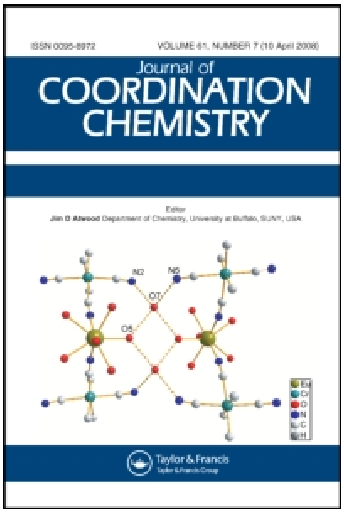

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A COPPER(II) COMPLEX CONTAINING THE PROTONATED FORM OF A DIAMINOPENTACARBOXYLIC ACID WITH AN UNSYMMETRICAL SKELETON

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A COPPER(II) COMPLEX CONTAINING THE PROTONATED FORM OF A DIAMINOPENTACARBOXYLIC ACID WITH AN UNSYMMETRICAL SKELETON

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Crystalline samples of $CuH_3L\cdot 3.5H_2O$ (L = anion of *N,N,N',N'*-tetrakis(carboxymethyl)-2,4-diaminobutyric acid; $H_5TDB = H_5L$) have been characterized by X-ray diffraction and other methods. The compound crystallizes in the monoclinic system, space group $P2_1/n$ ($a = 6.260(2)$, $b = 18.505(5)$ $c = 15.659(3)$ Å, $\beta = 91.78(3)°$ and $Z = 4$). Final $R = 0.049$ and $R_w = 0.054$ for 1400 independent observed reflections. The structure consists of one-dimensional chains of CuH_3L complex units and non-coordinated water molecules linked together in a network of hydrogen bonds. Only two [H(062) and H(N2)] of the three "acid" hydrogen atoms of the ligand (H_3L^{2-}) have been located in the structure. Each H_3L^{2-} anion acts as a tetradentate chelating agent for a Cu(II) ion by means of the C-substituted hydrogen nitrilotriacetato (NTA) group (Cu-N(1) 2.026(9), Cu-O(11) 1.971(8), Cu-O(81) 2.003(8) and Cu-O(61) 2.186(6)Å. The O(11) and O(61) atoms are part of carboxylato and carboxylic groups, respectively. The distorted five coordination of each Cu(II) ion is achieved by a rather short Cu-O(121^i) bond (1.893(8)Å) with a carboxylate oxygen atom of the zwitterionic *N*-carboxymethyl-glycinato group in the adjacent CuH_3L unit. The C(10)-carboxy group of the ligand IDA group exhibits two different statistical configurations with an unequal ratio of C-O distances. In addition, two and half water molecules in the formula $CuH_3TDB\cdot 3.5H_2O$ were also disordered. The Cu(11) coordination polyhedron is best described as an intermediate state between a trigonal bipyramid (wtih N(1) and O(121^i) apices) and a square-based pyramid (with O(61) apex) both correlated by the "Berry twist" mechanism.

KEYWORDS: copper(II), diaminopentacarboxylic acid, crystal structure, properties

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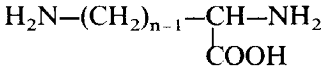
INTRODUCTION

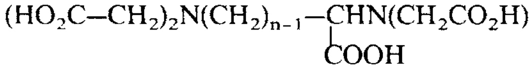
N,*N*,*N'*,*N'*-tetrakis(carboxymethyl) substitution of α,ω-diamino-carboxylic acids(**I**) yields the corresponding α-carboxypolymethylenediaminotetraacetic acids(**II**):



$H_2N{-}(CH_2)_{n-1}{-}\underset{\displaystyle COOH}{\underset{|}{CH}}{-}NH_2$

I

n = 2, 2,3-diaminopropionic acid (Hdap)
n = 3, 2,4-diaminobutyric acid (Hdab)
n = 4, ornithine
n = 5, lysine



$(HO_2C{-}CH_2)_2N(CH_2)_{n-1}{-}\underset{\displaystyle COOH}{\underset{|}{C}}HN(CH_2CO_2H)_2$

II

n = 2 H_5CEDTA
n = 3 $H_5TDB = H_5L$
n = 4 H_5TCO
n = 5 H_5TCL

The synthesis of the Hdap derivative in **II**[1,2], namely α-carboxyethylenediaminotetraacetic acid (H_5CEDTA)[1,2] has promoted extensive work on the stoichiometry and stability of metal-chelates of the four acids (**II**) in solution.[3–11]

