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LETTER

New Mixed-ligand Copper(II) Complex with Iminodiacetate and Imidazole: Bis[bis(imidazole)(iminodiacetato)copper(II)] Dihydrate

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The Cu–imidazole–aminodiacetato (or peptide) and related complexes can serve as model compounds for some copper proteins. Recent results [1] propose an imidazolate-bridged heterodinuclear (iminodiacetato)copper(II)pentaammine)cobalt(III) complex, $[(IDA)Cu(Im)Co(NH_3)_5]^{2+}$, as a model for superoxide dismutase (a Cu–Zn enzyme). In this connection, we report the synthesis, structure and properties of a new ternary complex of Cu(II), imidazole (ImH) and iminodiacetate or (*N*-carboxymethyl)glycinate(2–) ion (IDA).

Experimental

The title complex $[Cu(IDA)(ImH)_2]_2 \cdot 2H_2O$ can be obtained by reaction of 5.0 g (21.67 mmol) of $[Cu(IDA)(H_2O)_2]$ [2] and 4.34 g (65.01 mmol) of ImH (50% excess) in 200 ml of water at room temperature. The dark blue solution was filtered and allowed to crystallize for several days. The dark blue crystals of the desired product were filtered off, washed with cold water and air-dried. This compound needs to be recrystallized from concentrated water solutions ($\geqslant$4%); yield > 70%. *Anal.* Calc. for $Cu_2C_{20}H_{30}N_{10}O_{10}$: C, 34.44; H, 4.33; N, 20.07; Cu, 18.21. Found: C, 34.37; H, 4.33; N, 20.44; Cu, 18 ± 1% (complexometry). The thermal (TG-DTA), spectral (IR, reflectance, ESR) and magnetic susceptibility data were obtained as reported earlier [3].

The studied compound crystallizes in the triclinic system, space group $P\bar{1}$, with $a = 8.087(1)$, $b = 9.334(1)$, $c = 9.817(1)$ Å; $\alpha = 77.80(1)$, $\beta = 77.01(2)$, $\gamma = 82.88(1)°$; $V = 703.4$ Å^3 and $Z = 1$; $D_{exp} = 1.26$, $D_{calc} = 1.27$ Mg m^{-3}. For 2162 independent observed reflections ($I \geqslant 3\sigma(I)$), $R = 0.022$ and $R_w = 0.024$. Intensity data were collected on a Nonius-Enraf CAD4 diffractometer and corrected for Lorentz and polarization effects, but not for absorption effects. Structure determinations and other calculations were performed as in ref. 3.

Results and Discussion

Positional parameters are given in Table 1. Bond lengths and angles are given in Table 2. The compound consists of dinuclear centrosymmetrical units $[Cu(IDA)(ImH)_2]_2$ (see Fig. 1) and water molecules which are not bonded to the metal ion. Each Cu(II) atom exhibits a very flattened square-pyramidal coordination, lying at –0.056 Å from the mean plane P_1 of the square base atoms N(1), O(1), N(13) and N(23), towards the apical atom O(4), but a very weak interaction Cu···O(2^i) (symmetry code *i*: $1-x$, $1-y$, $-z$) with distance of 2.873(1) Å (the so-called 'partial coordination') completes the unsymmetrical elongated octahedral polyhedron (type 4 + 1 + 1) around the Cu atom. Two symmetrically related and long contacts of this kind make up the dinuclear unit shown in Fig. 1. In the crystal, the stability of each dimeric unit is reinforced by four hydrogen bonds, the N(1)–H(N1)···OW^i (3.158(2) Å, 168(2)° and OW–H1(OW)···O(2) (2.902(3) Å, 149(3)°) interactions and their centrosymmetrically related ones. In addition each dinuclear entity is bonded to six other units by means of hydrogen bonds, which involve the remaining OW–H2(OW) bond of the two water molecules and the N–H bond of the four ImH ligands of the dimer.

The IDA ligand acts as a tridentate chelating agent, making up two five-membered Cu–glycinate rings, nearly perpendicular (dihedral angle between their mean planes $\phi = 83.1°$) and sharing the Cu–N(1) bond. This situation agrees well with the chelating

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TABLE 1. Relative atomic coordinates and thermal parameters (e.s.d.s in parentheses)

