Inorganica Chimica Acta

LETTER

Synthesis, crystal structure and properties of aqua(*C*-benzyl-iminodiacetato) copper(II): [Cu(CMPhe)(H_2O)]* with a tridentate-bridged carboxylate group to copper(II) coordination

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(Received March 28, 1990; revised June 13, 1990)

In preceding papers, we reported the synthesis, crystal structure and properties of some copper(II) complexes with *N,N*-bis(carboxymethyl)amino acids (β-alanine or glycine) [1, 2]. Moreover, some new mixed-ligand copper(II) complexes with imidazole and iminodiacetic acid or *N,N,N',N'*-tetrakis-(carboxymethyl)cystamine were investigated recently by the authors [3, 4]. As a part of our program, this work deals with the preparation, crystal structure and properties of the title compound, where it will be of interest to study the influence of the *C*-benzyl substituent in the iminodiacetate skeleton of the ligand.

Experimental

C-Benzyl-iminodiacetic acid or *N*-carboxymethyl-L-phenylalanine (H_2CMPhe) was obtained from the reaction of equimolar amounts of chloroacetate and L-phenylalaninate potassium salts in alkaline (KOH) aqueous solution, by a procedure reported elsewhere [5].

The reaction of H_2CMPhe (22.4 mmol) and $Cu_2CO_3(OH)_2$ (11.2 mmol) in 300–500 ml of water (60 °C), stirring under vacuum to remove the CO_2, gives a dark blue solution, which is cooled slowly at room temperature and filtered (to remove insoluble by-products). The resulting clear solution is left to evaporate at room temperature and the dark blue crystals formed are filtered and washed with cold water, ethanol and acetone and then air-dried. The analytical data of this product gives the formula [Cu(CMPhe)]·$2H_2O$. This starting material is dissolved in the minimum amount of hot water (70 °C) and its recrystallization at room temperature yields well shaped blue crystals of the purified compound, with analytical data according with the actual formula [Cu(CMPhe)·(H_2O)]. Yield: 70%. *Anal.* Calc. for $C_{11}H_{13}CuNO_5$: C, 43.6; H, 4.3; N, 4.6; Cu, 21.0. Found: C,43.5; H, 4.3; N, 4.6; Cu, 20 ± 1 (complexometry)%.

The title compound crystallizes in the orthorhombic system, space group $P2_12_12_1$ with $a = 6.017(5)$, $b = 7.680(1)$, $c = 26.244(6)$ Å, $V = 1166$ Å^3 and $Z = 4$; $D_{exp} = 1.72$ and $D_{calc} = 1.71$ g cm^{-3}. For 1018 independent observed reflections ($I \geq 3\sigma(I)$), $R = 0.042$ and $R_w = 0.030$. Intensity data were collected on a Enraf-Nonius CAD4 diffractometer and corrected for Lorentz and polarization effects. Structure determination and other calculations were performed as in ref. 4.

Results and discussion

Positional parameters are given in Table 1. Bond lengths and angles of [Cu(CMPhe)(H_2O)] are given in Table 2. Figure 1 shows a view of this copper(II) complex with the atom labelling.

In the complex [Cu(CMPhe)(H_2O)], each copper(II) ion is bonded to one water molecule and two CMPhe^{2-} ligands. The atoms involved in these bonds are: N(21), O(25), O(12) (from one ligand), together with the O(11^i) atom (from an adjacent ligand referred with a superscript i: $\frac{1}{2}+x, \frac{3}{2}-y, 1-z$); they are roughly placed at the corners of the square

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*(CMPhe) = (*C*-benzyl-iminodiacetato) or (*N*-carboxymethyl-L-phenylalaninato)(2 −).

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0020-1693/90/$3.50

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

	x/a	y/b	z/c	B_{eq} (Å^2)^a
Cu	0.4956(2)	0.9466(1)	0.53240(3)	2.80
OW	0.286(1)	1.1687(7)	0.5287(4)	8.03
C(1)	0.248(1)	0.6548(9)	0.5472(3)	2.27
C(2)	0.422(1)	0.6462(9)	0.5920(3)	2.37
C(3)	0.334(1)	0.547(1)	0.6402(3)	2.84
O(11)	0.1154(8)	0.5337(6)	0.5423(2)	3.13
O(12)	0.2612(9)	0.7823(6)	0.5154(2)	2.75
N(21)	0.493(1)	0.8246(6)	0.6027(2)	2.42
C(22)	0.722(2)	0.844(1)	0.6240(4)	4.32
C(23)	0.855(1)	0.986(1)	0.5968(3)	3.41
O(24)	1.0414(9)	1.0187(9)	0.6144(2)	4.80
O(25)	0.7611(9)	1.0637(7)	0.5583(2)	3.93
C(31)	0.522(2)	0.5015(8)	0.6785(2)	2.47
C(32)	0.520(2)	0.5751(9)	0.7289(3)	3.35
C(33)	0.703(2)	0.539(1)	0.7626(3)	4.11
C(34)	0.869(2)	0.433(2)	0.7469(4)	4.59
C(35)	0.863(2)	0.355(1)	0.6972(4)	4.19
C(36)	0.689(1)	0.390(1)	0.6636(3)	3.33