We note that the *N*,*N*,*N'*,*N'*- tetrakis(carboxymethyl)diaminoacids **II** consist of one C-substituted nitrilotriacetic acid (NTA) group and one N-substituted iminodiacetic acid (IDA) group linked together by a central polymethylene $(CH_2)_{n-1}$ chain. Indeed, the properties of the higher (n = 3 to 5) members of these acids have been correlated with the ability of the NTA and IDA groups to cooperate or to compete in chelation of a variety of metal(II) ions.[10] In dilute aqueous solutions ($\sim 10^{-3}$M) of first-row transition metal(II) ions, these ligands yield MH_2L, MHL, ML or M_2L_2 and M_2L complexes (as well as $M_2L(OH)$ and/or $M_2L(OH)_2$ hydroxo-species).[6,10] In more concentrated acid solutions, neutral MH_3L species would be expected. Indeed, the molecular and crystal structure of the complex $[Cu(H_3DTPA)]\cdot H_2O$ containing diethylenetriaminepentaacetic acid (H_5DTPA) was reported some years ago. [12] On this basis and as a part of our programme on "acid" copper(II) chelates with *N*-(carboxymethyl)aminoacid derivatives, we attempted to isolate $CuH_3L\cdot nH_2O$ compounds for the four known members of the acid series (**II**).

The reaction of stoichiometric amounts of the acids with copper(II) hydroxycarbonate in water yields concentrated solutions of the hypothetical CuH_3L complexes. However, these strongly acid solutions lead to the precipitation of free acid H_5L and then form a blue glass, except for the case of $H_5L = H_5TDB$ which gives crystalline samples of $CuH_3TDB\cdot 3.5H_2O$ (hereafter $CuH_3L\cdot 3.5H_2O$). All attempts to obtain analogous Cu(II) compounds with the other three acids and $MH_3TDB\cdot nH_2O$ (with M = Co, Ni and Zn) were unsuccessful.

EXPERIMENTAL

Ligand synthesis

N,*N*,*N'*,*N'*-tetrakis(carboxymethyl)-2,4-diaminobutyric acid ($H_5TDB = H_5L$) was prepared as its dihydrate by condensation of *D*,*L*-2,4-diaminobutyric acid dihydrochloride (Sigma) and chloroacetic acid in alkaline medium (KOH) by the method reported earlier.[13]

$CuH_3L \cdot 3.5H_2O$ synthesis

This compound is obtained in aqueous solution by reaction of $H_5TDB \cdot 2H_2O$ and $Cu_2CO_3(OH)_2$ (Merck) in a molar ratio of 2:1. To 1.30 mmol of $H_5TDB \cdot 2H_2O$ in 100 cm^3 of CO_2-free water, 0.65 mmol of $Cu_2CO_3(OH)_2$ was added and the reaction mixture heated (60–70°C) and stirred *in vacuo* to remove the CO_2 by-product until a clear blue solution was obtained. The solution was left to cool slowly and then filtered *in vacuo*. After several days, evaporation at room temperature yielded an abundance of well-shaped crystals of the desired product, which was filtered, washed with cold water and air-dried. The product was recrystallized from hot water (70°C). Yield 90%. Anal: calcd. for $C_{12}H_{23}CuN_2O_{13.5}$: C, 3.35; H, 4.88; N, 5.90; Cu, 13.38; H_2O, 13.28%. Found: C, 30.39; H, 4.86; N, 5.96; Cu, 13.2 (complexometry); H_2O, 11.55% (TG, 293–423K). Molecular weight: calcd: 474.86; exp: 467 ± 4 (potentiometry). The crystals of $CuH_3TDB \cdot 3.5H_2O$ lose water easily on heating (up to 10% from room temperature to 363 K) and old samples (or those washed with ethanol or acetone) of the product yield analytical results for $CuH_3L \cdot nH_2O$ with $n < 3.5$.

X-ray structure determination

Crystallographic measurements were made at room temperature using an Enraf-Nonius CAD-4 diffractometer with graphite-monochromatized MoKα radiation and a crystal with dimensions 0.36 × 0.25 × 0.17 mm. Intensities of 2819 independent reflections were measured within the range $2° < 2\theta < 50°$, using the $\theta/2\theta$ scan-mode with a θ scan-width of $0.90 + 0.34 \tan \theta$. A data summary is given in Table 1.

Table 1 Summary of crystal data, intensity collection and structure refinement.

