A Mixed-ligand Homodinuclear Copper(II) Complex with Weak Disulfide–Metal Interactions: Synthesis, Properties and Molecular and Crystal Structure of μ-(*N,N,N',N'*-Tetrakis(carboxymethyl)cystaminato(4–))-bis(imidazole)-diaquodicopper(II) Dihydrate, $[Cu_2(TTC)(ImH)_2(H_2O)_2]\cdot 2H_2O$

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Abstract

μ-(*N,N,N',N'*-Tetrakis(carboxymethyl)cystaminato-(4–))-bis(imidazole)diaquodicopper dihydrate, $[Cu_2(TCC)(ImH)_2(H_2O)_2]\cdot 2H_2O$ (I) (where TCC = $(O_2CCH_2)_2{-}NC_2H_4{-}S{-}S{-}C_2H_4N(CH_2CO_2)_2{}^{4-}$), has been obtained in good yield by reaction of $[Cu_2(TCC)(H_2O)_2]\cdot 4H_2O$ (II) with excess of imidazole (ImH) in water. The new product I has been characterized by chemical analysis, TG-DTA diagram, infrared, reflectance and ESR spectra and the single-crystal X-ray diffraction method. The compound crystallizes in the monoclinic system, space group $P2_1/n$ ($a = 20.800(2)$, $b = 10.191(2)$, $c = 13.419(2)$ Å, $\beta = 92.41(1)°$). Final $R = 0.036$ and $R_w = 0.035$ for 2784 independent observed reflections. Instead of the polynuclear layered crystal structure of II, the crystal of I consists of hydrogen bonded water molecules and discrete dinuclear units $[Cu_2(TCC)(ImH)_2(H_2O)_2]$ linked together in a tridimensional hydrogen bonding network. Both crystallographic independent copper atoms of the mixed dinuclear unit show analogous distorted elongated octahedral coordination (of the type 4 + 1 + 1). The two Cu–N(ImH) bonds are shorter than the homologous bond in a variety of copper(II)–imidazole derivatives, lying in the lowest limit of the corresponding bond lengths in Cu(II)–(ImH)–aminoacidato (or peptide) complexes (1.95–1.98 Å). However, the ImH ligands do not play any π acceptor role (the Cu–N(ImH) bonds are tilted with respect to the ImH planes, which are twisted with respect to the mean equatorial coordination planes of the copper(II) atoms). By reacting ImH with II to give I, the copper coordinated water molecule in the equatorial position in II is replaced by an ImH molecule in I and moves to an apical position; this results in the lengthening of the Cu–S(disulfide) bonds, from 2.721(3) Å in II to 2.959(2) Å average in I.

Introduction

The mixed-ligand copper(II) complexes containing imidazole-coordinating groups are the subject of extensive works, both in solution and in the solid state [1–4]. As pointed out by Sigel [3] in such complexes, the imidazole (ImH) and very closely related ligands (like histamine) exhibit discriminating qualities, which favour the formation of mixed-complexes with O-donor ligands more strongly than they do with amino groups. The crystal structures of a considerable number of copper(II) complexes containing ImH or imidazole-derivative ligands are known, among which the imidazole–Cu(II)–O–ligand compounds seem to be the most frequent ones. In these compounds, the copper(II) ion is commonly in a distorted octahedral six-coordinate or in a square-pyramidal five-coordinate environment; the ImH groups are preferentially linked among the closest ligands of the copper, whereas the axial ligand–metal bonds are significantly lengthened. In most of the

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cases, the copper(II) atom lies out of the ImH planes. In addition, an appreciable dihedral angle should be defined between each ImH plane and the nearly square plane (of the closest donor atoms) of the referred complexes with distorted octahedral coordination. These and other findings have been rationalized on the basis of the poor ability of the imidazole to act as an effective π acceptor ligand [2], in addition to their σ donor properties. It is well known that ternary metal–ligand complexes play very important roles in biological systems [3]. In this context, the imidazole–copper(II)–aminoacidato and the imidazole–copper(II)–peptide complexes are of particular interest [1], since it is believed (known in some cases) that the imidazole side-chain group of the histidine residues is involved in the metallic center of several copper proteins and in some substrate–copper–enzyme complexes [3]. In their structural aspects, the mixed imidazole–copper(II)–aminoacidato (or peptide) complexes and related compounds (histidine-containing peptide complexes) serve as models for copper–protein interactions.

