Inorganica Chimica Acta, *174* (1990) 145–148

Inorganica Chimica Acta

LETTER

Additional Contribution to the Study of Iminodiacetate (IDA) and Imidazole (ImH) Mixed-ligand Copper(II) Complexes; Crystal Structure of [Cu(IDA)(ImH)(CH_3OH)]·0.37H_2O

NGUYEN-HUY DUNG*

Laboratoire de Chimie Minérale et Structurale, U.F.R. des Sciences Pharmaceutiques, 1 rue Vaubénard, F-14032 Caen Cedex (France)

B. VIOSSAT

Laboratoire de Chimie Générale, U.F.R. de Médecine et Pharmacie, 34 rue du Jardin des Plantes, 86034 Poitiers Cedex (France)

A. BUSNOT

Laboratoire de Chimie Minérale et Bioinorganique, U.F.R. des Sciences, Esplanade de la Paix, F-14032 Caen Cedex (France)

J. M. GONZÁLEZ PÉREZ, J. NICLÓS GUTIÉRREZ

Department of Inorganic Chemistry, Faculty of Pharmacy, University of Granada, G-18071 Granada (Spain)

and F. GARDETTE

Laboratoire de Chimie Minérale et Structurale (associé au C.N.R.S., U.R.A. 200) Faculté des Sciences Pharmaceutiques et Biologiques, Université de Paris-V, 4 Avenue de l'Observatoire, F-75270-Paris Cedex 06 (France)

(Received February 27, 1990; revised April 23, 1990)

In a previous letter, we reported the synthesis, structure and properties of a new ternary complex of copper(II), imidazole (ImH) and iminodiacetate (2–) ion (IDA), [Cu(IDA)$(ImH)_2$]·2H_2O called hereafter compound **I** [1]. By modifying the experimental procedure, one new compound called hereafter **II** was synthesized, and the crystal structure determination leads to the formula [Cu(IDA)(ImH)(CH_3OH)]·0.37H_2O.

Experimental

Instead of compound **II**, when the reactants are mixed in equimolar ratio (1:1:1), the reaction of copper(II), iminodiacetate (2–) ion and imidazole in aqueous media yields another mixed-ligand complex, with a probable formula Cu(IDA)(ImH)·2H_2O (**III**). Accordingly, the slow evaporation of an equimolar solution of the complex [Cu(IDA)$(H_2O)_2$] (**IV**) [2] (5 g, 21.67 mmol) and ImH (1.47 g, 21.68 mmol) in water (100 ml) gives dark blue crystals of compound **III** (yield >90%). *Anal.* (%) Calc. for $CuC_7H_{13}N_2O_6$: C, 28.13; H, 4.39; N, 14.04; Cu, 21.27. Found: C, 28.54; H, 4.15; N, 14.07; Cu; 21 ± 1 (complexometry). In spite of many attempts, no suitable crystal for X-ray structure determination of this air-stable 1:1:1 'dihydrate form' has yet been obtained. However, the recrystallization at room temperature of a solution of this product in hot methanol gives air(moisture)-sensitive crystals of the methanol-containing derivative (**II**) suitable for the crystallographic study.

[Cu(IDA)(ImH)(CH_3OH)]·0.37H_2O crystallizes in the monoclinic space group $P2_1$ with $a = 9.649(5)$, $b = 7.772(4)$, $c = 9.856(2)$ Å, $\beta = 103.10(3)°$; $Z = 2$; $V = 719.9$ Å^3; $D_{calc} = 1.39$ g cm^{-3}; μ(Mo Kα) = 1.53 mm^{-1} ($\lambda = 0.71069$ Å). A dark blue crystal (approx. 0.18 × 0.25 × 0.35 mm) handled under nitrogen atmosphere was sealed in a glass capillary. Diffraction data were collected on a Syntex $P2_1$ diffractometer. Lattice constants were fitted with 25 reflections in the range ($11.34 < 2\theta < 334.84°$). Isotropic extinction corrections were performed, but absorption correction was not necessary. The structure was solved by direct methods (MULTAN 80 and DIRDIF) and refined, as described in ref. 3. A total of 2677 independent reflections up to $2\theta = 58°$ was measured of which 1145 reflections ($I > 3\sigma(I)$) were used in the refinement to find residuals $R = 0.039$ and $R_w = 0.062$. The oxygen atom of the water molecule was found to be in statistical disorder with a refined occupational factor of 0.37 and large B isotropic temperature factor. See also 'Supplementary Material'.