Formula	$(CuC_{12}H_{16}N_2O_{10}, 3.5H_2O)_n$
M_r	474.85
Monoclinic space group	$P2_1/n$
a(Å)	6.260(2)
b(Å)	18.550(5)
c(Å)	15.659(3)
β(°)	91.78(3)
V(Å^3)	1817(2)
Z	4
D_{meas}(g cm^{-3})	1.68(2)
D_{exp}(g cm^{-3})	1.71
μ(MoKα)(mm^{-1})	1.275
Scan type	$\theta - 2\theta$
Scan range	$2 < 2\theta < 50°$
Octants collected	$-10 \le h \le 10$; $0 \le k \le 15$; $0 \le l \le 20$
No. independent reflections measured	2819
Final R	0.049
Final R_w	0.054

Data were corrected for Lorentz and polarization effects but not for absorption. Unit-cell parameters and the orientation matrix were determined and refined using setting angles for 25 well-spaced reflections with $15 < \theta < 16°$. Direct methods [14](MULTAN II/82) were used to solve the structure by locating the copper atom and in a second step, carbon, nitrogen and oxygen atoms. The structure was refined by full-matrix least-squares methods to final residuals $R = 0.049$ and $R_w = 0.054$ with $w = 1/\sigma^2 (F)$, minimizing the function $\Sigma w(|F_o| - |kF_c|)^2$ The O(101) and O(102) atoms were disordered; their occupancies were 50:50; water molecules O(501), O(502), O(503), O(504) and O(505) were also disordered with an occupancy factor of 0.50. Only fifteen hydrogen atoms were found in difference electron-density maps. They were included in the structure refinement with an overall isotropic thermal parameter. Final atomic positional parameters and equivalent isotropic temperature factors are listed in Table 2. All calculations were performed with the local system of programs adapted for the VAX 11/725 computer.[15,16]

Table 2 Atomic coordinates and equivalent isotropic thermal parameters (esd's are given in parentheses); $U_{eq} = 1/3$ trace U.

Atom	x	y	z	U_{eq}(Å^2)	U_{iso}(Å^2)
Cu(1)	-0.4780(2)	0.49596(8)	0.21850(9)	0.0267	
C(1)	-0.378(2)	0.3539(7)	0.2497(6)	0.0187	
C(2)	-0.587(2)	0.3674(6)	0.2978(6)	0.0202	
C(3)	-0.715(2)	0.2978(6)	0.3142(8)	0.0272	
C(4)	-0.653(2)	0.2599(6)	0.3971(7)	0.0252	
C(5)	-0.807(2)	0.3978(6)	0.1703(7)	0.0241	
C(6)	-0.827(2)	0.4584(7	0.1060(6)	0.0219	
C(7)	-0.862(2)	0.4624(7)	0.3044(7)	0.0254	
C(8)	-0.785(2)	0.5365(8)	0.3311(7)	0.0308	
C(9)	-0.336(2)	0.2173(7)	0.4811(7)	0.0268	
C(10)	-0.214(3)	0.2839(8)	0.5084(8)	0.0399	
C(11)	-0.462(2)	0.1496(6)	0.3527(7)	0.0228	
C(12)	-0.248(2)	0.1180(6)	0.3322(7)	0.0194	
N(1)	-0.705(1)	0.4240(5)	0.2509(5)	0.0197	
N(2)	-0.439(1)	0.2221(5)	0.3941(5)	0.0201	
O(11)	-0.310(1)	0.4067(4)	0.2076(5)	0.0244	
O(12)	-0.287(1)	0.2950(4)	0.2563(5)	0.0293	
O(61)	-0.711(1)	0.5118(4)	0.1133(4)	0.0229	
O(62)	-0.967(1)	0.4469(4)	0.0471(5)	0.0268	
O(81)	-0.618(1)	0.5604(4)	0.3030(5)	0.0374	
O(82)	-0.905(1)	0.5699(5)	0.3817(6)	0.0506	
O(121)	-0.263(1)	0.0522(5)	0.3085(5)	0.0305	
O(122)	-0.088(1)	0.1548(4)	0.3372(5)	0.0328	
O(101)	-0.264(3)	0.3398(9)	0.455(1)		0.034(4)
O(102)	-0.099(2)	0.2741(9)	0.5756(9)		0.034(4)
O(101')	-0.155(3)	0.3291(9)	0.455(1)		0.035(4)
O(102')	-0.213(3)	0.2930(9)	0.587(1)		0.030(4)
O(500)	-0.096(1)	0.8802(5)	0.4810(5)	0.0479	
O(501)	-0.518(3)	0.530(1)	0.532(1)		0.059(5)
O(502)	-0.769(3)	0.519(1)	0.574(1)		0.054(5)
O(503)	-0.265(3)	0.591(1)	0.465(1)		0.059(5)
O(504)	-0.433(3)	0.700(1)	0.356(1)		0.051(5)
O(505)	-0.307(3)	0.682(1)	0.368(1)		0.050(5)

Physical measurements

Potentiometric titrations, TG-DTA measurements, IR, reflectance and ESR spectra and magnetic susceptibility data were obtained in similar modes to those described in ref. 17 for $[Cu(HL)(H_2O)]$ where H_3L = N-(2-carboxyethyl)iminodiacetic acid.