$^a B_{eq} = \frac{4}{3}\Sigma_i \Sigma_j \beta_{ij}\, \vec{a}_i \cdot \vec{a}_j$.

base of a pyramid whose apex is occupied by the oxygen OW atom of one water molecule. The atoms of the square base deviate from the mean plane in the range of −0.184 to 0.242 Å. The copper atom inside the pyramid is displaced from the mean plane towards the apical water molecule (−0.349 Å). The $CMPhe^{2-}$ ligand acts as a tridentate chelating agent and forms three shorter bonds Cu–N(21), Cu–O(12) and Cu–O(25) of two nearly coplanar metal glycinate rings. The Cu(II)–OW bond is longer and lies almost perpendicular to the five-membered chelate rings. Moreover, the adjacent $CMPhe^{2-}$ ligand may supply a very weak bond with the referred copper(II) ion via the $O(12^{i})$ atom. It is noticeable that, both oxygen $O(11^{i})$ and $O(12^{i})$ atoms of the α-carboxylate group of the L-phenylalanine moiety are involved in the bonds to the referred copper(II) ion. This double carboxyl–copper interaction is typically unsymmetrical. Because the carboxyl group is less susceptible to distortion than the coordination polyhedron of the Cu(II) ion, the longer Cu(II)–$O(12^{i})$ interaction is necessarily very weak. In accordance with Freeman [6], where a Cu(II) atom is bonded to both oxygens of a single carboxyl group, the 'bond number' to be assigned to the weaker quasi-apical Cu–O interaction is 3/4 for a length range of 2.5–2.8 Å, and 1/2 for a distance of 2.9–3.0 Å. If we assume these approximations, the best description for the coordination of the copper(II) ion in $[Cu(CMPhe)(H_2O)]$ is a strongly distorted octahedral polyhedron. As suggested by Hathaway [7], the copper polyhedron of coordination might be described as belonging to the (4+1+1*) type [7]. In this case, the α-carboxyl group of the L-phenylalanine residue would play an unsymmetrical tridentate bridged role. The same type of tridentate carboxylate group was reported for one of the acetate arms of the nitrilotriacetate ion, $NTA^{3-} = N(CH_2CO_2)_3{}^{3-}$ in the crystal structure of nona-coordinated praseodymium(III) and neodymium(III) nitrilotriacetates, $[M(NTA)(H_2O)_2]\cdot H_2O$ (M = Pr, Nd) [8]. In the crystal structure of $[Cu(CMPhe)(H_2O)]$, each ligand $CMPhe^{2-}$ chelates two metal ions. To account for the consequences of the *C*-benzyl substituent in the iminodiacetate skeleton of the ligand $CMPhe^{2-}$, it is instructive to compare the studied complex with the structure of diaqua(iminodiacetato)copper(II), $[Cu(IDA)(H_2O)_2]$ [9]. In this compound, the IDA^{2-} ligand acts as a tridentate chelating agent for a copper atom, thus forming two Cu(II)–glycinate rings nearly perpendicular, with a dihedral angle of 107° between their mean planes. Similarly, in the $[Cu(IDA)(ImH)_2]\cdot 2H_2O$ complex [3], the mean planes between the two five-membered Cu–glycinate rings are nearly perpendicular (83.1°). In these complexes, the two carboxylate groups never play a tridentate-bridged role. In the title complex, the first structural consequence of the *C*-benzyl-substituent in the ligand $CMPhe^{2-}$ is the closure of the corresponding chelate ring and of the angles Cu–N(21)–C(2), N(21)–C(2)–C(1) and C(2)–C(1)–O(12). This results in the fairly coplanarity of the two five-membered chelate rings in $[Cu(CMPhe)(H_2O)]$, with a dihedral angle of 21.7°. Both rings have an asymmetric envelope conformation, the C-substituted cycle being slightly more distorted. The Cu(II) ion lies virtually in these mean planes. The torsion angles of the ligand $CMPhe^{2-}$ also reflect the stronger distortion of the C-substituted acetate arm (as shown by significatively higher values of Cu–N–C–C and N–C–C–O torsion angles around the N–C and C–C bonds in the C-substituted chelate ring than in unsubstituted analogous one). The view of the unit-cell of the studied complex (Fig 2) shows the overall extension of polynuclear zigzag chains along the $\vec{a}$ axis, by infinite repetition of double-complex units $[Cu(CMPhe)(H_2O)]_2$. In these chains, two consecutive units of the complex are related by a 2_1 axis parallel to [100]. Both hydrogen atoms of the water molecule are involved in hydrogen bonding formation, but the N–H bond is not. In the crystal, every one of the zigzag chains is reinforced by intrachain hydrogen bonds OW–HA(OW)...$O(24^{iv})$(2.86(1) Å; 142°) linking two alternate complex units (iv = $-1+x, y, z$) which are related by the $\vec{a}$ axis translation.

