Mixed-ligand copper(II) complexes with iminodiacetato and 2- or 4-methylimidazole: molecular and crystal structure of the 'remote' isomer iminodiacetato(5-methylimidazole)copper(II) monohydrate, $[Cu(IDA)(5MeImH)]\cdot H_2O$

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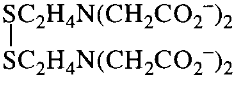
Abstract

Diaqua(iminodiacetato)copper(II), $[Cu(IDA)(H_2O)_2]$ (I), reacts with 2-methylimidazole to yield $[Cu(IDA)(2MeImH)]$ nH_2O ($n=3$, 1/2) or $[Cu(IDA)(2MeImH)_2]_2$ $4H_2O$. However, the reaction of I with 4MeImH (even in excess) only gives the 1:1:1 ternary complex in the form of the 'remote' tautomer derivative $[Cu(IDA)(5MeImH)]\cdot H_2O$. This compound crystallizes in the monoclinic system, space group $P2_1/n$ ($a=13$ 875(1), $b=5.748(1)$, $c=14.739(3)$ Å, $\beta=106.32(1)°$, $Z=4$, final $R=0.059$ and $R_w=0.060$ for 1169 independent reflections). The crystal consists of H_2O molecules non-bonded to the metal and zigzag chains of the complex The Cu(II) atom shows a flattened square base pyramidal coordination (type 4+1) One N of 5MeImH and one N and two O of the same IDA ligand are at the coordination square base. One longer Cu–O bond with the next adjacent IDA ligand of the chain complex accomplishes the Cu(II) distorted five-coordination The new mixed-ligand copper(II) complexes were characterized by thermal, spectral and magnetic methods. The results are discussed in connection with the reported data for analogous compounds with an unsubstituted imidazole ligand.

Key words Crystal structures; Copper complexes; Amino acid complexes, Imidazole complexes

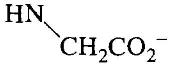
Introduction

Copper(II)-imidazole-aminoacidato or peptide and related compounds (such as Cu(II)–histidine containing peptide complexes) have a broad interest as structural models for some copper proteins. In this sense we have reported the synthesis, structure and/or properties of several Cu(II) complexes having iminodiacetato(2–) (IDA) or *N,N,N',N'*-tetrakis(carboxymethyl)cystaminato(4–) (TCC) ions as primary ligands and coordinated imidazole (ImH) as the secondary one [1–3]. In addition, we have reported the crystal structure of $[Cu_2(TCC)(5MeImH)_2]\cdot 2H_2O$ [4]. This compound was obtained by reaction of $[Cu_2(TCC)(H_2O)_2]\cdot 4H_2O$ [5] and 4-methylimidazole (4MeImH), which is coordinated as its 'remote' tautomer form 5MeImH. Various reports on Co(III), Cu(II) or Ni(II) mixed-ligand complexes [6–10] suggest that the coordination of 4/5-MeImH as 5MeImH implies steric advantages. In this connection, we report a comparative study of the reactions of $[Cu(IDA)(H_2O)_2]$ with 2-methylimidazole (with only this neutral ligand form) and 4MeImH (which could to be coordinated to the metal as itself – 'adjacent' isomer – as well as 5MeImH – 'remote' isomer).



$SC_2H_4N(CH_2CO_2^-)_2$ | $SC_2H_4N(CH_2CO_2^-)_2$

TCC^{4-} ion



IDA^{2-} ion

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Experimental

Synthesis of the complexes

The three new mixed-ligand Cu(II) complexes were obtained by reaction of [Cu(IDA)(H_2O)$_2$] (**I**) [11] and the required amount of 2MeImH or 4MeImH (Sigma) in aqueous media, by the procedures previously reported for [Cu(IDA)(ImH)]·2H_2O (**II**) [2] or [Cu(IDA)-(ImH)$_2$]$_2$·2H_2O (**III**) [1] but using a methyl-substituted imidazole instead of ImH.

