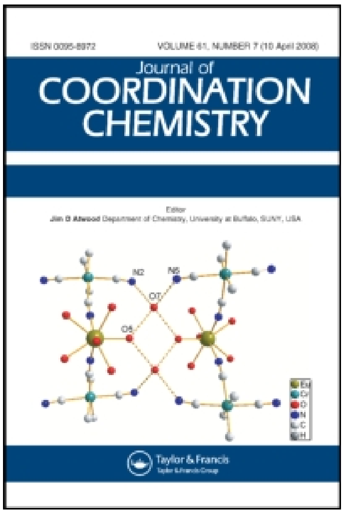

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COPPER(II) COMPLEXES OF N-CARBOXYMETHYL-D,L-THREONINE IN AQUEOUS SOLUTION. STRUCTURE OF AQUA (N-CARBOXYMETHYL-D,L-THREONINATO (2-)) COPPER(II)

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Formation constants for Cu(II) complexes with *N*-carboxymethyl-*D,L*-threonine ($H_2CMT = H_2L$) have been determined ($I = 0.1M$ KNO_3, 25°C) using the HYPERQUAD program with 652 potentiometric data from the titration of twelve solutions having different H_2L concentrations and/or Cu(II)/H_2L ratios. Refined values of long β_{pqr} for the species $Cu_pL_qL_r$ = CuL, CuL_2, CuL(OH) and $CuL(OH)_2$ allow simulation of experimental titration curves with good agreement.

Aqua (*N*-carboxymethyl-*D,L*-threoninato (2-)) copper(II) was synthesized and studied by X-ray diffraction and other physical methods. The structure (monoclinic system, space group $P2_1/c$, final $R = 0.044$ and $R_w = 0.051$) consists of infinite zigzag chains of [Cu(CMT) (H_2O)] groups linked together by hydrogen bonds. The Cu(II) atom exhibits square pyramidal coordination with an additional sixth weak interaction (Cu–O = 2.568(4)Å) which involves a terdentate-bridged carboxylate group closely related to that already claimed in the structure of [Cu(CMPhe) (H_2O)], with CMPhe = *N*-carboxymethyl-*L*-phenylalaninato (2−).

KEYWORDS: copper(II), *N*-carboxymethyl-D,*L*-threonine, stability constants, X-ray structure

INTRODUCTION

Several papers on iminodiacetato(IDA)-copper(II) chelates with water,[1] imidazole (ImH)[2,3] or bipyridines (2,2′- or 4,4′-bipy)[4,5] and closely related ligands[6] have reported significant structural data concerning the Cu-N(IDA) bond length, preferences of the heterocyclic nitrogen atom for specific coordination position(s) around the Cu(II) atom, and the nearly coplanar or perpendicular conformation of the two

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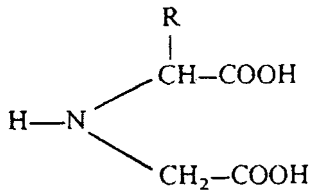
five-membered chelate rings in the Cu(IDA) moiety as a consequence of the number of heterocyclic *N*-donor atoms per copper(II) centre.[4]

To verify the scope of the above findings we have studied a selected of *C*- and *N*-substituted derivatives of H_2IDA and/or ImH[6] derivatives. We have prepared *N*-carboxymethyl-*D,L*-threonine (H_2 CMT = H_2L).[7] There are no references in the literature to copper(II)/H_2CMT systems in solution or solid state.[7] The aim of the present work is to address this deficiency.