TABLE 2. Bond lengths (Å) and angles (°) with e.s.d.s. in parentheses[a]

Copper environment			
Cu–OW	2.123(6)	Cu–N(21)	2.006(5)
Cu–O(12)	1.941(5)	Cu–O(11^{i})	2.023(4)
Cu–O(25)	1.946(6)	Cu–O(12^{i})	2.665(5)
Cu–Cu^{i}	4.566(1)		
OW–Cu–O(12)	94.7(2)	O(12)–Cu–O(12^{i})	84.65(5)
OW–Cu–O(25)	97.5(3)	O(25)–Cu–N(21)	85.6(3)
OW–Cu–N(21)	114.2(3)	O(25)–Cu–O(11^{i})	89.2(2)
OW–Cu–O(11^{i})	96.4(3)	O(25)–Cu–O(12^{i})	88.0(2)
OW–Cu–O(12^{i})	150.0(3)	N(21)–Cu–O(11^{i})	149.4(2)
O(12)–Cu–O(25)	166.2(2)	N(21)–Cu–O(12^{i})	95.5(2)
O(12)–Cu–N(21)	83.5(2)	O(11^{i})–Cu–O(12^{i})	54.1(2)
O(12)–Cu–O(11^{i})	95.8(2)		
Ligand CMPhe^{2-}			
C(1)–O(11)	1.232(9)	C(23)–O(24)	1.231(10)
C(1)–O(12)	1.269(8)	C(23)–O(25)	1.272(10)
C(1)–C(2)	1.540(10)	C(31)–C(32)	1.393(9)
C(2)–N(21)	1.462(9)	C(32)–C(33)	1.417(14)
C(2)–C(3)	1.530(10)	C(33)–C(34)	1.345(14)
C(3)–C(31)	1.527(11)	C(34)–C(35)	1.392(14)
N(21)–C(22)	1.487(13)	C(35)–C(36)	1.372(13)
C(22)–C(23)	1.519(13)	C(36–C(31)	1.376(12)
O(11)–C(1)–O(12)	124.0(6)	N(21)–C(22)–C(23)	113.2(7)
O(11)–C(1)–C(2)	118.8(6)	C(22)–C(23)–O(24)	117.5(7)
O(12)–C(1)–C(2)	117.1(6)	C(22)–C(23)–O(25)	116.7(8)
C(1)–C(2)–C(3)	111.8(6)	O(24)–C(23)–O(25)	125.9(8)
C(1)–C(2)–N(21)	107.2(5)	Cu–O(25)–C(23)	113.9(5)
C(3)–C(2)–N(21)	115.1(6)	C(3)–C(31)–C(32)	118.8(8)
C(2)–C(3)–C(31)	111.2(6)	C(3)–C(31)–C(36)	120.7(6)
Cu–O(11^{i})–C(1^{i})	105.6(4)	C(32)–C(31)–C(36)	120.5(8)
Cu–O(12)–C(1)	114.1(4)	C(31)–C(32)–C(33)	117.6(9)
Cu–O(12^{i})–C(1^{i})	74.9(4)	C(32)–C(33)–C(34)	121.2(8)
Cu–O(12^{i})–Cu^{i}	164.8(2)	C(33)–C(34)–C(35)	120.4(8)
C(2)–N(21)–C(22)	115.7(6)	C(34)–C(35)–C(36)	119.5(10)
Cu–N(21)–C(2)	106.1(4)	C(35)–C(36)–C(31)	120.7(8)
Cu–N(21)–C(22)	105.6(5)		

[a] Symmetry code i: $\frac{1}{2}+x$, $\frac{3}{2}-y$, $1-z$.

Properties of the complex [Cu(CMPhe)(H$_2$O)]

TG and TDA diagrams of single crystal and powdered samples of [Cu(CMPhe)(H$_2$O)] show the loss of the water molecule (5.57% exp., 5.97% calc.loss) at 453–498 K, immediately followed by a sharp decarboxylation step (498–503 K) and the pyrolysis of the organic ligand residue in two or more overlapped steps (503–770 K) to give impure CuO (31% exp., 26.3% calc. residue).