RESULTS AND DISCUSSION

Description of the structure

The compound $CuH_3TDB\cdot 3.5H_2O$ ($CuH_3L.3.5H_2O$ hereafter) consists of one-dimensional chains of CuH_3L complex units and non-coordinated water molecules. Figure 1 shows a view of the complex with the atom labelling. Bond lengths and angles are listed in Table 3.

Copper(II) coordination

In the CuH_3L complex unit, the copper(II) ion exhibits very distorted five-coordination with the N(I), O(11), O(61) and O(81) donor atoms from the tetradentate C-substituted NTA group of the ligand (H_3L^{2-}) and the $O(121^i)$ atom from the N-substituted IDA group of the ligand from one adjacent CuH_3L unit (symmetry code *i*: -1/2-*x*, 1/2 + *y*, -1/2- *z*) related to the former by the 2_1 screw axis. If we consider the O(61) atom as the apex of a distorted square-based pyramid, each *trans*-pair N(1), $O(121^i)$ and O(11), O(81) are displaced by 0.25 ± 0.02Å in an opposite sense from the mean tetragonal plane and Cu(II) (0.333Å) is moved to the apex, O(61). Alternatively, we can consider the copper(II) atom in an unsymmetrically flattened bipyramidal coordination with the *trans*-bonds Cu-N(1) and Cu-$O(121^i)$ deviating 3.7(3)° and 9.7(3)° from the normal to the plane defined by O(11), O(61) and O(81). However, Cu(II) is 0.279Å out of the plane, being nearer the $O(121^i)$ apex. Thus, the best description for the Cu(II) coordination in $CuH_3L\cdot 3.5H_2O$ is intermediate between a trigonal bipyramid and a square-based tetragonal pyramid, the two idealized polyhedra being related by the 'Berry twist' mechanism.[18]

The description of Cu(II) coordination is further complicated by the fact that only two of the three acid hydrogen atoms of the ligand (H_3L^{2-}) have been located (they are linked to O(62) and N(2) atoms). Furthermore, the O(101) and O(102) atoms linked to the C(10) atom are in statistical disorder. The O(11) and $O(121^i)$ atoms belong to unidentate carboxylate groups and O(61) to an unionized carboxylic acid group.

The Cu-N(1) and Cu-O(11) distances agree well with those of Cu-N and Cu-O (carboxylato) bonds in the tetragonal plane of the distorted octahedral Cu(II) coordination sphere reported for the related "acid" complexes $[Cu(H_2EDTA)(H_2O)]$,[19] $[Cu(H_3DTPA)]\cdot H_2O$,[12] $[Cu(HNPDA)(H_2O)]$[17] and $[Cu(H_2NTA)_2]\cdot 2H_2O$,[20] where H_3NPDA and H_3NTA are nitrilopropionicdiacetic and nitrilotriacetic acid, respectively. The Cu-$O(121^i)$ carboxylato bond is shorter than corresponding bonds in related compounds (usually 1.95–1.97(1)Å). This could be due to the coordination number of five, the lack of chelate ring formation through the $O(121^i)$ atom, and of the corresponding constraint, and the simple unidentate role of the C(12)- carboxylato group in CuH_3L instead of the bridging