Some aminopolycarboxylate ligands (like iminodiacetate (IDA) or nitrilotriacetate (NTA)) also form mixed ligand–Cu(II)–ImH complexes in solution [5]. To be stable enough, such complexes require that the imidazole ligand could be coordinated to the copper(II) ion in one position of the four closest donor atoms. We are interested in the investigation of such complexes in the solid state [6, 7], where the crystal structure analysis would report more conclusive results [8]. In this context, we have reported the crystal structure of a Cu(II) derivative of the *N,N,N′,N′*-tetrakis(carboxymethyl)cystamine (H_4-TCC = $[(HO_2CCH_2)_2NC_2H_4\text{-}S]_2$) having the formula $\{[Cu_2(TCC)(H_2O)_2]\cdot 4H_2O$ and a polynuclear layered crystal structure [9]. In this compound, each copper(II) atom has an elongated octahedral coordination where an iminodiacetate-N-substituted moiety of the ligand and one H_2O molecule supply the four closest donor atoms, and one sulfur–disulfide atom forms an axial Cu–S bond (2.721(3) Å), shorter than the analogous bond in the dinuclear copper(II) complexes of penicillamine disulfide [10] or oxidized glutathione [11]. This compound has essentially the molecular skeleton to give mixed Cu–TCC–ImH complexes suitable to check some of the referred suggestions of the literature cited and, in addition, the possible influences of the imidazole coordination on the S(disulfide)–Cu(II) interaction.

Experimental

Preparation

Synthesis of TCC

TCC was obtained by reaction of potassium chloroacetate and cystamine (or bis(2-aminoethyl)-disulfide) in alkaline (KOH) aqueous medium, at room temperature (cold method) or on heating in a water bath (hot method). Details of both procedures have been published earlier [12]. To avoid the formation of large quantities of *N,N,S*-(triscarboxymethyl)-cysteamine, $(HO_2CCH_2)\text{–S–}CH_2CH_2\text{–}N(CH_2CO_2H)_2$, a by-product of the TCC synthesis [13], it is better to use the highest purity samples of cystamine dihydrochloride and a stoichiometric amount or moderate excess (<25%) of chloroacetate (hot and cold methods, respectively). The mixture of both reactants must be carried out in the cold (<10 °C).

Synthesis of μ-(N,N,N′,N′-Tetrakis(carboxymethyl)cystaminato(4–))bis(imidazole)diaquodicopper(II) dihydrate $[Cu_2(TCC)(ImH)_2(H_2O)_2]\cdot 2H_2O$

This compound can be obtained in aqueous solution by reaction of dissolved $[Cu_2(TCC)(H_2O)_2]\cdot 4H_2O$ [9] (method I) and imidazole or by the direct reaction of the free acid H_4TCC with copper(II) hydroxycarbonate and ImH (method II).

Method I. A mixture of microcrystalline solid samples of $[Cu_2(TCC)(H_2O)_2]\cdot 4H_2O$ (1.6 mmol) and ImH in the molar ratio 1:2.5 was slowly added to 150 ml of water (60 °C) gently stirred. The resulting dark blue solution was cooled, filtered and then evaporated at room temperature in a crystallizing flask, where blue powder or crystals of the desired product were formed on several days. This starting material should be recrystallized in water with excess of ImH. Several samples of well shaped crystals were filtered off, washed with cold water and ethanol and air-dried. Yield: ≥60%. *Anal.* Calc. for $C_{18}H_{32}Cu_2N_6O_{12}S_2$: C, 30.21; H, 4.51; N, 11.74; S, 8.96; Cu, 17.76. Found: C, 29.86; H, 4.35; N, 11.84; S, 8.85; Cu, 17.5%.

Method II. To 1.2 mmol of $H_4TCC\cdot nH_2O$ ($n = 2\text{–}4$) in 200 ml of water was slowly added a mixture of $Cu_2CO_3(OH)_2$ (1.2 mmol) and ImH (3 mmol, 25% excess). The reaction mixture was heated (60 °C) and stirred and the CO_2 (by product) removed under vacuum. The dark blue solution was cooled and filtered and then allowed to evaporate at room temperature for several days. The crude product obtained was recrystallized with excess of imidazole and collected as in method I.

Both procedures enable good samples of the desired product, but the former method gives highest yields because when starting with purified $[Cu_2(TCC)(H_2O)_2]\cdot 4H_2O$, the required stoichiometric amounts of Cu(II) and TCC are ensured.

Crystallography

Data collection

Diffraction data for compound **I** were collected at room temperature on a CAD4 Enraf-Nonius diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). The blue single crystals were shaped as parallelepipeds with dimensions $0.35 \times 0.25 \times 0.22$ μm. Intensities of 4975 reflections were measured within $1.5 < \theta < 25.0°$ using the ω–2θ scan mode with a scan range of $1.12 + 0.34 \tan\theta$. Data were corrected for Lorentz and polarization effects but not for absorption. Unit-cell parameters and orientation matrix were determined and refined using setting angles for 25 well spaced reflections using $14 < \theta < 15°$.

Crystal data

$a = 20.800(2)$, $b = 10.191(2)$, $c = 13.419(2)$ Å, $\beta = 92.41(1)°$; $V = 2841.9$ Å^3; $M_r = 715.7$; $\rho_{obs} = 1.67$, $\rho_{calc} = 1.67$ g cm^{-3}. Space group monoclinic $P2_1/n$; $Z = 4$; μ(Mo Kα) = 1.70 mm^{-1}. Formula: $Cu_2C_{18}H_{32}N_6O_{12}S_2$. Octants collected: $-25 \leqslant h \leqslant 25; 0 \leqslant k \leqslant 12; 0 \leqslant l \leqslant 15$.