R	Acid
$-H$	H_2IDA
$-\underset{\displaystyle OH}{\underset{\vert}{CH}}-CH_3$	H_2CMT

EXPERIMENTAL

N-carboxymethyl-D,L-threonine ($H_2CMT = H_2L$)

This compound was obtained in good yield (75%) as reported earlier[7] by reaction of chloroacetic acid and *D,L*-threonine potassium salts (mol ratio 2:1) in alkaline (KOH) aqueous solution at room temperature. The procedure has several advantages[7] as against those proposed by Snyder and Angelici[8] and by Miyazawa (with 40% yield).[9]

Aqua(N-carboxymethyl-D,L-threoninato(2-))copper(II)

This compound was obtained by reacting H_2CMT (354 mg, 2 mmol) and $Cu_2CO_3(OH)_2$ (221 mg, 1 mmol) in water (150 ml), heating (60°C) and stirring under vacuum to remove CO_2. The resulting solution was left to cool and then filtered. Evaporation at room temperature yielded clear, blue crystals of the desired product, and which were twice recrystallized from water, filtered off and air-dried. Yield: 85%. Calcd. for $C_6H_{11}CuNO_6$: C, 28.07; H, 4.32; N, 5.46; Cu, 24.75; H_2O, 7.02. Found: C, 28.04; H, 4.31; N, 5.59; Cu, 24.5 ± 0.5%; H_2O (TG), 6.72 ± 0.2%.

Potentiometric study and formation constant calculations

All solutions were prepared with CO_2-free, doubly distilled water. Stock solutions of recrystallized H_2CM (anhydrous)[7] and $CuNO_3 \cdot 3H_2O$ (AGR, Merck) were titrated by conventional alkalimetric and complexometric[10] methods, respectively.

The starting solutions for the potentiometric study were carefully prepared by dilution with water into volumetric flasks (100 ml) of the required amount of H_2CMT, copper(II) nitrate and background electrolyte (KNO_3 1M) stock solutions. Solutions with Cu(II)/H_2CMT ratios about equal to 0.25/1, 0.50/1, 1/1 and 2/1 with three different H_2L concentrations for each metal/ligand ratio were used. Aliquots (50 ml) of these twelve solutions were titrated against CO_2-free, standarized KOH (0.1M) solution. The titrant and the mixed metal/ligand solutions were prepared with ionic strength $I = 0.1$ mol dm^{-3} in KNO_3. The potentiometric measurements were made using a Metrohm Dosimat 665 Titroprocessor equipped with a Crison 2002 digital (mV/pH)-meter and a combined Ingold electrode (internal reference Ag/AgCl). Temperature in the reaction cell was maintained at 25.00±0.05°C by circulating thermostatted water and the titrations were performed under a slow and constant stream of pre-saturated (KNO_3, 0.1 mol dm^{-3}) N_2. The standard electrode potential E°, the concentration of the KOH solution and $Kw = 0.166.10^{-13}$ were determined before and after each experiment by titration of a known amount of HCl in 0.1 mol dm^{-3} KNO_3 with KOH by a similar procedure to that of Leporati.[11,12]

The determination of the equilibrium model and Cu(II) complex formation constants ($\log\beta_{pqr}$) defined as

$$pCu + qL + rH \rightleftharpoons Cu_pL_qH_r; \beta = [Cu_pL_qH_r]/[Cu]^p[L]^q[H]^r$$

(charges omitted for simplicity) were carried out with 625 data from twelve solutions using the HYPERQUAD program supplied by Prof. A. Vacca.[13] Unlike the SUPERQUAD[14] program for the treatment of potentiometric data, HYPERQUAD can treat potentiometric and/or spectrophotometric data. The range of starting concentrations were 1.76×10^{-4} to 6.03×10^{-3} mol dm^{-3} for Cu(II) and 7.05×10^{-4} to 3.18×10^{-3} mol dm^{-3} for H_2CMT. To avoid the influence of metal ion hydrolysis, the data for three solutions with $Cu(II)/H_2L = 2$ (metal excess) fall in the range $2.25 \leq pH < 3.70$. The data of the other nine solutions with $Cu(II)/H_2L \leq 1$ fall in the range $2.30 \leq pH \leq 10.94$. Overall protonation constants of H_2CMT were determined previously[7] with the same conditions and methods ($\log\beta_{11} = 8.73(1)$, $\log\beta_{12} = 11.22(1)$ and $\log\beta_{13} = 12.76(2)$); these were introduced as fixed values in the refinement of complex formation constants ($\sigma_V = 0.002$ and $\sigma_E = 0.1$ mV were used). Protonation constants of the ligand and Cu(II) complex formation constants were used for simulation of a potentiometric curve set by using the HYDRAPH subprogram of HYPERQUAD.[13]