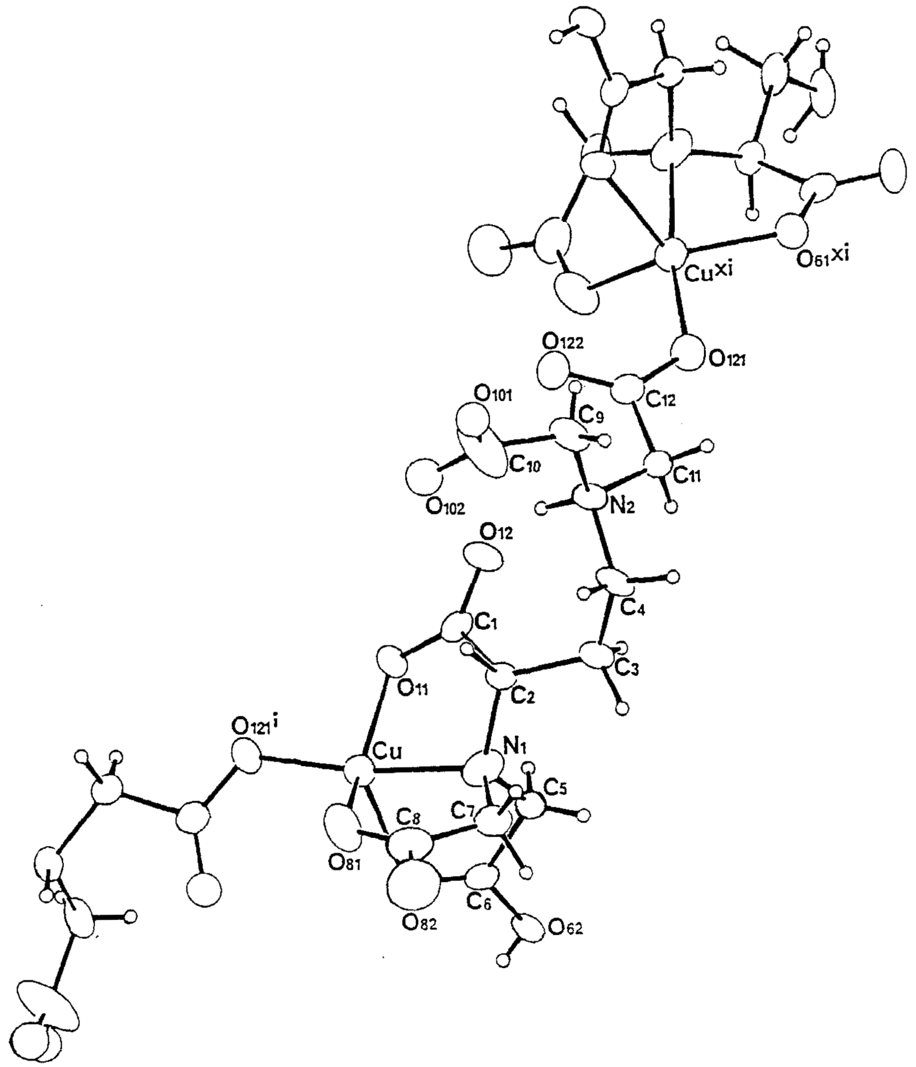


Figure 1 ORTEP view of the complex (the water molecules are not drawn). Only one statistical configuration for each of the O(101) and O(102) atoms is shown. The O(61) atom is hidden by O(82) atom but is seen as the symmetrical equivalent $O(61^{xi})$ atom (symmetry code: $i = -1/2 - x, 1/2 + y, 1/2 - z$; $xi = -1/2 - x, -1/2 + y, 1/2 - z$).

role Cu-O-C-O-Cu^i found in $[Cu(HNPDA)(H_2O)]$[17] or in $[Cu(IDA)(H_2O)_2]$[21] for iminodiacetic acid (H_2IDA). In addition, the longest Cu-O(61) carboxylic bond in CuH_3L is clearly shorter than the corresponding Cu-O(carboxylic) bond (2.321(2)–2.518(2)Å) in the related "acid" copper(II) chelates.[12,17,19,20] Again, this shortening could be attributed to the five (instead of six) Cu(II) coordination in CuH_3L (other factors being comparable). In this connection, the Cu-O(81) distance and the C(8)-O(82)/C(8)-O(81) ratio suggest that the third unlocated "acid"

Table 3 Bond lengths (Å) and angles (°) for the complex.