Atom	x/a	y/b	z/c	U_{eq} [a]
Cu	0.28336(3)	0.32094(2)	0.13126(2)	0.0260
O(1)	0.2975(2)	0.5122(1)	0.0068(1)	0.0345
O(2)	0.3616(2)	0.7402(1)	−0.0159(2)	0.0486
O(3)	−0.0042(2)	0.3151(1)	0.5370(1)	0.0320
O(4)	0.0331(1)	0.3868(1)	0.3017(1)	0.0323
OW	0.2652(2)	0.7321(2)	−0.2815(2)	0.0564
N(1)	0.3676(2)	0.4225(2)	0.2657(1)	0.0286
N(11)	0.1141(2)	0.2488(2)	−0.2090(2)	0.0420
N(13)	0.2085(2)	0.2454(2)	−0.0172(2)	0.0339
N(21)	0.2078(2)	−0.0846(2)	0.3867(2)	0.0363
N(23)	0.2901(2)	0.1240(2)	0.2569(1)	0.0303
C(1)	0.3578(3)	0.5821(2)	0.2083(2)	0.0351
C(2)	0.3380(2)	0.6161(2)	0.0550(2)	0.0336
C(3)	0.2683(2)	0.3832(2)	0.4120(2)	0.0296
C(4)	0.0840(2)	0.3611(2)	0.4158(2)	0.0251
C(12)	0.1348(3)	0.3271(2)	−0.1166(2)	0.0390
C(14)	0.2362(3)	0.1069(2)	−0.0490(2)	0.0457
C(15)	0.1790(3)	0.1089(3)	−0.1672(3)	0.0501
C(22)	0.1631(3)	0.0406(2)	0.3061(2)	0.0380
C(24)	0.4219(3)	0.0474(2)	0.3104(3)	0.0460
C(25)	0.3700(3)	−0.0815(3)	0.3916(3)	0.0530

[a] $U_{eq} = \frac{1}{3}\text{trace}\,(U)$.

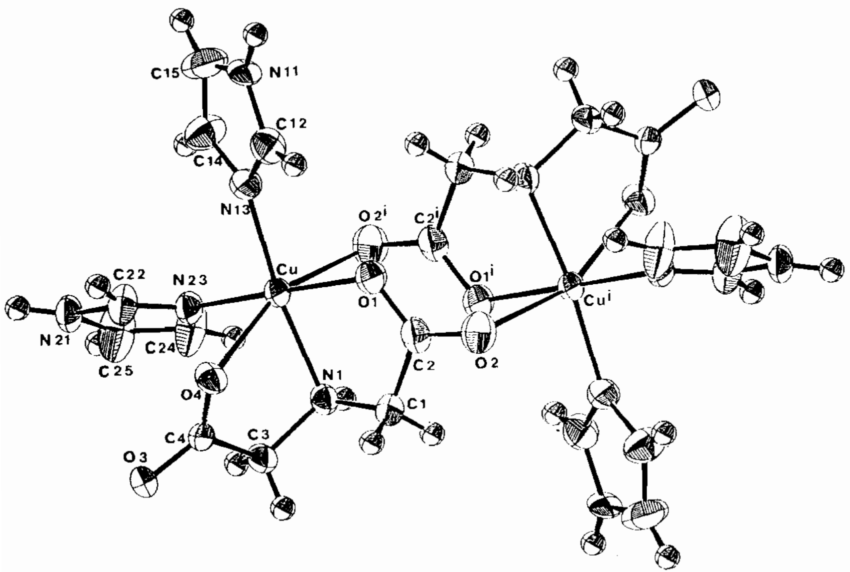

Fig. 1. $[Cu(IDA)(ImH)_2]_2$.

role of IDA in $[Cu(IDA)(H_2O)_2]$ ($\phi = 107°$) [2]. However, in this latter case, each IDA ligand supplies the O(3) atom to the next Cu^i atom in a short Cu^i–O(3) bond, thus forming chains of the Cu–IDA–$(H_2O)_2$ complex, whereas in the new $[Cu(IDA)(ImH)_2]_2$ complex, the IDA ligand plays a singular bridging role, giving rise to the referred dimeric unit.

The *cis*-coordination of two ImH molecules to the same Cu(II) atom is sterically hindered. Hence it follows that the Cu–N(ImH) distances fall in the upper limit of the range (1.95–1.98 Å) of the Cu–imidazole bonds in Cu(II)–ImH–aminoacidato (or peptide) and related compounds [3], and both the ImH-1 and ImH-2 planes define a noticeable dihedral

TABLE 2. Bond lengths (Å) and angles (°) within the dimeric unit (e.s.d.s in parentheses)