X-ray diffraction, structure solution and refinement

Crystals suitable for X-ray diffraction were obtained by slow evaporation of an aqueous solution of the complex. Data collection was carried out using a sky-blue crystal of dimensions 0.05 × 0.10 × 0.25 mm at 293K on an automated CAD4 diffractometer (Enraf-Nonius, Delft). MoKα radiation ($\lambda = 0.71073$Å) and the w/2θ scan technique were used throughout the experiment. Cell parameters were determined from 25 high angle settings ($4.6 < \theta < 15.0$). Of 3767 reflections measured, 1495 independent reflections with $I > 3\sigma(I)$ were used in structure solution and refinement. The space group ($P2_1/c$) was evident from systematic absences. Direct methods were applied for the structure solution. All non-hydrogen atoms were refined with anisotropic displacement factors. Hydrogen atoms were located in a difference map and refined with B_{iso} fixed at 4.0Å^2. Empirical absorption[15] and extinction corrections[16] were applied. Refinement converged at $R = 0.044$ ($R_w = 0.051$) with a final shift to error ratio of 0.001 for 161 parameters refined**. The most intense peak in the final Fourier map was 0.50 eA^{-3}. Programs used were VAX-SDP,[17] SHELXS86,[18] and SCHAKAL.[19]

**Further details of the structure determination and full lists of thermal parameters, H atom positions and observed and calculated structure factors are available from the authors upon request.

Physical measurements

TG, DTA and IR data were recorded as in previous papers.[5,6] Reflectance spectra were recorded on a Perkin-Elmer Lamda 15 spectrophotometer. The ESR spectrum was obtained using a Brucker 200 spectrometer.

RESULTS AND DISCUSSION

Solution Study

Formation constants for the Cu(II) complexes with *N*-carboxymethyl-*D,L*-threonine (H_2CMT) are given in Table 1. Under the experimental conditions of this work, no complex with protonated forms of CMT^{2-} ion are present. In contrast, we have obtained reliable values for stability constants of the mono- and di-hydroxo ternary complexes with pqr = 11 – 1 and 11 – 2, respectively. This is noticeable because in the copper(II)-iminodiacetato (IDA or *N*-carboxymethylglycinato) system it is well known that the Cu(IDA) complex undergoes alkaline hydrolysis to give Cu(IDA) $(OH)^-$ followed by disproportion to $Cu(IDA)_2^{2-}$ (in solution) and $Cu(OH)_2$ (precipitate).[20] The stability constant of Cu(IDA) $(OH)_2^{2-}$ remains unknown.[21] It seems reasonable to suppose that the C-(1-hydroxyethyl)-substituent present in the IDA skeleton to give the CMT ligand will increase the solubility of its "products" in a polar solvent such as water. Indeed H_2CMT is clearly more soluble than H_2IDA in aqueous solution.[7]

Appropriate comparison of formation constants reveals that the Cu(II)-CMT complexes are of comparable stability to those of IDA and various *C*-alkyl or *C*-hydroxyalkyl-IDA complexes with Cu(II). For example logβ values for CuL complexes are 10.57, 10.97, 10.93 and 10.83 for H_2IDA, *N*-carboxymethyl-*L*-valine, *N*-carboxymethyl-*L*-serine and H_2CMT, respectively.

Protonation constants of the ligand[7] and formation constants for its copper(II) complexes allows simulation of the potentiometric titration curves with reasonably good agreement with experimental data points (Fig. 1). To obtain a more complete view of the Cu(II)/H_2CMT system it is interesting to consider species distribution diagrams for representative mixed Cu(II)/H_2CMT solutions (Fig. 2). In equimolar solution, CuL is the most abundant species in acid with maximum abundance near pH = 6. This neutral complex undergoes hydrolysis in alkaline solution to give $CuL(OH)^-$ and $CuL(OH)_2$. No precipitation occurs in the concentration range of our experiments. In solutions with Cu(II)/H_2CMT = 1/2, the maximum concentration of CuL (with 50% free ligand) is reached at pH = 4.5. As pH becomes less

Table 1 Copper(II) complex formation constants with *N*-carboxymethyl-*D,L*-threonine (standard deviations are given in parentheses; Z = 625[a], χ^2 = 21.18[b], σ = 3.87[c]).