Results and Discussion about Compound II (Fig. 1)

Positional parameters of [Cu(IDA)(ImH)(CH_3OH)]·0.37H_2O are listed in Table 1. The bond lengths and angles around the copper atom are given in Table 2. The copper(II) atom is bonded to two nitrogen and four oxygen donor atoms, thus forming a distorted octahedral polyhedron of coordination (type 4 + 2). The nitrogen atom N(13) of the imidazole and the N, O(1) and O(4) atoms belonging to the iminodiacetato group are roughly placed at the corners of the square cross section of the tetragonally elongated octahedral polyhedron; the apical sites are occupied by the oxygen atom O(3^i) of an adjacent

---

*Author to whom correspondence should be addressed.

0020-1693/90/$3.50

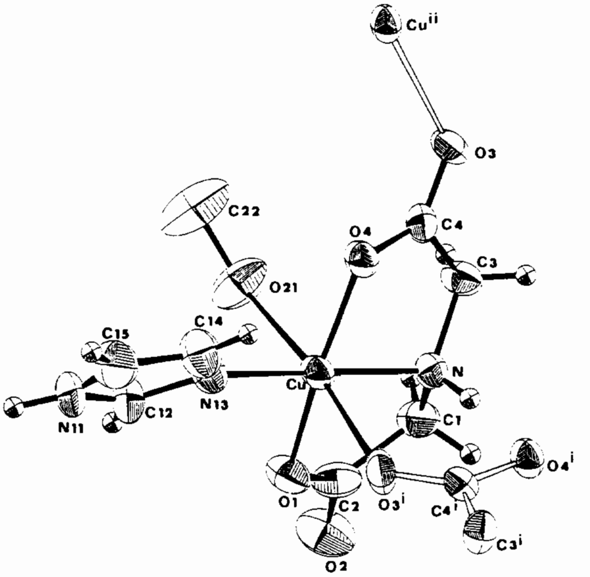

Fig. 1. View of the title complex showing the atom numbering. i: $1 - x, \frac{1}{2} + y, -z$; ii: $1 - x, -\frac{1}{2} + y, -z$.

iminodiacetato group (symmetry code i: $1-x, \frac{1}{2}+y, -z$) and the oxygen atom O(21) of the methanol molecule. The copper(II) atom lies 0.056 Å off the least-squares mean and equatorial plane P(1). It is displaced toward the apical position occupied by the atom O(3^{i}). The two *trans* axial bonds Cu–O(3^{i}) and Cu–O(21) are nearly equivalent and typically much longer than the other four coordination bonds to the equatorial donor atoms. Coordinated methanol molecules have been observed for a number of copper(II) complexes in the range 2.16–2.60 Å [4–8] and the copper–oxygen distance agrees well with the value (2.413 Å) found in one of these compounds [4]. The coordination type is different from that observed in compound **I** in which the Cu(II) atoms exhibit a very flattened square pyramidal coordination and a very weak interaction Cu..O(2) 2.873(2) Å. In this latter case, the coordination type is (4 + 1 + 1). The water molecule is not bonded to the metal ion.

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

Copper environments	
Cu–N(13)	1.940(7)
Cu–N	1.977(7)
Cu–O(4)	1.979(6)
Cu–O(1)	1.986(7)
Cu–O(3^{i})	2.438(7)
Cu–O(21)	2.468(9)
N(13)–Cu–N	176.6(4)
N(13)–Cu–O(4)	95.2(3)
N(13)–Cu–O(1)	97.5(3)
N(13)–Cu–O(3^{i})	86.8(3)
N(13)–Cu–O(21)	90.0(3)
N–Cu–O(4)	83.5(3)
N–Cu–O(1)	84.2(3)
N–Cu–O(3^{i})	90.3(3)
N–Cu–O(21)	93.0(3)
O(4)–Cu–O(1)	164.7(2)
O(4)–Cu–O(3^{i})	98.4(3)
O(4)–Cu–O(21)	86.9(3)
O(1)–Cu–O(3^{i})	90.7(3)
O(1)–Cu–O(21)	84.7(3)
O(3^{i})–Cu–O(21)	174.0(3)