Structure determination

Direct methods [14] (MULTAN 80) were used to solve the structure, by locating the copper atoms. Carbon, nitrogen and oxygen atoms were found by direct methods (DIRDIF) [14] or by Fourier and difference Fourier synthesis. The structure was then refined by the full-matrix least-squares method [15] to final residuals $R_F = 0.036$ and $R_w = 0.035$ with $w = 1/\sigma^2(F)$, minimizing the function $\Sigma_{hkl} w_{hkl}(|F_o| - |kF_c|)^2$. H atoms (excepted three) could be located from difference maps but were not refined and were assigned isotropic thermal parameters 1 Å higher than the isotropic factor of the corresponding C, O or N atoms. Final atomic positional parameters and equivalent isotropic temperature factors are listed in Table 1. All calculations were performed with the local system of programs adapted for the Univac 1110 computer [15]. Scattering factors and the anomalous dispersion correction terms were taken from ref. 16. The highest peak in the last difference Fourier map at the end of the refinement was less than 0.1 e Å^{-3}.

Physical Measurements

TG and DTA diagrams, IR, NIR–Vis–UV and ESR spectra data of the studied compound were obtained as described in a previous paper [17].

Results and Discussion

Crystal Structure

An ORTEP drawing of the complex is given in Fig. 1, with the labeling of the atoms. The unit cell of the studied compound contains four of these mixed ligand dinuclear entities and eight water molecules. Figure 2 represents a stereoscopic view of such a unit cell. Bond lengths and angles are given in Table 2.

TABLE 1. Atomic coordinates and equivalent isotropic thermal parameters with e.s.d.s in parentheses

	x	y	z	B_{eq} (Å^2)[a]
Cu(1)	0.65025(3)	0.24565(9)	0.25175(5)	2.25
Cu(2)	0.36358(3)	0.25684(9)	0.26086(5)	2.20
S(1)	0.53818(8)	0.3263(2)	0.1260(1)	3.00
C(2)	0.5860(3)	0.2688(7)	0.0238(4)	2.81
C(3)	0.6224(3)	0.1452(6)	0.0482(4)	2.33
N(4)	0.6763(2)	0.1585(5)	0.1250(3)	1.76
C(5)	0.7296(3)	0.2406(7)	0.0886(4)	2.15
C(6)	0.7184(3)	0.3833(6)	0.1170(4)	1.99
O(61)	0.6825(2)	0.4060(4)	0.1891(3)	2.37
O(62)	0.7461(2)	0.4699(4)	0.0704(3)	2.79
C(7)	0.6970(3)	0.0249(6)	0.1570(4)	2.24
C(8)	0.6518(3)	−0.0223(7)	0.2370(5)	2.42
O(81)	0.6242(2)	0.0647(4)	0.2876(3)	2.71
O(82)	0.6462(2)	−0.1422(5)	0.2500(3)	3.40
S(11)	0.47122(8)	0.1812(2)	0.1328(1)	3.08
C(12)	0.4152(3)	0.2289(7)	0.0315(4)	2.74
C(13)	0.3778(3)	0.3512(6)	0.0539(4)	2.41
N(14)	0.3285(2)	0.3318(5)	0.1306(3)	1.75
C(15)	0.2777(3)	0.2405(7)	0.0957(4)	2.07
C(16)	0.2924(3)	0.1008(6)	0.1309(4)	2.09
O(161)	0.3324(2)	0.0880(4)	0.2050(3)	2.40
O(162)	0.2638(2)	0.0101(4)	0.0882(3)	3.01
C(17)	0.3040(3)	0.4629(6)	0.1591(4)	2.24
C(18)	0.3491(3)	0.5215(7)	0.2394(5)	2.42
O(181)	0.3848(2)	0.4424(4)	0.2893(3)	2.58
O(182)	0.3463(2)	0.6404(4)	0.2553(3)	3.48
N(101)	0.6080(3)	0.3947(9)	0.5211(5)	5.62
C(102)	0.6253(3)	0.2999(8)	0.4609(5)	3.58
N(103)	0.6202(2)	0.3382(6)	0.3681(4)	2.68
C(104)	0.5992(4)	0.4646(8)	0.3698(6)	5.01
C(105)	0.5918(5)	0.5014(9)	0.4648(7)	6.57
N(201)	0.4116(3)	0.1079(6)	0.5352(4)	3.66
C(202)	0.3711(3)	0.1323(7)	0.4567(5)	3.22
N(203)	0.4025(2)	0.1871(5)	0.3843(3)	2.11
C(204)	0.4656(3)	0.1980(7)	0.4196(5)	2.89
C(205)	0.4725(3)	0.1494(7)	0.5111(5)	3.43
OW(1)	0.7543(2)	0.2112(4)	0.3345(3)	3.14
OW(2)	0.2601(2)	0.2742(4)	0.3332(3)	2.86
OW(3)	0.4062(3)	0.8764(5)	0.3007(5)	8.87
OW(4)	0.5176(3)	−0.228(1)	0.1930(5)	13.23

[a] $B_{eq} = \frac{4}{3}\Sigma_i \Sigma_j \beta_{ij} \vec{a}_i \vec{a}_j$.