Complex	pqr	logβ
CuL	110	10.83(1)
CuL_2	120	15.71(1)
CuL (OH)	11-1	1.95(1)
CuL $(OH)_2$	11-2	–8.25(1)

[a]Total number of experimental data points used in the refinement.
[b]Observed value of the goodness of fit.
[c]Sample standard deviation as defined in ref. 14.

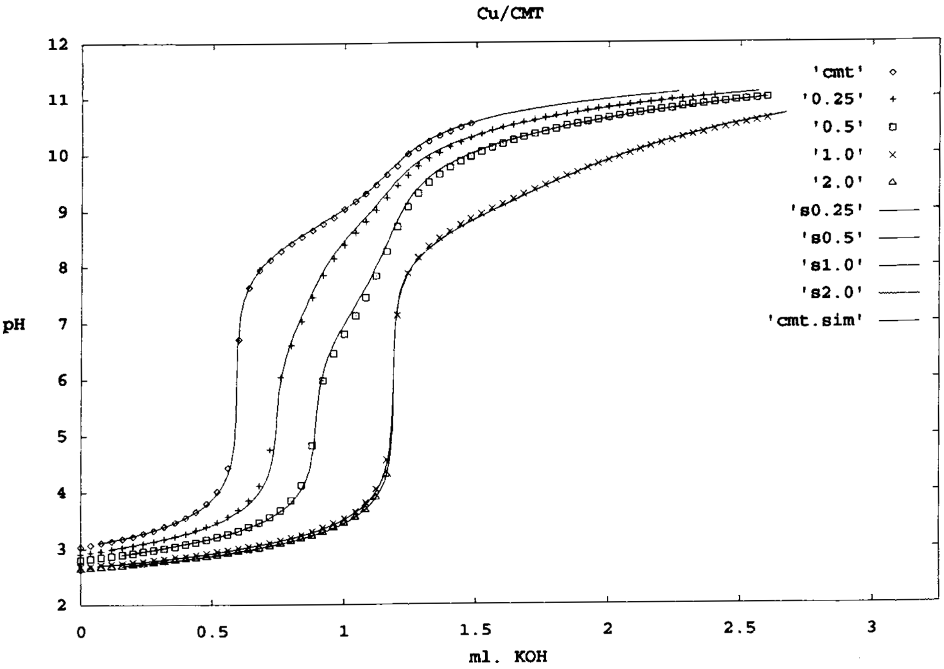


Figure 1 Titration pH data points for H_2CMT and $Cu(II)/H_2L$ solutions with corresponding simulated curves as a function of the volume of KOH added. $C_{HL} = 1.79.10^{-3}$ M, $C_{KOH} = 0.099$ M, $V_o = 50$ ml.

acid, CuL and HL give the anionic complex CuL_2 and free ligand L and the hydroxo complexes CuL(OH) and $CuL(OH)_2$. The formation of these ternary hydroxo-species plays an important role in basic solution by limiting the presence of CuL_2 (82% of CMT at pH = 8.8), and promoting the formation of free ligand (010) and the soluble anionic hydroxo species (11-1 and 11-2). It is evident that in an equimolar solution of Cu(II) and H_2CMT with pH 6 to 7 (Fig. 2-a) it is possible to attempt the crystallization of a solid compound with tentative formula Cu(CMT) $\cdot nH_2O$. The synthesis reported in the experimental part uses an equimolar Cu (II)/ligand ratio and a pH value near to neutrality and avoids the presence of counter-ions and by-products.