Lengths			
Cu-O(121^{i})	1.893(8)	Cu-N(1)	2.026(8)
Cu-O(11)	1.971(7)	Cu-O(61)	2.186(6)
Cu-O(81)	2.003(8)		
N(1)-C(2)	1.47(1)	C(5)-C(6)	1.51(2)
N(1)-C(5)	1.48(1)	C(6)-O(61)	1.23(1)
N(1)-C(7)	1.49(1)	C(6)-O(62)	1.27(1)
N(2)-C(4)	1.51(1)	C(7)-C(8)	1.51(2)
N(2)-C(9)	1.49(1)	C(8)-O(81)	1.23(1)
N(2)-C(11)	1.50(1)	C(8)-O(82)	1.27(2)
C(1)-O(11)	1.26(1)	C(9)-C(10)	1.51(2)
C(1)-O(12)	1.24(1)	C(10)-O(101)	1.36(2)
C(1)-C(2)	1.55(2)	C(10)-O(102)	1.27(2)
C(2)-C(3)	1.55(2)	C(10)-O(101′)	1.25(2)
C(3)-C(4)	1.52(2)	C(10)-O(102′)	1.24(2)
		C(11)-C(12)	1.50(2)
		C(12)-O(121)	1.28(1)
		C(12)-O(122)	1.22(1)
(b) Angles			
O(121^{i})-Cu-O(11)	90.7(3)	O(11)-Cu-N(1)	81.3(3)
O(121^{i})-Cu-O(81)	100.7(3)	O(11)-Cu-O(61)	113.1(3)
O(121^{i})-Cu-N(1)	171.6(3)	O(81)-Cu-N(1)	84.5(3)
O(121^{i})-Cu-O(61)	106.0(3)	O(81)-Cu-O(61)	97.1(3)
O(11)-Cu-O(81)	143.4(3)	N(1)-Cu-O(61)	79.7(3)
Cu-N(1)-C(2)	104.4(6)	N(1)-C(7)-C(8)	112(1)
Cu-N(1)-C(5)	106.9(6)	C(7)-C(8)-O(81)	120(1)
Cu-N(1)-C(7)	111.2(8)	C(7)-C(8)-O(82)	115(1)
Cu-O(11)-C(1)	114.7(7)	O(81)-C(8)-O(82)	125(1)
Cu-O(61)-C(6)	109.8(7)	N(2)-C(9)-C(10)	114(1)
Cu-O(81)-C(8)	114.5(8)	C(9)-C(10)-O(101)	110(1)
Cu-O(121^{i})- C(12^{i})	122.7(7)	C(9)-C(10)-O(102)	113(1)
C(2)-N(1)-C(5)	113.0(8)	O(101)-C(10)-O(102)	137(2)
C(2)-N(1)-C(7)	113.0(8)	C(9)-C(10)-O(101′)	112(1)
C(5)-N(1)-C(7)	111.2(8)	C(9)-C(10)-O(102′)	121(1)
C(4)-N(2)-C(9)	110.9(8)	O(101′)-C(10)-O(102′)	126(2)
C(4)-N(2)-C(11)	110.9(8)	N(2)-C(11)-C(12)	111.7(9)
C(9)-N(2)-C(11)	111.9(9)	C(11)-C(12)-O(121)	112(1)
N(1)-C(2)-C(1)	107.0(8)	C(11)-C(12)-O(122)	120(1)
N(1)-C(2)-C(3)	115(1)	O(12)-C(12)-O(122)	127(1)
C(1)-C(2)-C(3)	113(1)		
C(2)-C(1)-O(11)	116(1)		
C(2)-C(1)-O(12)	120(1)		
O(11)-C(1)-O(12)	125(1)		
C(2)-C(3)-C(4)	114(1)		
C(3)-C(4)-N(2)	113.0(9)		
N(1)-C(5)-C(6)	110.4(9)		
C(5)-C(6)-O(61)	120.1(9)		
C(5)-C(6)-O(62)	114(1)		
C(61)-C(6)-O(62)	126(1)		

Symmetry code: *i* = − 1/2 − *x*, 1/2 + *y*, 1/2 − *z*

hydrogen atom could be linked to the O(82) atom. The tetradentate role of the H_3L^{2-} ligand with respect to a single copper(II) atom yields three five-membered chelate rings (sharing N(1)) with an unsymmetrical envelope configuration.

The internal geometry of the ligand H_3L^{2-} agrees well with data reported in the literature, except for the C(10) "carboxyl" group which has two different conformations in statistical disorder (50%) for the atoms O(101) and O(101′); O(102) and O(102′) are related by a 38° rotation about C(9)–C(10). The differences between the C-O distances in the two conformations suggest that the O(101′)–C(10)–O(102′) is a carboxylate group, while the O(101)–C(10)–O(102) carboxyl group would be partially protonated (on O(101)).

In any case, it is interesting to note the zwitterionic-type configuration adopted by the IDA group of H_3L^{2-} ligand in the complex, in contrast with the structure of $[Cu(H_3DTPA)]\cdot H_2O$, where all three amino nitrogen atoms of the triply protonated ligand chelate the same Cu(II) ion.[12]

In addition to four CuH_3L complex units, the unit cell contains fourteen water molecules which contribute to crystal cohesion by hydrogen bonds. Two and a half of the water molecules in the formula $CuH_3TDB\cdot 3.5H_2O$ are in statistical disorder (50%). The two located "acid" hydrogen atoms of the ligand are involved in hydrogen bonding. HN(2) forms one intra-chain hydrogen bond with one oxygen atom of the α-carboxylato group of the same H_3L^{2-} ligand (N(2)-HN(2)...O(12), 2.74(1)Å, 155°).