Coordination of the Copper(II) Atoms

The discrete homodinuclear complex in the title compound $[Cu_2(TCC)(ImH)_2(H_2O)_2]\cdot 2H_2O$ (**I**) exhibits two independent copper(II) atoms which have very similar coordination environments. Each copper(II) atom has an unsymmetrically elongated octahedral coordination, of the type 4 + 1 + 1. The four closest donor atoms are one hydrogen-free imidazole nitrogen, the amino nitrogen and one oxygen of each carboxylate group from the same N-substituted-iminodiacetate moiety of the TCC ligand, $-N(CH_2CO_2^-)_2$, which forms two nearly coplanar metal–glycinate type rings. The four referred donor atoms define the mean coordination square planes P(1) [N(4), O(61), N(103), O(81)] and P(2) [N(14), O(161), N(203), O(181)]. The oxygen and nitrogen pairs are found on either side of each mean plane (max. deviation < 0.05 Å). The Cu(1) and Cu(2) atoms roughly lie in the mean planes P(1) and P(2), respectively (max. deviation < 0.03 Å). Each of these Cu(II) atoms is bound to one water molecule at 2.411(3) Å (on average). The bonds Cu(1)–OW(1) and Cu(2)–OW(2) only deviate 1.4° and 3.4° from the perpendicular to the mean planes P(1) and P(2), respectively. These Cu(II)–OW bonds are somewhat longer than the expected one (2.30 Å) for the 'smallest' Jahn–Teller distortion in complexes of this type [1]. The six-coordination of each copper-(II) ion in the dinuclear complex is achieved by formation of a very long and weak bond (or interaction) Cu–S(disulfide) of 2.959(2) Å (average), in the *trans* apical direction to the corresponding Cu(II)–OW bond. These Cu(II)–S(disulfide) linkages are significantly longer than the homologous bond (2.721(3) Å) found in the previously reported $\{[Cu_2(TCC)(H_2O)_2]\cdot 4H_2O\}$ and called hereafter **II** [18], but they fall in the range of the expected apical Cu(II)–S(disulfide) distances (2.7–3.0 Å) [10]. However, the longer Cu(II)–S(disulfide) distances have been taken into account in the Cu(II) derivatives of penicillamine disulfide, $[Cu_2(D\text{-}PDS)_2(H_2O)_2]\cdot 7H_2O$ (3.10(4) Å, on average) [10] and of oxidized glutathione $Na_4[Cu_2(GSSG)]\cdot 6H_2O$ (3.22(2) Å, on average) [11]. Neglecting these copper(II) disulfide interactions, we could consider that each copper(II) atom in the reported mixed-ligand complex exhibits a five-coordinated distorted square-pyramidal coordination. However, this approach seems unreasonable since the displacements of the Cu(I) (0.028 Å) and Cu(II) (0.014 Å) atoms from the mean-planes P(1) and P(2) respectively towards the corresponding

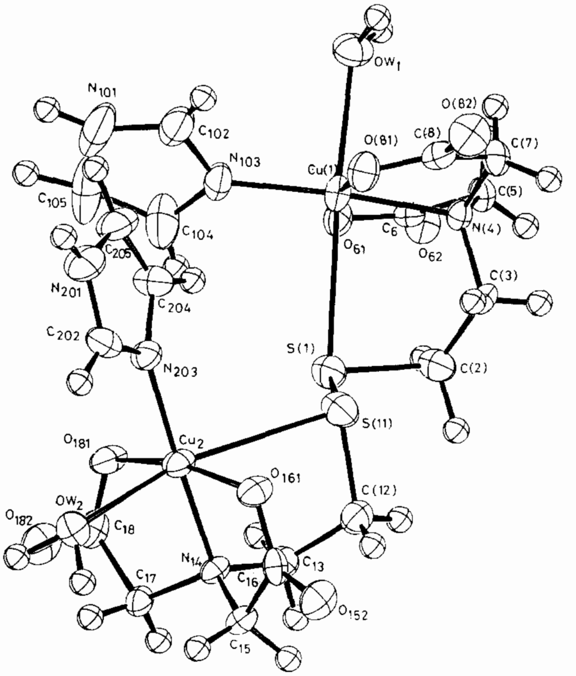

Fig. 1. ORTEP view of the dinuclear complex $[Cu_2(TCC)(ImH)_2(H_2O)_2]$.