Crystal and molecular structure of [Cu(CMT) (H_2O)]

A summary of crystal data is given in Table 2. Positional parameters and bond lengths and angles are given in Tables 3 and 4, respectively. A drawing of the complex [Cu(CMT) (H_2O)] with the atom numbering scheme is shown in Figure 3. Each Cu(II) atom is bonded to one water molecule and two CMT ligands. From Figure 3, we can consider the copper(II) atom to lie in a slightly distorted square pyramid (type 4 + 1) involving four short bonds to the atoms N, O(11) and O(41) from one terdentate CMT ligand and the O(42) atom from the CMT ligand of an adjacent complex unit (related to the former by the symmetry code ii = $-x, 0.5+y,$

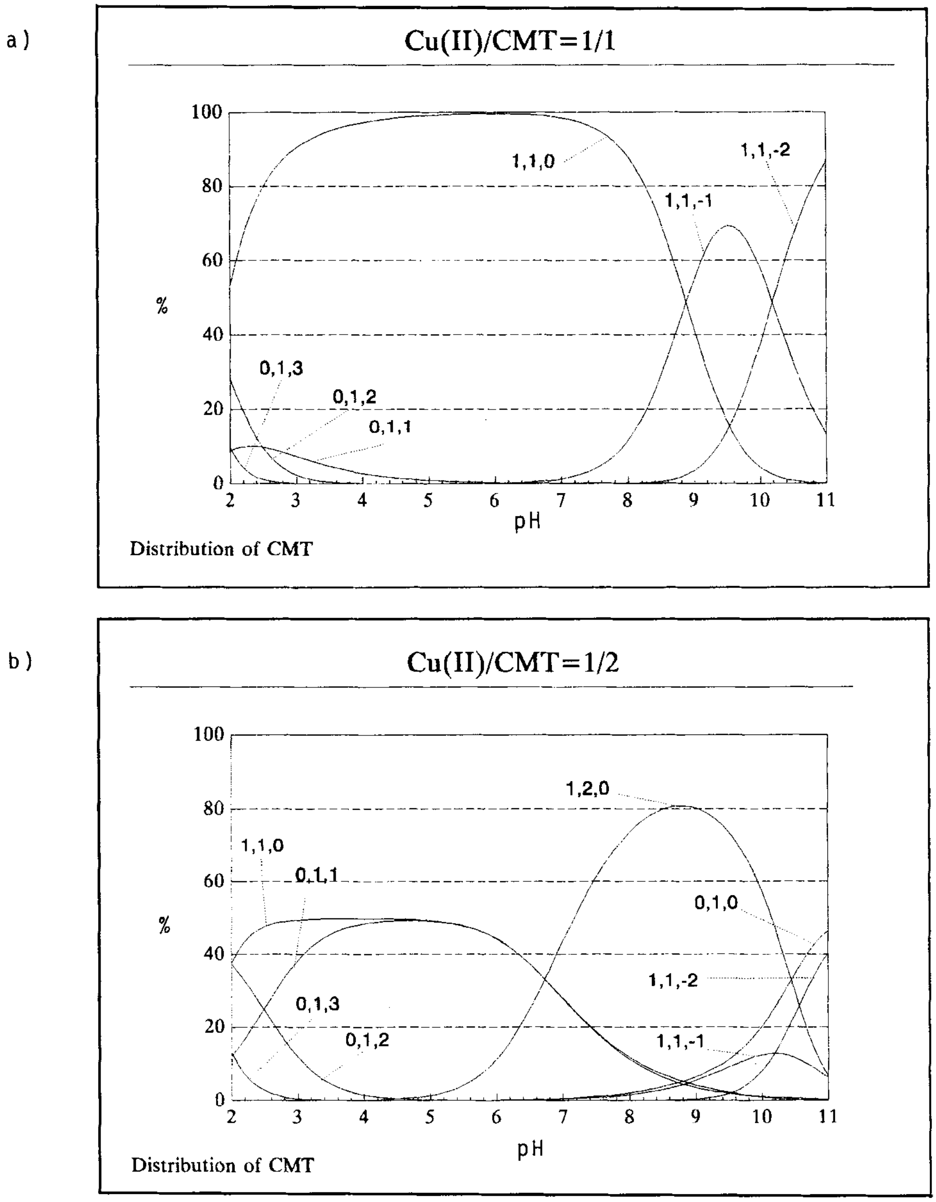


Figure 2 Distribution of species (%) in representative mixtures for the H_2CMT-Cu(II) system.

