameters and bond lengths and angles for compound **IV** are given in Tables 2 and 3, respectively. A drawing of the complex with the atom labelling is given in Figure 3. The atoms N(1), O(1) and O(3) from the same CMT ligand and N(2) of ImH define a slightly distorted square base. The Cu(II) atom is displaced 0.064(2) Å from the base mean plane, P(1), towards the fifth donor atom O(5^i) (symmetry code i = 0.5 − *x*, −*y*, 0.5 + *z*) that is the hydroxyl oxygen atom from the side chain of a neighbouring *N*-carboxymethyl-*D,L*-threoninato(2-) ion. The Cu(II) atom exhibits a flattened, square-based, pyramidal coordination in **IV**. From the square base there are nearly equivalent deviations (±0.04(1) Å) of both N donors towards the Cu(II) and O(5^i) atoms and of both O donor atoms in the opposite sense (τ = 6.3%). This coordination polyhedron (type 4 + 1) is closely related to, but less distorted than those of the compounds [Cu(IDA)(5MeImH)][5] and [Cu(IDA)(ImH)H_2O)]·H_2O (-**I** in this work) with τ = 20.7 and 30.2% and deviation of ±0.07(2) Å and ±0.12(1) Å from the corresponding mean plane, P(1), respectively.

In **IV** the Cu-O(5^i) bond is longer than the Cu-O(apical) bond with water in the related compounds [Cu(CMT)H_2O)](Cu-OW = 2.242(4) Å)[11] and **I**(Cu-OW =

Table 3 Bond lengths (Å) and angles (deg.) for **I** and **IV** with e.s.d.s in parentheses

Compound **I**

Distance		Angle	
Cu-O(1)	2.00(1)	O(1)-Cu-O(3)	160.1(5)
Cu-O(3)	1.98(1)	O(1)-Cu-O(5)	99.4(5)
Cu-O(5)	2.37(1)	O(1)-Cu-N(1)	84.0(5)
Cu-N(1)	2.01(1)	O(1)-Cu-N(2)	94.5(6)
Cu-N(2)	1.94(2)	O(3)-Cu-O(5)	96.6(5)
O(1)-C(1)	1.25(3)	O(3)-Cu-N(1)	84.0(6)
O(2)-C(1)	1.28(2)	O(3)-Cu-N(2)	97.2(6)
O(3)-C(4)	1.29(2)	O(5)-Cu-N(1)	90.5(5)
O(4)-C(4)	1.23(2)	O(5)-Cu-N(2)	90.9(6)
N(1)-C(2)	1.51(2)	N(1)-Cu-N(2)	178.2(5)
N(1)-C(3)	1.50(3)	C(2)-N(1)-C(3)	117(1)
N(2)-C(5)	1.31(2)	C(5)-N(2)-C(7)	107(2)
N(2)-C(7)	1.39(2)	C(5)-N(3)-C(6)	106(2)
N(3)-C(5)	1.37(2)	O(1)-C(1)-O(2)	123(2)
N(3)-C(6)	1.38(3)	O(1)-C(1)-C(2)	122(2)
C(1)-C(2)	1.49(3)	O(2)-C(1)-C(2)	115(2)
C(3)-C(4)	1.47(3)	N(1)-C(2)-C(1)	109(1)
C(6)-C(7)	1.36(3)	N(1)-C(3)-C(4)	111(2)
		O(3)-C(4)-O(4)	120(2)
		O(3)-C(4)-C(3)	119(2)
		O(4)-C(4)-C(3)	121(2)
		N(2)-C(5)-N(3)	111(2)
		N(3)-C(6)-C(7)	106(2)
		N(2)-C(7)-C(6)	110(2)