In addition to an expectable NIR spectrum of little structural significance, the UV–Vis reflectance spectrum shows a very strong UV absorption, characteristic of a ligand-to-metal charge transfer band in copper(II) complexes of amino acid and related ligands. Curiously, the remarkable unsymmetrical six-coordination of the copper(II) ion in [Cu(CMPhe)(H$_2$O)] gives only a rather symmetrical and broad band at 13 500 cm^{-1} in the visible reflectance spectrum. It seems obvious that this band overlaps the different components involved in a $^2T_{2g} \leftarrow {}^2E_g$ transition of a distorted octahedral Cu(II) coordination. The $\lambda_{max} = 741$ nm agrees well with the established shorter Cu–OW bond and longer Cu–O(12^{i}) bond; this later deviates markedly from the normal to the mean equatorial plane P1. The comparable shape and λ_{max} values of the Vis-reflectance spectra of these complexes support that the distortion caused by the forced coordination of O(12^{i}) in [Cu(CMPhe)(H$_2$O)] is roughly compensated by the shortening of the *trans*-axial water to copper(II) bond.

The observed powder ESR spectra at 298 and 77 K and the *g* parameters of the spin Hamiltonian show that the complex obtained is in the form of

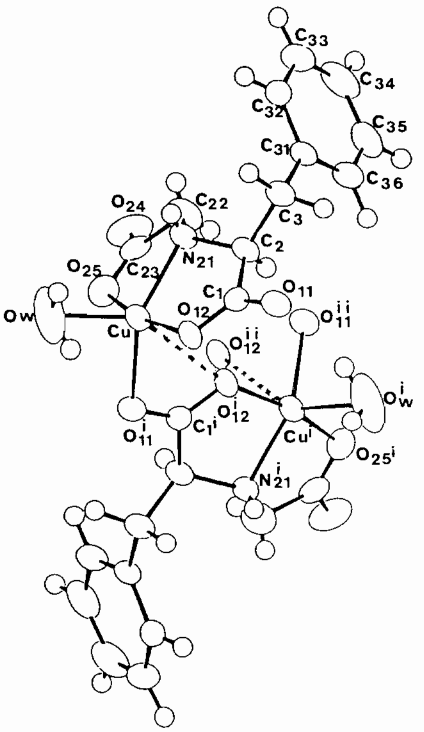

Fig. 1. View of the [Cu((CMPhe)(H_2O)] complex with the atom labelling. Symmetry code i: $\frac{1}{2}+x$, $\frac{3}{2}-y$, $1-z$; ii: $-\frac{1}{2}+x$, $\frac{3}{2}-y$, $1-z$.

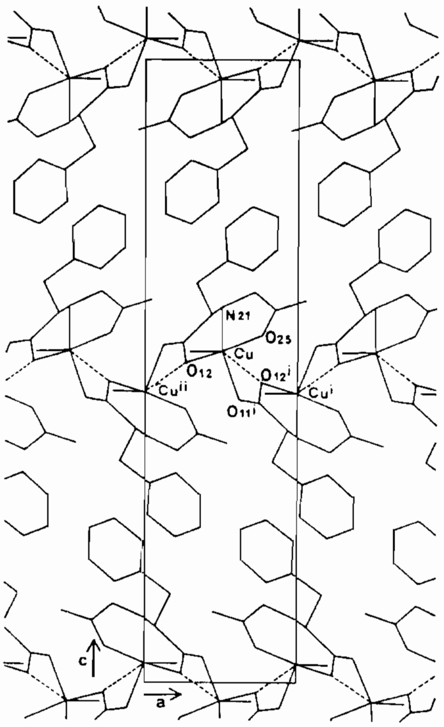

Fig. 2. Projection of the unit-cell along the *b*-axis.

a distorted octahedra in the polycrystalline state [7]. The observed *g* values are $g_{\perp}=2.05$ and $g_{\parallel}=2.26$ at 77 and 298 K, respectively. These spectra have the large linewidth typical of dipolar interaction. The lack of hyperfine structure in the ESR suggests that intermolecular exchange interactions are operative, in accordance with the distance Cu–Cu^i = 4.566(1) Å in the crystal structure of [Cu(CMPhe)(H_2O)]. The value of μ_{eff}(Cu) = 1.82 BM at room temperature and plot of χ data versus *T*(K) (*T* = 80–298 K) are typical of mononuclear distorted octahedral Cu(II) complexes. This plot approximately follows Curie's law and the complex has mainly ionic or weakly covalent metal–ligand bonds.

Supplementary material

The anisotropic thermal parameters U_{ij}, hydrogen atomic coordinates, C–H, O–H and N–H distances, mean planes, torsion angles and a listing of the observed and calculated structure factors are available from the authors.

Acknowledgement

We thank Professor S. González García (Granada, Spain) for his interest in this work.

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