0.5 - *z*). The copper(II) atom is typically displaced (0.269Å) from the mean plane P(1) of the base atoms towards the fifth ligand, that is the O atom of the apical water molecule. The compound exhibits a polymeric zigzag chain structure which extends parallel to the *b* axis, with adjacent units related each other by the binary screw axis

Table 2 Crystal data for [Cu (CMT) (H_2O)].

Chemical formula	$C_6H_{11}CuNO_6$
Formula weight	256.70
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 13.330 (5)
	b = 5.978 (1)
	c = 12.469 (4) Å
	β = 115.45 (1)°
	V = 897.3 (8) Å^3
Z	4
d_{calc}	1.900
F (000)	524
$\mu_{MoK\alpha}$ (mm)	2.442

of symmetry. Moreover, it is interesting to consider one additional weak interaction between the Cu(II) atom and the O(41^{ii}) atom (2.568(4) Å) belonging to the same carboxylate group as O(42) atom in Figure 3. This means that the carboxylate group from the *C*-unsubstituted arm of CMT takes part simultaneously in the chelation of the Cu(II) ion and in a typically unsymmetrical double interaction[22–24] with the Cu(II)^i atom. On this basis, the copper(II) coordination polyhedron might be described as the type 4 + 1 + 1*, where 1* corresponds to the weak Cu-O interaction.[22,24] Recently, we reported the crystal structure of the closely related compound [Cu(CMPhe)(H_2O)] (CMPhe = *N* - carboxymethyl-*L*-phenylalaninate (2 -) ion) with a terdentate carboxylate group involved with copper(II) coordination, where the distance of the corresponding weak Cu-O interaction is 2.665(5) Å. In that complex, the terdentate carboxylate group belongs to the *C*-benzyl-substituted arm of the CMPhe ligand. The same structural type of terdentate-bridged carboxylate group is known in nitrilotriacetates of praseodymium(III)[27] and of neodymium(III).[27]

Other structural features in the studied compound worthy of note are the nearly coplanar glycinate-Cu(II) rings (with dihedral angle Ø between mean planes P(2) / P(3) of 23.4 (3)°). This CMT conformation agrees well with that of CMPhe

Table 3 Fractional positional parameters for the atoms in [Cu($C_6H_9NO_5$) (H_2O)] with e.s.d.s. in parentheses (for numbering see Fig. 3).

Atom	*x/a*	*y/b*	*z/c*	*B* (Å^2)
Cu	0.11486(5)	0.1836(1)	0.38024(5)	1.576(9)
O1	0.1747(3)	- 0.0610(8)	0.5311(3)	2.53(9)
O11	0.2000(3)	0.4487(8)	0.4553(3)	2.39(8)
O12	0.3106(3)	0.7020(8)	0.4327(4)	3.0(1)
O20	0.4477(4)	0.2261(9)	0.4737(4)	3.5(1)
O41	0.0326(3)	- 0.0514(8)	0.2650(3)	1.92(7)
O42	- 0.0210(3)	0.2825(7)	0.3977(3)	2.01(8)
N	0.2270(3)	0.1422(7)	0.3170(3)	1.40(8)
C1	0.2652(4)	0.515(1)	0.4113(5)	2.1(1)
C2	0.2841(4)	0.3598(9)	0.3241(5)	1.8(1)
C3	0.1702(4)	0.041(1)	0.1989(5)	2.7(1)
C4	0.0690(4)	- 0.085(1)	0.1886(4)	1.7(1)
C20	0.4077(4)	0.329(1)	0.3595(5)	2.6(1)

Table 4 Bond lengths (Å) and angles (deg.) for [Cu (CMT) (H_2O)]*.