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

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

	x	y	z	B_{eq} (Å^2)^a
Cu	0.36427(9)	0.2741	0.1240(1)	2.46
N	0.5548(7)	0.367(1)	0.2089(8)	2.37
C(1)	0.557(1)	0.419(1)	0.354(1)	3.21
C(2)	0.405(1)	0.443(2)	0.374(1)	3.38
O(1)	0.3044(7)	0.402(1)	0.2757(7)	3.25
O(2)	0.3921(8)	0.509(1)	0.4845(7)	4.78
O(3)	0.6864(6)	0.025(1)	0.0282(7)	3.34
O(4)	0.4701(6)	0.1362(9)	0.0121(7)	2.66
C(3)	0.661(1)	0.241(1)	0.188(1)	2.84
C(4)	0.6022(9)	0.125(1)	0.067(1)	2.63
N(11)	−0.0418(8)	0.097(1)	−0.006(1)	4.28
C(12)	0.070(1)	0.150(2)	0.088(1)	3.61
N(13)	0.1780(7)	0.189(1)	0.0305(8)	2.75
C(14)	0.128(1)	0.163(2)	−0.109(1)	3.60
C(15)	−0.007(1)	0.104(2)	−0.131(1)	4.61
O(21)	0.393(1)	0.028(1)	0.2863(9)	5.11
C(22)	0.370(2)	−0.138(2)	0.233(1)	6.49
OW	0.898(5)	0.839(8)	0.477(5)	13.06

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

The Cu–N(13) bond (1.940 Å) is shorter than the homologous Cu(II)–ImH bonds in compound **I** (1.98 Å) and falls below the range of the reported values for the copper(II)–imidazole bond in Cu(II)–aminodiacetato–ImH and related compounds (1.95–1.98 Å) [2]. The strictly planar ImH ligand gives a dihedral angle of 36.8° with the tetragonal plane of coordination P(1). Again, in the case reported here, we found the preference of the imidazole ligand for a position in the tetragonal plane of the copper coordination polyhedron, and the Cu(II)–ImH bond is of the σ (ligand → metal) nature.

As in the two previous structures of compounds **I** and **IV**, the IDA ligand acts as a tridentate chelating agent, by means of two five-membered glycinate–copper(II) rings, nearly coplanar (dihedral angle between their mean planes: 15.5(3)°), in contrast with the observed dihedral angle (83 and 73° in compounds **I** and **III**, respectively). This might be explained in the title complex by the location of the three donor atoms of the tridentate ligand in the equatorial plane. In compounds **I** and **II**, the tridentate chelating role of IDA places two donor atoms in equatorial sites and the third atom in one axial site of the copper(II) coordination. In compound **I**, the ligands are *cis*-coordinated to the copper(II) in equatorial positions. The substitution of one ImH ligand in **I** by a coordinated methanol molecule in **II** allows the remaining ImH to be in an equatorial site (the CH_3OH molecule occupying an axial position) but gives rise to a noticeable change in the coordinating role of the IDA group (for the chelated Cu(II) atom and for the adjacent Cu^i atom).

Figure 2 shows that each IDA^{2-} ligand is coordinated to two copper(II) ions which are themselves bonded to two different IDA^{2-} ligands, thus forming infinite polynuclear zigzag chains $[Cu(IDA)(ImH)(CH_3OH)]_n$ of the complex, in contrast with the dinuclear centrosymmetrical units $[Cu(IDA)(ImH)_2]_2$ in compound **I**. Each one of these zigzag chains is reinforced by one intrachain hydrogen bond N–H(N)...O(4^i) (2.99(1) Å, 157°). In addition, the crystal structure seems stabilized by two other interchain hydrogen bonds (N(11)–H(N11)...O(3^{iii}) (2.78(1) Å, 171°) and probably O(21)–H(O21)...O(2^{iv}) (2.70(1) Å) (symmetry code iii: $-1 + x, y, z$; iv: $1 - x, -\frac{1}{2} + y, 1 - z$).