Compound **IV**

Distance		Angle	
Cu-O(1)	1.95(1)	O(1)-Cu-O(3)	170.0(5)
Cu-O(3)	1.94(1)	O(1)-Cu-O(5)	89.0(5)
Cu-O(5)	2.44(1)	O(1)-Cu-N(1)	83.6(5)
Cu-N(1)	2.01(1)	O(1)-Cu-N(2)	96.3(5)
Cu-N(2)	1.95(1)	O(3)-Cu-O(5)	91.9(4)
O(1)-C(1)	1.26(2)	O(3)-Cu-N(1)	86.4(5)
O(2)-C(1)	1.21(2)	O(3)-Cu-N(2)	93.5(5)
O(3)-C(4)	1.27(2)	O(5)-Cu-N(1)	90.8(4)
O(4)-C(4)	1.23(3)	O(5)-Cu-N(2)	95.3(5)
O(5)-C(5)	1.42(2)	N(1)-Cu-N(2)	173.8(6)
N(1)-C(2)	1.51(3)	C(2)-N(1)-C(3)	118(1)
N(1)-C(3)	1.49(2)	C(7)-N(2)-C(9)	109(1)
N(2)-C(7)	1.35(2)	C(7)-N(3)-C(8)	112(2)
N(2)-C(9)	1.37(2)	O(1)-C(1)-O(2)	126(1)
N(3)-C(7)	1.37(2)	O(1)-C(1)-C(2)	117(1)
N(3)-C(8)	1.38(2)	O(2)-C(1)-C(2)	118(1)
C(1)-C(2)	1.54(3)	N(1)-C(2)-C(1)	108(1)
C(2)-C(5)	1.55(2)	N(1)-C(2)-C(5)	114(1)
C(3)-C(4)	1.55(3)	C(1)-C(2)-C(5)	111(1)
C(5)-C(6)	1.54(3)	N(1)-C(3)-C(4)	110(1)
C(8)-C(9)	1.38(3)	O(3)-C(4)-O(4)	125(2)
		O(3)-C(4)-C(3)	118(1)
		O(4)-C(4)-C(3)	117(1)
		O(5)-C(5)-C(2)	111(1)
		O(5)-C(5)-C(6)	111(1)
		C(2)-C(5)-C(6)	112(1)
		N(2)-C(7)-N(3)	105(2)
		N(2)-C(9)-C(8)	110(2)
		N(3)-C(8)-C(9)	104(2)
		O(3)-N(1)-O(4)	118.9(5)