Lengths			
Cu-O(1)	2.242(4)	O(42)-C(4)	1.265(6)
Cu-O(11)	1.940(4)	N-C(2)	1.491(7)
Cu-O(41)	1.972(4)	N-C(3)	1.468(7)
Cu-O(42)	2.003(4)	N-H(1)	0.91(9)
Cu-N	1.982(5)	C(1)-C(2)	1.53(1)
O(11)-C(1)	1.274(9)	C(2)-C(20)	1.523(8)
O(12)-C(1)	1.246(8)	C(3)-C-(4)	1.501(9)
O(20)-C(20)	1.427(8)	C(20)-C(21)	1.51(1)
O(41)-C(4)	1.259(8)		
Angles			
O(1)-Cu-O(11)	101.8(2)	O(11)-C(1)-O(12)	123.0(6)
O(1)-Cu-O(41)	91.9(2)	O(11)-C(1)-C(2)	118.0(5)
O(1)-Cu-O(42)	96.5(2)	O(12)-C(1)-C(2)	118.9(6)
O(1)-Cu-N	101.2(2)	N-C(2)-C(1)	109.6(5)
O(11)-Cu-O(41)	163.9(2)	N-C(2)-0(20)	111.8(5)
O(11)-Cu-O(42)	94.3(2)	C(1)-C(2)-C(20)	110.8(4)
O(11)-Cu-N	84.8(2)	N-C(3)-C(4)	110.5(5)
O(41)-Cu-O(42)	92.6(2)	O(41)-C(4)-O(42)	121.6(5)
O(41)-Cu-N	84.3(2)	O(41)-C(4)-C(3)	118.7(5)
O(42)-Cu-N	162.0(2)	O (42)-C(4)-C(3)	119.6(6)
C(2)-N-C(3)	116.8(5)	O(20)-C(20)-C(2)	103.6(5)
C(2)-N-H(1)	106(6)	O(20)-C(20)-C(21)	112.1(7)
C(3)-N-H(1)	115(6)	C(2)-C(20)-C(21)	113.9(4)

* Numbers in parentheses are estimated standard deviations.

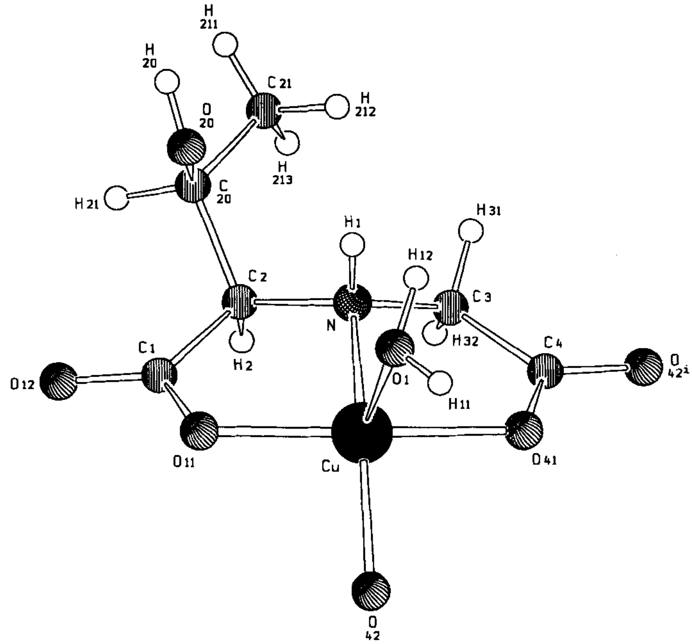


Figure 3 Perspective view of the complex unit showing the atom numbering scheme and the copper(II) coordination geometry (Cu-O (41^{ii}) and Cu^i-O (41) (2.568 (4) Å) omitted). Symmetry codes i: $-x$, y–0, 5, 0.5 − z; ii: $-x$, 0.5 + y, 0.5 − z.