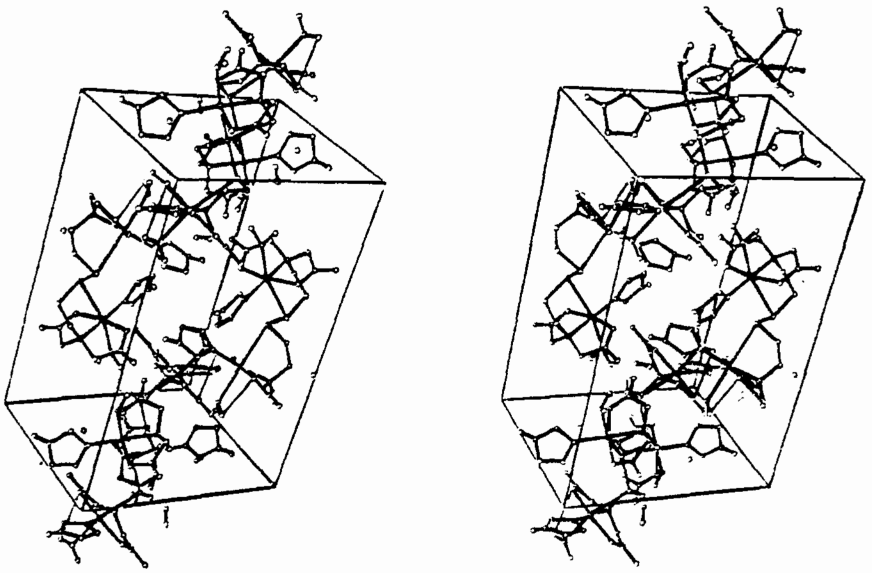

Fig. 2. ORTEP stereoscopic view of the unit cell of $[Cu_2(TCC)(ImH)_2(H_2O)_2]\cdot 2H_2O$.

TABLE 2. Bond lengths (A) and angles (°) with e.s.d.s in parentheses

Copper environments			
Cu(1)–N(103)	1.949(5)	Cu(2)–N(203)	1.947(5)
Cu(1)–N(4)	2.012(4)	Cu(2)–N(14)	2.016(4)
Cu(1)–O(61)	1.968(4)	Cu(2)–O(161)	1.975(4)
Cu(1)–O(81)	1.987(4)	Cu(2)–O(181)	1.975(4)
Cu(1)–S(1)	2.937(2)	Cu(2)–S(11)	2.981(2)
Cu(1)–OW(1)	2.417(4)	Cu(2)–OW(2)	2.405(4)
Cu(1)...Cu(2)	5.970(1)		
N(103)–Cu(1)–O(61)	93.8(2)	N(203)–Cu(2)–O(181)	95.9(2)
N(103)–Cu(1)–O(81)	98.9(2)	N(203)–Cu(2)–O(161)	97.1(2)
N(103)–Cu(1)–N(4)	175.5(2)	N(203)–Cu(2)–N(14)	176.6(2)
N(103)–Cu(1)–OW(1)	90.8(2)	N(203)–Cu(2)–OW(2)	91.8(2)
N(103)–Cu(1)–S(1)	92.9(2)	N(203)–Cu(2)–S(11)	95.8(1)
O(61)–Cu(1)–O(81)	167.3(2)	O(181)–Cu(2)–O(161)	167.0(2)
O(61)–Cu(1)–N(4)	84.1(2)	O(181)–Cu(2)–N(14)	82.8(2)
O(61)–Cu(1)–OW(1)	90.1(1)	O(181)–Cu(2)–OW(2)	92.8(2)
O(61)–Cu(1)–S(1)	78.4(1)	O(181)–Cu(2)–S(11)	101.1(1)
O(81)–Cu(1)–N(4)	83.2(2)	O(161)–Cu(2)–N(14)	84.2(2)
O(81)–Cu(1)–OW(1)	90.1(2)	O(161)–Cu(2)–OW(2)	86.1(2)
O(81)–Cu(1)–S(1)	100.4(1)	O(161)–Cu(2)–S(11)	78.4(1)
N(4)–Cu(1)–OW(1)	93.2(2)	N(14)–Cu(2)–OW(2)	91.4(2)
N(4)–Cu(1)–S(1)	82.7(1)	N(14)–Cu(2)–S(11)	81.5(1)
OW(1)–Cu(1)–S(1)	168.1(1)	OW(2)–Cu(2)–S(11)	163.4(1)
Ligand TCC^{4-}			
S(1)–S(11)	2.036(2)		
S(1)–C(2)	1.824(6)	S(11)–C(12)	1.819(6)
C(2)–C(3)	1.499(8)	C(12)–C(13)	1.506(8)
C(3)–N(4)	1.497(7)	C(13)–N(14)	1.497(7)
N(4)–C(5)	1.487(7)	N(14)–C(15)	1.469(7)
C(5)–C(6)	1.524(8)	C(15)–C(16)	1.527(9)
C(6)–O(61)	1.269(6)	C(16)–O(161)	1.275(7)
C(6)–O(62)	1.238(7)	C(16)–O(162)	1.227(7)
N(4)–C(7)	1.486(7)	N(14)–C(17)	1.485(7)
C(7)–C(8)	1.533(8)	C(17)–C(18)	1.522(8)
C(8)–O(81)	1.269(7)	C(18)–O(181)	1.268(7)
C(8)–O(82)	1.241(7)	C(18)–O(182)	1.232(7)
C(2)–S(1)–S(11)	101.3(2)	S(1)–S(11)–C(12)	101.0(2)
S(1)–C(2)–C(3)	113.0(4)	S(11)–C(12)–C(13)	113.1(4)
C(2)–C(3)–N(4)	115.5(5)	C(12)–C(13)–N(14)	113.7(5)
C(3)–N(4)–C(5)	111.8(4)	C(13)–N(14)–C(15)	111.6(4)
C(3)–N(4)–C(7)	108.4(5)	C(13)–N(14)–C(17)	108.1(5)
C(5)–N(4)–C(7)	113.5(5)	C(15)–N(14)–C(17)	113.7(5)
N(4)–C(5)–C(6)	109.3(5)	N(14)–C(15)–C(16)	111.1(5)
C(5)–C(6)–O(61)	117.8(5)	C(15)–C(16)–O(161)	116.9(5)
C(5)–C(6)–O(62)	118.4(5)	C(15)–C(16)–O(162)	118.1(6)
O(61)–C(6)–O(62)	123.8(6)	O(161)–C(16)–O(162)	125.0(6)
N(4)–C(7)–C(8)	108.1(5)	N(14)–C(17)–C(18)	109.1(5)
C(7)–C(8)–O(81)	117.4(6)	C(17)–C(18)–O(181)	117.0(6)
C(7)–C(8)–O(82)	118.1(6)	C(17)–C(18)–O(182)	118.4(6)
O(81)–C(8)–O(82)	124.4(6)	O(181)–C(18)–O(182)	124.4(6)
Cu(1)–N(4)–C(3)	113.6(3)	Cu(2)–N(14)–C(13)	114.3(4)
Cu(1)–N(4)–C(5)	105.1(3)	Cu(2)–N(14)–C(15)	105.4(3)
Cu(1)–N(4)–C(7)	104.2(3)	Cu(2)–N(14)–C(17)	103.5(3)
Cu(1)–O(61)–C(6)	113.3(4)	Cu(2)–O(161)–C(16)	113.6(4)
Cu(1)–O(81)–C(8)	112.6(4)	Cu(2)–O(181)–C(18)	112.7(4)
Cu(1)–S(1)–C(2)	84.1(2)	Cu(2)–S(11)–C(12)	83.6(2)
Cu(1)–S(1)–S(11)	107.4(1)	Cu(2)–S(11)–S(1)	111.7(1)