Properties of $CuH_3TDB\cdot 3.5H_2O$

To obtain the n value in the formula $CuH_3L\cdot nH_2O$, several powdered and polycrystalline samples (4.5–33.3mg) of the compound were studied by thermal methods (TG-DTA). The compound loses most of the unbound water molecules very easily (310–365K, endo-effect at 343–353K). Powdered samples result with $n \leq 3$. Freshly polycrystalline samples lose only 10% of the 13.38% calculated for 3.5 H_2O in this step. The remaining water is lost very slowly (365–575K) before the pyrolytic decomposition of the organic ligand (575–675K, exo-effects at 510 and 630K) to yield a residue of $Cu(NO_3)(OH)$ (calcd. 23.5, exp. 25.5) with IR bands at 3400 and 500 cm^{-1} of OH^- ion and 1380 and 1355 cm^{-1} of NO_3^-.

An IR spectrum of the compound shows υ(O-H) bands of carboxylic groups and water molecules at 3600, 3530 and 3400 (shoulder) cm^{-1}. The stretch υ(C = O) reveals the existence of different carboxylic groups (1735, 1720 (sh) and 1690 cm^{-1}. The deformation mode $\delta(H_2O)$ gives a strong band (163 cm^{-1}) with a broad shoulder (~1590 cm^{-1}) for the antisymmetric stretching mode of the carboxylate groups. The carboxylic groups also show a peak (1410 cm^{-1}) and bands (~1200 cm^{-1} and ~900 cm^{-1}) due to the modes υ(C-O) + δ(OH) and π(OH). The symmetric mode υ(COO) shows a band at 1390 cm^{-1}(sh. at 1370 cm^{-1}); splitting values $(\Delta\upsilon(\upsilon_{as} - \upsilon_s)$ = 210 and 220 cm^{-1}) agree well with the unidentate carboxylato groups established in the CuH_3L complex with quite ionic Cu-O (carboxylato) bonds.[20] An IR spectrum of a sample heated to 423K (almost anhydrous) also shows three υ(C = O) bands due to carboxylic groups (at 1755, 1730 and 1680 cm^{-1}). A diffuse reflectance spectrum shows a band (υ_{max} = 11730 cm^{-1} and shoulder near 14000 cm^{-1}) with shape and frequencies expected for the $CuNO_4$ chromophore with square-pyramidal to trigonal-bipyramidal intermediate character.[18,22]

ESR spectra at 77 and 298K are of axial type with an apparently ill-defined $g_{//}$ value of 2.34 ± 0.01 and $g_{\perp}$ = 2.07. In addition, at high amplification (×200), a weak $\Delta M_s = 2$ signal also reported for dinuclear Cu(II) complexes with rather short Cu-Cu distances (4.4 – 5.5Å)[23] was recorded. On this basis, an approximate $g_{//}$ value of 2.14 could be estimated.[24,25] However, in the reported Cu(II) complex, the shortest Cu-Cu^{iii} distance is 6.260(1)Å (symmetry code iii: 1 + x, y, z) and the observed half-field signal could not be interpreted as a $\Delta M_s = 2$ forbidden transition in the triplet state, but would reflect, in any mode, interactions between Cu(II) atoms at larger distances in the CuH_3L chain. Several examples of mononuclear and chain polynuclear Cu(II) complexes with Cu-Cu distances ~7Å have been reported with a weak half-field signal in the ESR spectrum at low and/or at room temperature.[26,27] The inverse molar susceptibilities (77–298K) of the new Cu(II) compound follows Curie-Weiss behaviour with $\mu_{eff} = 1.80$ B.M. in accordance with the rather long Cu-Cu distances in the crystal (≥ 6.260(1)Å).

The present work establishes that the H_3L^{2-} ion of H_5TDB chelates the Cu(II) ion in $CuH_3L \cdot 3.5H_2O$ by means of its partially protonated C- substituted NTA group, while the ligand retains as an N-protonated zwitterion its N-substituted IDA group. In spite of the triple "acid" form of the ligand, Cu(II) prefers to form three five-membered chelate rings rather than two of these plus one six-membered *N,N'*-diamino-Cu(II) chelate ring.

Supplementary material

Hydrogen atomic coordinates, C-H, O-H and N-H distances, anisotropic thermal parameters, van der Waals distances and a list of observed and calculated structure factors are available from the authors.