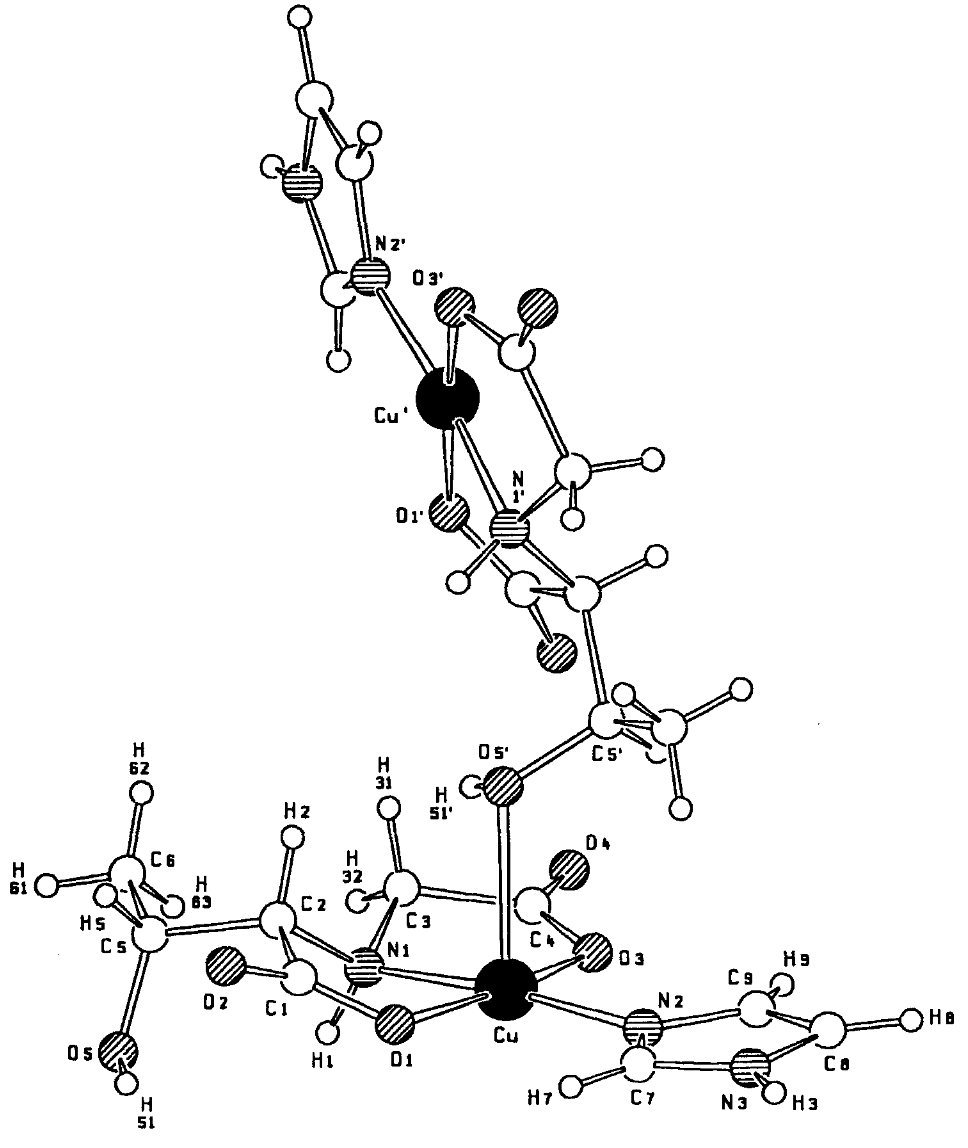


Figure 3 Perspective view of compound **IV** showing the unusual Cu(II) coordination of the side chain OH group from a neighbouring CMT (symmetry code i − 0.5 − x, y, 0.5+ z for primed atoms).

2.37(1)Å), but agrees well with the range of distances [Cu(II)-O(methanol) (2.16–2.60Å)] reported for a variety of cases, including [Cu(IDA)(ImH)(CH_3OH)]·0.37H_2O(2.438(7)Å).[3] Nevertheless, the coordinating role of the CMT side chain hydroxyl group is not established in the structure of or parent compound [Cu(CMT)(H_2O)][11] nor in those of [Cu(*L*-Thr)$_2$]·H_2O[20] and [Cu(*L*-His)(*L*-Thr)

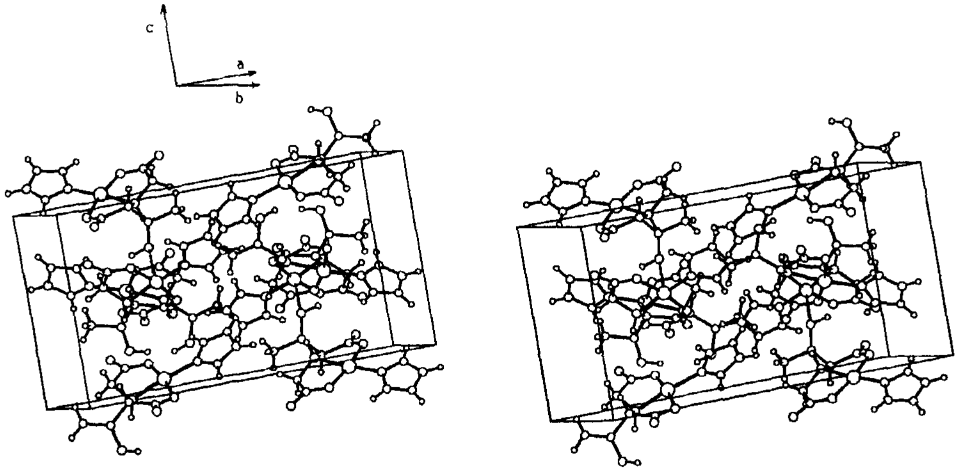


Figure 4 Stereo view of **IV** with Cu-O(5) bonds indicated as broken lines.

$(H_2O)]^{21}$ (*L*-thr = *L*-threonine, *L*-His = *L*-histidine). All other bonds in **IV** have normal values. The structure of **IV** consists of polymeric chains of [Cu(CMT) (ImH)]$_n$ linked together by hydrogen bonds N(1)-H(1)...O(4^{ii}) (3.20(2)Å, 168.2(8)°, ii = x, 0.5 - y, z - 0.5) and N(3)-H(3)...O(2^{ii})(2.80(2)Å, 172.7(9)°, iii = 1 - x, $-y$, $-z$). The hydroxyl group of CMT is not involved in hydrogen bonding.