(continued)

TABLE 2. *(continued)*

Imidazole ligands			
N(101)–C(102)	1.320(9)	N(201)–C(202)	1.343(7)
N(101)–C(105)	1.36(1)	N(201)–C(205)	1.387(8)
C(102)–N(103)	1.306(8)	C(202)–N(203)	1.318(7)
N(103)–C(104)	1.360(9)	N(203)–C(204)	1.381(7)
C(104)–C(105)	1.34(1)	C(204)–C(205)	1.326(8)
C(102)–N(101)–C(105)	108.3(7)	C(202)–N(201)–C(205)	108.1(5)
N(101)–C(102)–N(103)	110.6(7)	N(201)–C(202)–N(203)	110.1(6)
C(102)–N(103)–C(104)	106.3(6)	C(202)–N(203)–C(204)	105.9(5)
N(103)–C(104)–C(105)	109.3(8)	N(203)–C(204)–C(205)	110.6(6)
N(101)–C(105)–C(104)	105.5(8)	N(201)–C(205)–C(204)	105.4(6)
Cu(1)–N(103)–C(102)	127.1(5)	Cu(2)–N(203)–C(202)	125.5(4)
Cu(1)–N(103)–C(104)	125.8(5)	Cu(2)–N(203)–C(204)	128.2(4)

apical water molecules are very short with respect to the usual values found (≥0.15 Å) in related five-coordinated compounds [1]. In the present case, the Cu(II)–N(imidazole) bonds are as short as the lowest limit of the range of such bonds (1.95(1)–1.98(2) Å) in related Cu(II)–ImH–aminoacidato and Cu(II)–ImH–peptide complexes [18–24]. The Cu(1) and Cu(2) atoms lie out of the corresponding ImH ligand planes P(3) and P(4) (0.25 and 0.18 Å respectively) and the Cu(1)–N(103) and Cu(2)–N(203) bonds are inclined with respect to these planes (7.4° and 5.3°, respectively). In addition, the ImH plane P(3) is tilted with respect to the mean square plane P(1) (35.4°) and the ImH plane P(4) with P(2) (62.6°). Analogous dihedral angles (31° and 57°) are formed between each of the ImH ligands and the best fit-plane of the four closest ligand atoms in glycylglycinato–bis(imidazole) copper(II) perchlorate [24]. The observed behaviour of the studied complex is consistent with a σ donor role for the ImH ligands, without appreciable dπ–pπ metal–ligand interaction (back donation). Other bond distances and angles of the copper(II) environments are in the range of comparable values reported in the literature for analogous Cu(II) complexes [9–11].