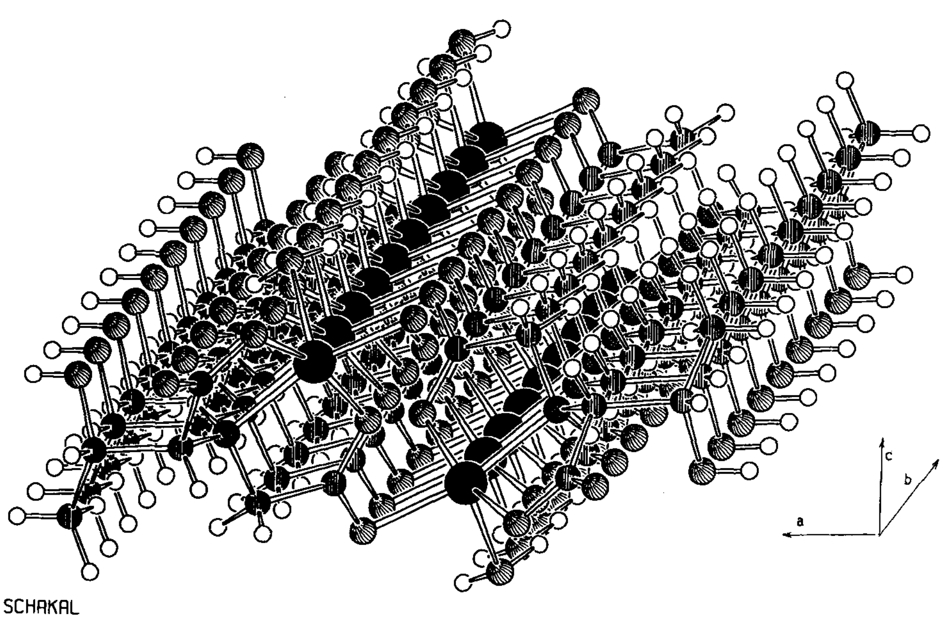


Figure 4 A SCHAKAL drawing of the repeating infinite zigzag chain along the *b* axis in the *ca* plane of [Cu (CMT) (H_2O)].

in [Cu(CMPhe)(H_2O)][25] (Ø = 21.7°), but contrast with the nearly perpendicular chelate rings in [Cu(IDA)$(H_2O)_2$][1] Ø = 73°). The presence of the terdentate carboxylate group in both [CuL (H_2O)] compounds is consistent with short Cu - Cu^{i} distances (4.507 (1) Å for L = CMT, 4.566 (1) Å for L = CMPhe[25]). The hydroxyl group of CMT is not involved in coordination. Neither OH group of *L*-threoninate (L-thr) is bonded to Cu(II) in [Cu(*L*-thr)$_2$].H_2O[28] and [Cu(*L*-His)(*L*-thr)(H_2O)][29] (*L*-His = *L*-histidinate ion).

In the crystal of the studied compound the zigzag chains are hydrogen bonded. The N-H bond of CMT is involved in one unsymmetrical bifurcated hydrogen bond with the hydroxyl atom O(20) of the same ligand and with the carboxylate atom O(12^{iii}) of an adjacent chain of complexes (symmetry code iii = x, $y - 1$, z). Also, both H atoms of the water molecule are hydrogen bonded, one to the O(12^{iii}) atom and the other to O(42^{iv}) (iv = $-x$, $-y$, $1 - z$).

The apical water molecule is lost at 415–450K. Pyrolysis of the organic ligand (483–633K) yields a residue of CuO (calc. 30.6%, exp. 31.5%). The reflectance spectrum shows an unsymmetrical d-d band with ν_{max} = 14,340 cm^{-1} and the ESR spectrum at 298K is of the "reverse" type with $g_{\parallel}$ = 2.06 and $g_{\perp}$ = 2.19. The lower g value is consistent with a $d_{x^2-y^2}$ ground state for Cu(II). IR spectra show the expectable bands (cm^{-1}) for H_2O ($\nu \sim 3450$, δ 1650, π 680), and for the CMT ligand: hydroxyl ($\nu \sim 3450$, $\delta \sim 1600$), N-H (ν 3240, δ 1510 shoulder), carboxylate (ν_{as} 1580 and 1590, ν_s 1380). The assignment of the first TG-DTA step to the loss of H_2O has been confirmed by the absence of the δ (H_2O) band (1650 cm^{-1}) in the IR spectrum of a sample heated in the thermobalance to 460K.

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