Cu coordination			
Cu–N(1)	2.049(1)	O(2^i)–Cu–O(1)	87.72(5)
Cu–O(1)	1.939(1)	O(4)–Cu–O(1)	96.67(5)
Cu–O(4)	2.424(1)	O(4)–Cu–O(2^i)	157.76(4)
Cu–N(13)	1.981(1)	N(1)–Cu–O(1)	83.91(5)
Cu–N(23)	1.987(1)	N(1)–Cu–O(2^i)	85.10(5)
Cu–O(2^i)	2.873(2)	N(1)–Cu–O(4)	73.76(5)
Cu–Cu^i	5.0295(3)	N(13)–Cu–O(1)	88.97(6)
		N(13)–Cu–O(2^i)	93.38(6)
		N(13)–Cu–O(4)	108.45(5)
		N(13)–Cu–N(1)	172.77(6)
		N(23)–Cu–O(1)	175.17(6)
		N(23)–Cu–O(2^i)	87.74(5)
		N(23)–Cu–O(4)	86.93(5)
		N(23)–Cu–N(1)	94.04(6)
		N(23)–Cu–N(13)	92.96(6)
IDA			
O(1)–C(2)	1.270(2)	C(2)–O(2)–Cu^i	96.2(1)
O(2)–C(2)	1.232(2)	C(4)–O(4)–Cu	103.2(1)
O(3)–C(4)	1.260(2)	C(1)–N(1)–Cu	107.8(1)
O(4)–C(4)	1.245(2)	C(3)–N(1)–Cu	110.2(1)
N(1)–C(1)	1.476(2)	C(3)–N(1)–C(1)	113.4(1)
N(1)–C(3)	1.474(2)	C(2)–C(1)–N(1)	112.0(1)
C(1)–C(2)	1.512(3)	O(2)–C(2)–O(1)	123.7(2)
C(3)–C(4)	1.521(2)	C(1)–C(2)–O(1)	116.9(1)
		C(1)–C(2)–O(2)	119.4(2)
		C(4)–C(3)–N(1)	112.6(1)
		O(4)–C(4)–O(3)	125.5(1)
		C(3)–C(4)–O(3)	115.8(1)
		C(3)–C(4)–O(4)	118.7(1)
		C(2)–O(1)–Cu	117.2(1)
ImH-1			
N(11)–C(12)	1.328(3)	C(15)–N(11)–C(12)	107.3(2)
N(11)–C(15)	1.360(3)	C(12)–N(13)–Cu	124.6(1)
N(13)–C(12)	1.313(2)	C(14)–N(13)–Cu	129.3(1)
N(13)–C(14)	1.373(3)	C(14)–N(13)–C(12)	105.7(2)
C(14)–C(15)	1.338(2)	N(13)–C(12)–N(11)	111.1(2)
		C(15)–C(14)–N(13)	109.0(2)
		C(14)–C(15)–N(11)	106.8(2)
ImH-2			
N(21)–C(22)	1.325(3)	C(25)–N(21)–C(22)	107.2(2)
N(21)–C(25)	1.328(3)	C(22)–N(23)–Cu	126.1(1)
N(23)–C(22)	1.308(2)	C(24)–N(23)–Cu	128.8(1)
N(23)–C(24)	1.352(3)	C(24)–N(23)–C(22)	105.1(2)
C(24)–C(25)	1.352(3)	N(23)–C(22)–N(21)	111.7(2)
		C(25)–C(24)–N(23)	109.1(2)
		C(24)–C(25)–N(21)	106.9(2)

angle (66.0°). These ligands are twisted with respect to the square coordination plane (26.0 and 56.1°, respectively), the Cu–N(13) and Cu–N(23) bonds are differently inclined versus the corresponding ImH plane (5.1 and 0° respectively) and the Cu(II) atom lies 0.176 and 0.002 Å out of these ligand planes. In the reported compound, the imidazole ligands act as σ(N–Cu) donors, without any π metal-to-ligand acceptor role.

The compound loses all water molecules at 403–418 K and decomposes at 430–620 K. The IR spectrum (cm^{-1}) shows N–H bands of ImH (3200,

1545) and IDA (3140, 1500), carboxylate bands of IDA (1605 (shoulder), 1590, 1380) and the H_2O deformation (1650). An unsymmetrical d–d band (ν_{max} at 16075 and 17275 (shoulder) cm^{-1}; the intensity barycentre at 16500 cm^{-1}) agrees with the spectral data reported for square-pyramidal Cu(II)–ImH–aminoacidato (or peptide) complexes (ν_{max} = 16000–17000 cm^{-1}). In addition to an axial type signal ($g_{\parallel} = 2.23$, $g_{\perp} = 2.03$ at 298 K) as expected for the $\Delta M_s = 1$ transition of the Cu(II) atom in a $d_{x^2-y^2}$ ground state, the ESR spectra (77 and 298 K) of the complex show a very weak signal at $g \approx 4$ for the forbidden transition $\Delta M_s = 2$, typical in dinuclear Cu(II) complexes with a $Cu\cdots Cu^i$ distance of 4.4–5.5 Å [4]. In the reported example, the internuclear $Cu\cdots Cu^i$ distance is 5.029(1) Å and the inverse molar susceptibilities (77–298 K) show a Curie–Weiss behaviour with $\mu_{eff} = 1.65$ BM for Cu(II), a value slightly lower than the spin-only value (1.73 BM). These properties agree well with the crystal and/or molecular structure of the studied compound.

Supplementary Material

Anisotropic thermal parameters, hydrogen atomic coordinates, 'mean planes' and a listing of the observed and calculated structure factors are available from the authors on request.

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