The mean tetragonal planes of the copper(II) atoms P(1) and P(2) form a dihedral angle of 51.2° while the imidazole ligands of the same dinuclear unit remain roughly perpendicular with a dihedral angle value of 83.3°.

Chelating Rings and Conformation of the Ligand TCC

In the dinuclear complex **I**, the TCC ligand plays both bridging and octadentate chelating roles. Each half ligand chelates (as tetradentate) one of the two crystallographically independent copper(II) atoms in the mixed complex. This chelation involves one puckered metal–(β-mercaptoethylamino) ring and two nearly planar metal–glycinate type rings. Both moieties of TCC are not symmetrically related but their overall conformations are closely similar (see 'Supplementary Material'). All the metal–glycinate rings of TCC have slightly distorted asymmetric envelope conformations. The mean planes P(5), P(6) and P(9), P(10)* of every two metal–glycinate rings sharing the same Cu–N(amino) bond contain the corresponding metal atom (maximum deviation <0.006 Å) and form dihedral angles (171°–172°) which reflect their rough coplanarity. Among the small structural differences of the two halves of the ligand TCC, the most remarkable seems to be the symmetrical puckered conformation of the chelate ring Cu(1)–S(1)–C(2)–C(3)–N(4), with the carbon atoms at 0.38 Å on either side of the plane P(7) defined by Cu(1), N(4), S(1), in contrast with the unsymmetrical puckering of the homologous ring Cu(2)–S(11)–C(12)–C(13)–N(14), with unequal distances of the atoms C(12) and C(13) (0.36 and –0.43 Å respectively) from the plane P(8) defined by Cu(2), N(14) and S(11). This difference is probably attributable to the inequality in the Cu–S(disulfide) bonds (0.04 Å), since both Cu(1)–S(1) and Cu(2)–S(11) bonds are tilted with respect to the normal to their coordination square planes P(1) and P(2) in similar magnitude (12.4° and 13.5° respectively). The bond distances and angles of the ligand TCC in the studied compound agree well with the reported values for related Cu(II) complexes [9–11]. However, from one to another, significant differences are observed in the values (and the chirality) of the torsion angles about the disulfide bond. Thus, the TCC ligand shows different left-handed torsion angles C–S–S–C in **II** (–113.1°) and in **I** (–80.4°), whereas the corresponding angle in $Na_4[Cu_2(GSSG)]\cdot 6H_2O$ has a right-handed value (+108.5°) [11].

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*P(5): Cu(1), N(4), C(5), C(6), O(61); P(6): Cu(1), N(4), C(7), C(8), O(81); P(9): Cu(2), N(14), C(15), C(16), O(161); P(10): Cu(2), N(14), C(17), C(18), O(181).

Observations on Imidazole Coordination to the Dicopper(II)–TCC Chelate

It is instructive to compare the structures of the compounds **I** and **II**. The Cu–O (carboxylate) apical bond (2.621(8) Å) in **II** is shortened by about 0.210 Å in the Cu–OW (apical) bond in **I**. This change results in the lengthening of the *trans*-apical Cu(II)–S(disulfide) bond (0.238 Å in average). The evolution of a layered crystal structure (**II**) to a packing of discrete dinuclear units (**I**) increases the Cu(II)...Cu(II) shortest distance from 4.632(2) to 5.970(1) Å.

Crystal Packing

The crystal of the title compound shows a bidimensional hydrogen bonded network in which seem to be involved all N–H and O–H groups of the discrete dinuclear complex units and the non-coordinated water molecules (OW(3) and OW(4)) (see 'Supplementary Material'). These data suggest that the N–H bond of both ImH ligands might be involved in unsymmetrical 'bifurcated' hydrogen bonding interactions with two oxygen atoms of the same carboxylate group of an adjacent complex unit.