References

1. S. González García, F.J. Sánchez Santos and M.F. Morales Ayala, *Ars Pharmaceutica*, **17**, 295 (1976).
2. G.N. Tyurenkova, L.G. Egorova, N.V. Serebriankova ans S.L. Mertsalov, *Zh. Anal. Khim.*, **31**, 2310 (1976).
3. Yu. Kozlov and V.A. Babich, *Zh. Ovshch*, **50**, 1116 (1980); **51**, 1115 (1981).
4. Yu. Kozlov and V.A. Babich, *Russ. J. Inorg. Chem.*, **25**, 940, 1547 (1980).
5. S. González García, F.J. Sánchez Santos and M.F. Morales Ayala, *An. Quim.*, **78B**, 22 (1982).
6. J. Niclós Gutiérrez, S. González García, A. Matilla Hernández and J.M. Tercero Moreno, *An. Quim.*, **79B**, 517 and 525 (1983).
7. A. Matilla Hernández, S. González García, J. Niclós Gutiérrez and J.M. Tercero Moreno, *An. Quim.*, **82B**, 22 (1986).
8. J.M. Tercero Moreno, S. González García, A. Matilla Hernández and J. Niclós Gutiérrez, *An. Quim.*, **84B**, 39 (1988).
9. S. González García, J. Niclós Gutiérrez and A. Matilla Hernández, *An. Quim.*, **79B**, 24 (1983).
10. J.M. Tercero Moreno, S. González García, A. Matilla Hernández, J. Niclós Gutiérrez and M.T. Fernández Martínez, *An. Quim.*, **85B**, 10 (1989).
11. A. Matilla Hernández, S. González García, J.M. Tercero Moreno, M.C. Vaz and L. Villas-Boas, *Talanta*, **34**, 519 (1987).
12. R.C. Secombe, B. Lee and G.M. Henry, *Inorg. Chem.*, **14**, 1147 (1975).
13. A. Matilla Hernández, S. González García, J. Niclós Gutiérrez and J.M. Tercero Moreno, *An. Quim.*, **81B**, 297 (1985).
14. P. Main, S.J. Fiske, S.E. Hull, L. Lessinger, G. Germain, J.P. Declercq and M.M. Woolfson, *Multan 11/82. A system of computer programs for the automatic solution of crystal structures from X-ray diffraction data*, (Univ. of York, U.K., and Univ. of Louvain, Belgium, 1982).
15. J.R. Carruthers and D.J. Watkin, *Crystals*, (Chemical Crystallography Laboratory, Univ. of Oxford, U.K., 1984).
16. C.K. Johnson, *ORTEPII, Rep. ORNL-5138*, (Oak Ridge National Laboratory, Oak Ridge, TN, 1976).

17. Nguyen-Huy Dung, B. Viossat, A. Busnot, J.M. González Pérez, S. González García and J. Niclós Gutiérrez, *Inorg. Chem.*, **26**, 2365 (1987).
18. a) B.J. Hathaway, *Struct. Bonding*, **57**, 55 (1984); b) S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).
19. F.S. Stephens, *J. Chem. Soc.*, (A), 1723 (1969).
20. Nguyen-Huy Dung, B. Viossat, A. Busnot, J.M. González Pérez, S. González García and J. Niclós Gutiérrez, *Inorg. Chem.*, **27**, 1227 (1988).
21. A. Podder, J.K. Dattagupta, N.N. Saha and N. Saenger, *Acta Crystallogr.*, **B35**, 53 (1979).
22. M. Duggan, N. Ray, B. Hathaway, G. Tomlinson, P. Brint and K. Pelin, *J. Chem. Soc.*, Dalton Trans., 1342 (1980).
23. J.F. Boas, J.R. Pilbrow, C.R. Hartzell and T.D. Smith, *J. Chem. Soc.*, (A), 572 (1969).
24. M. Chikira, H. Kon, R.A. Hawley and K.M. Smith, *J. Chem. Soc.*, Dalton Trans., 25 (1979).
25. A. Busnot, F. Busnot. J.F. Hemidy and J.F. Le Querler, *Thermochim. Acta*, **179**, 135 (1991).
26. M. Julve, M. Verdaguer, J. Faus, F. Tinti, J. Moratal, A. Monge and E. Gutiérrez-Puebla, *Inorg. Chem.*, **26**, 3520 (1987).
27. X. Solans, M. Aguiló, A. Gleizes, J. Faus, M. Julve and M. Verdaguer, *Inorg. Chem.*, **29**, 775 (1990).