Appropriate comparisons of the structures of **I**, **IV** and [Cu(CMT)(H_2O)] reveal interesting structural correlations. As expected, the ImH ligand in **IV** is linked to the Cu(II) atom *trans* to the Cu-N(CMT) bond and the two Cu(CMT) chelate rings exhibit a nearly coplanar conformation (dihedral angle between mean planes = 15.6°). However, compound **IV** does not show a shortening of the Cu-N(CMT) bond (2.01(1)Å in **IV** and 1.982(5) Å in the parent compound [Cu(CMT) (H_2O)]). In contrast, the Cu-N(IDA) bond in [Cu(IDA) $(H_2O)_2$](2.014(3)Å) is shortened in [Cu(IDA)(ImH)(CH_3OH)]·0.37H_2O (1.977(7) Å, ϕ = 25.1°). The available data reveal that the shortening of the Cu-N(IDA) bond by *trans*-coordination of one ImH ligand applies in Cu(II) complexes with unsubstituted IDA if the dihedral angle between the Cu(IDA) chelate rings (ϕ) is lowered from 73° in [Cu(IDA)$(H_2O)_2$] to ϕ 15°. This is not attained in **I** (ϕ = 25.1°) and it seems ruled out for Cu(II) complexes with *C*-substituted-IDA such as CMT. Indeed, the coordination of ImH in **IV** instead of H_2O in [Cu(CMT)(H_2O)]^{11} produces an opening of ϕ from 23.4° to 15.6°, and a lengthening of the Cu-N(CMT) bond from 1.982(5) to 2.01(1) Å. In addition, the noticeable flexibility of unsubstituted IDA for Cu(II) coordination is also reflected in the nearly perpendicular conformation of the Cu(IDA) chelate rings established in complexes with a Cu(II):IDA:*N*-heterocyclic donor ratio of 1:1:2 like **II**, [Cu(IDA)$(ImH)_2]_2$·2H_2O (ϕ = 83.1°)[4] and [Cu(IDA)(2,2'-bipy)]·6H_2O.[6] In clear contrast, all our attempts to obtain ternary Cu(II) complexes with CMT and two ImH or one bidentate 2,2-bipy have failed.[20]

The anhydrous compound **IV** decomposes at 473–730 K to give impure CuO (cald. 25.93, found 29.52%). The IR spectrum (cm^{-1}) shows ν(O-H) of the hydroxyl side chain (3430), N-H of ImH (3240, 1550 shoulder) and N-H (3180+3150, 1505) and carboxylate groups (1625, 1580 shoulder, 1400) of the CMT ligand.

The electronic spectrum shows the expected d-d band with ν_{max} = 15,725 cm^{-1} (14,340 cm^{-1} for $[Cu(CMT)(H_2O)]$[11] and 14,750 cm^{-1} in $[Cu(IDA)(5MeImH)]\cdot H_2O$).The ESR spectrum at 298K is of the "reverse" type with $g_{\parallel} = 2.06$ and $g_{\perp} = 2.20$ (2.06 and 2.19 for $[Cu(CMT)(H_2O)]$[11]). The lack of hyperfine structure in this spectrum is in accord with intermolecular exchange (shortest distance $Cu\text{-}Cu^{ii} = Cu\text{-}Cu^{iv} = 5.642(3)$ Å with ii = x, $0.5 - y$, $-0.5 + z$ and iv = x, $0.5 - y$, $0.5 + z$).

On the basis of the results of this and related work we conclude that C-(1-hydroxyethyl)-substitution in the iminodiacetate skeleton introduces steric constrains which permit the roughly in-plane Cu(II) coordination of a terdentate *N*-(carboxymethyl-*D,L*-threoninate(2-) ion and one H_2O[11] or ImH (this work) unidentate. On the other hand, in contrast with the nearly perpendicular configuration of the two five-membered chelate rings in the Cu(IDA) moiety of ternary Cu(II) complexes of IDA and H_2O[2] or two *N*-heterocyclic donors (as two ImH[4] or one 2,2'-bipy[6]), it seems clear that the *C*-(1-hydroxyethyl)-substitution in IDA to give CMT makes it unable to chelate the copper(II) ion with a perpendicular configuration of the chelate rings. It is interesting to note that such perpendicular chelate rings involve the formation of two short and one long bonds around the distorted Cu(II) coordination polyhedron.

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