Properties of the Compound $[Cu_2(TCC)(ImH)_2(H_2O)_2]\cdot 2H_2O$

Thermal stability

The dihydrated form of the studied compound is relatively stable at room temperature. On heating, the product loses all water molecules at 360–400 K, in an overall endothermic process (calc. loss 10.06%; exp. loss 8.81%). The anhydrous residue initiates the pyrolytic decomposition over 435 K and several steps yield $CuSO_4\cdot CuO$ at 800 K (calc. residue 33%, exp. 35%). The overlapped dehydration process is in accordance with the reported structural data. Analogous examples are known. The mixed-copper(II) complex of L-glutamato (L-glu) and 1,10-*o*-phenanthroline (*o*-phen), having the formula $[Cu(L\text{-}glu)(o\text{-}phen)(H_2O)]\cdot 3H_2O$ and Cu(II)–OW axial bond of 2.26(1) Å (average) [22] loses the uncoordinated water at 308–373 K and the coordinated water at 383–423 K [22]. In the here studied compound, with the longest Cu(II)–OW (apical) bonds, it seems reasonable to expect an overlap of the free and metal-bonded water loss.

Infrared spectrum

The infrared spectrum of **I** shows several absorptions in the region of 3100–3600 cm^{-1}, of ν(O–H) and ν(N–H) modes. A band at 3210 cm^{-1} can be attributed to the mode ν(N–H) of the hydrogen bonded N–H bond of the ImH ligands [25]. The absorptions of the deformation modes $\delta(H_2O)$ and δ(N–H) at 1645 and ~1500–1540 cm^{-1}, respectively, overlap the intense band of ν_{as}(COO) at 1600 cm^{-1}. The ν_s(COO) band is recorded at 1380–1370 cm^{-1}. The value of $\Delta(COO) = \nu_{as}(COO) - \nu_s(COO) =$ 220–230 cm^{-1} is typical of monodentate carboxylate group-to-copper(II) coordination of remarkable ionic character. No information can be obtained about the disulfide group from the discussed spectrum.

Reflectance spectrum

The reflectance spectrum of the title compound shows an unsymmetrical and broad band with ν_{max} = 14 000 cm^{-1}. If we assume $\Delta_0 = \bar{\nu}$ (at the barycenter of intensity = 14 600 cm^{-1}), a rough value of ligand field stabilization energy of 8800 cm^{-1} could be obtained. In all instances, this spectrum supports the distorted octahedral description of the copper(II) coordination environment in compound **I**. The electronic spectra of mixed Cu(II) (aminoacidato)–imidazole complexes with square-pyramidal and discrete square-planar copper(II) coordination polyhedra show electronic spectra with ν_{max} in the ranges 16 000–17 000 and 17 500–18 200 cm^{-1}, respectively [22]. The electronic spectrum of the mixed Cu(II)–TCC–imidazole complex agrees well with the corresponding spectrum for the Cu(II)–TCC–imidazole–free analogous solid (ν_{max} = 13 250 cm^{-1}) [26], taking into account that the ImH ligand is more basic than the water molecule.

Electron spin resonance

The powder spectra of **I** recorded at 298 and 77 K are axial ESR spectra, with g values of $g_{\parallel} = 2.24$ and $g_{\perp} = 2.07(\pm 0.01)$ and without hyperfine structure because of the magnetic interactions between neighbouring copper(II) ions ('Supplementary Material', Table S-IX). In the observed axial spectra, the lowest g value is greater than 2.04 and the expression [27] $(G = g_{\parallel} - 2)/(g_{\perp} - 2)$ gives $G = 3.43 < 4.00$. These results suggest a significant exchange coupling between crystallographically independent copper(II) ions with an appreciable misalignment of the local 'tetragonal axes' [28]. In agreement with this, the molecular structure of **I** clearly shows misalignment of the 'tetragonal' axes of both crystallographically independent copper(II) ions.

Conclusions

A comparison of the present results on the compound $[Cu_2(TCC)(ImH)_2(H_2O)_2]\cdot 2H_2O$ (**I**) with the known crystal structure and properties of $[Cu_2(TCC)(H_2O)_2]\cdot 4H_2O$ (**II**) shows several interesting features.

First, the preference of the ImH ligand is to be coordinated in an equatorial position (of the tetragonal plane) in the environment of the copper(II) ion. This does not disturb the chelating properties of the *N,N,N',N'*-tetrakis(carboxymethyl)-

cystaminate(4−) ion (TCC) against the two copper(II) ions but it is made by moving water molecules from equatorial positions to apical sites of the elongated octahedral polyhedron of the metal ions. Two of these rearrangements lead to the lengthening of the Cu(II)–S(disulfide) linkages to the limit of the very weak bonds or weak interactions.

Second, the σ donor properties are without any significant π acceptor role of the ImH ligands as evidenced by the tilt of these ImH planes with respect to the corresponding Cu–N(ImH) bonds and the twist of these ligands with respect to the tetragonal coordination planes of copper(II).

Supplementary Material

Tables S-I to S-IX giving thermal motion factors, atomic coordinates and isotropic thermal parameters of hydrogen atoms, C–H, O–H and N–H distances, hydrogen bonds and van der Waals distances, least-squares mean plane equations; and Figures 3–6 showing TG and DTA diagrams, infrared, reflectance and ESR spectra of $[Cu_2(TCC)(ImH)_2]\cdot 2H_2O$, a listing of observed and calculated structure factors are available from the authors on request.

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