Properties of the Dihydrate Form of the Complex: $Cu(IDA)(ImH)\cdot 2H_2O$

The air-stable 'dihydrate-form', compound **III**, loses the two water molecules at 373–418 K, and the anhydrous residue decomposes at 458–673 K to yield basic Cu(II)–oxy-nitrate. The water loss temperatures might correspond to hydrogen bonded (uncoordinated) as well as to weakly coordinated water molecules or to one molecule of each of these types. The IR spectrum (cm^{-1}) shows the expected N–H bands of ImH (3280, 1550) and IDA (3150, 1500), carboxylate bands of IDA (1610(shoulder), 1585, 1390) and water absorption (3440, ~3340, 1655). The electronic spectrum shows one unresolved d–d band with $\nu_{max} = 14\,180$ cm^{-1} of little diagnostic value. The magnetic data (77–298 K) are typical of magnetically dilute Cu(II) complexes ($\mu_{eff} = 1.75$ BM at 298 K), but the 'reverse' axial ESR spectra at 77 and 298 K (with $g_\parallel = 2.06$; $g_\perp = 2.18 \pm 0.01$) suggest several possible distorted (square pyramidal, trigonal, bipyramidal or elongated octahedral) coordination structures.

In view of all the reported results, we find it reasonable to assume that the more probable formula for the studied dihydrate compound is $[Cu(IDA)(ImH)]\cdot 2H_2O$ (with a five-coordinated structure of transition between square pyramidal and trigonal bipyramidal coordination) or $[Cu(IDA)(ImH)(H_2O)]\cdot H_2O$, the latter with a similar octahedral structure to that of Fig. 1, but with water instead of methanol.

Supplementary Material

The anisotropic thermal parameters U_{ij}, hydrogen atomic coordinates distances and angles in the

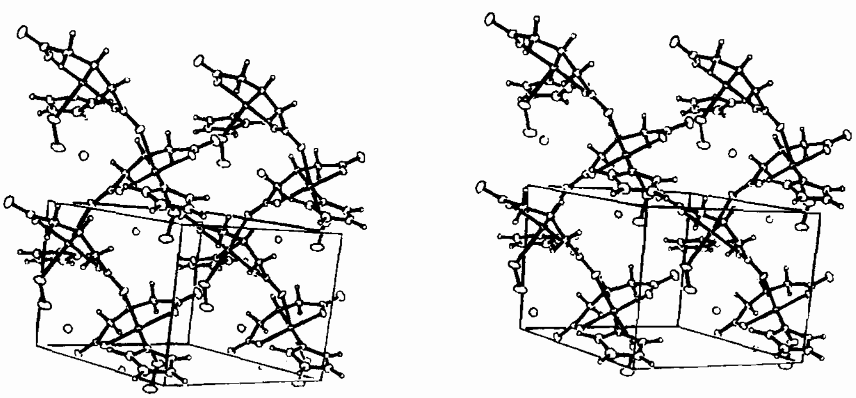

Fig. 2. Stereoscopic view of the unit cell.

ligands, 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.

References

1 Nguyen-Huy Dung, B. Viossat, A. Busnot, A. G. Sicilia Zafra, J. M. González Pérez and J. Niclós Gutiérrez, *Inorg. Chim. Acta, 169* (1990) L9.

2 A. Podder, J. K. Dattagupta, N. N. Saha and N. Saenger, *Acta Crystallogr., Sect. B, 35* (1979) 53.

3 J. M. González Pérez, Nguyen-Huy Dung, B. Viossat, A. Busnot, M. L. Vicente Gelabert and J. Niclós Gutiérrez, *Inorg. Chim. Acta, 166* (1989) 115.

4 S. K. Mandal, L. K. Thompson, K. Nag, J. P. Charland and E. J. Gabe, *Can. J. Chem., 65* (1987) 2815, and refs. therein.

5 E. Bulitta, U. Casellato, P. Guerriero, P. A. Vigato and R. Graziani, *Inorg. Chim. Acta, 134* (1987) L3.

6 C. B. Castellani, O. Carugo and A. Coda, *Acta Crystallogr., Sect. C, 44* (1988) 267.

7 Y. Nishida and K. Takahashi, *J. Chem. Soc., Dalton Trans.*, (1988) 691.

8 L. L. Borer and E. Sinn, *Inorg. Chim. Acta, 142* (1988) 197.