Equimolar amounts (15 mmol) of **I** and 2MeImH react in water (150 ml) to give by slow evaporation blue crystals of [Cu(IDA)(2MeImH)]·3H_2O (**IVa**). Yield 70%. *Anal.* Calc. for $CuC_8H_{17}N_3O_7$: C, 29.05; H, 5.18; N, 12.70; Cu, 19.1. Found: C, 29.02; H, 5.14; N, 13.08; Cu, 19.21%. This compound slowly loses water at room temperature to give [Cu(IDA)(2MeImH)]·1/2H_2O (**IVb**) *Anal.* Calc for $CuC_8H_{12}N_3O_{4.5}$: C, 33.63; H, 4.23; N, 14.70; Cu, 22.24. Found: C, 33.63; H, 4.26; N, 14.77; Cu, 22.2%

The reaction of **I** (15 mmol) with 2MeImH (45 mmol, 50% in excess) in 150 ml of water gives dark blue crystals of [Cu(IDA)(2MeImH)$_2$]$_2$·4H_2O (**V**) (assumed dimer). Yield 60% *Anal.* Calc. for $Cu_2C_{24}H_{42}O_{10}N_{10}$: C, 36.50; H, 5.36; N, 17.74; Cu, 16.09. Found: C, 36.37; H, 5.35; N, 17.58; Cu, 15.9%

Reaction of **I** and 4MeImH (in equimolar amounts or in large excess) only gives [Cu(IDA)(5MeImH)]·H_2O (**VI**) as well formed dark blue crystals. Yield 80%. *Anal.* Calc for $CuC_8H_{13}N_3O_5$: C, 32.60; H, 4.45; N, 14.26; Cu, 21.56. Found: C, 32.42; H, 4.35; N, 14.58; Cu, 21.5%.

Crystal structure determination

A prismatic blue single crystal of compound **VI** with approximate dimensions 0.15×0.10×0.15 mm was mounted on an Enraf-Nonius CAD-4 diffractometer. The unit cell was determined and refined from angle data of 25 randomly selected reflections in the range $8.19 < \theta < 13.42°$. Intensities were measured at room temperature with filtered Mo Kα radiation by the $\omega/2\theta$ scan technique Crystal data are in Table 1. Of 3397 reflections collected in the range $3 < \theta < 29°$, 1169 with $I > 3\sigma(I)$ were used in structure determination and refinement. Lorentz–polarization and empirical absorption [12] corrections were applied (with linear absorption coefficients: min. 0.484, max. 1.299, av. 0.958). The structure was solved by direct methods [13] and refined by full-matrix least-squares with unit weights and anisotropic thermal parameters for non-H atoms. The positions of the H atoms were located on a $\Delta\rho$ map with the exception of H(10) which was assumed as N–H = 0.95 Å. The hydrogen atoms of the water molecule were not calculated. The required H atoms were included in structure factor calculations with $B_{iso} = 4.0$ Å^2, but not refined. Secondary-extinction coefficient [14] refined to $g = 6.25 \times 10^{-8}\{F_o = F_c/[1 + g(F_c)^2\mathrm{Lp}]\}$. $\Delta/\sigma_{max} < 0.001$, $\Delta\rho$ max. 1.06 e Å^{-3} Final R factor = 0.059, $R_w = 0.061$, $S = 2.228$ for 155 parameters. See also 'Supplementary material'. Atomic scattering factors were taken from the International Tables for X-ray Crystallography [15] Calculations were performed on a DEC MicroVAXII computer with the SPD program package [16] Molecular graphics were from SCHAKAL [17].

TABLE 1 Crystallographic data for [Cu(IDA)(5MeImH)]·H_2O (**VI**)

Chemical formula	$C_8H_{13}CuN_3O_5$
Formula weight	294.75
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	13.875(1)
b (Å)	5.748(1)
c (Å)	14.739(3)
β (°)	106.32(1)
V (Å^3)	1128.2
Z	4
λ (Mo Kα) (Å)	0.70930
ρ_{calc} (g cm^{-3})	1.735
μ (cm^{-1})	19.525
$F(000)$	604

Physical measurements

TG and DTA diagrams, IR, near-IR–Vis–UV and ESR spectra and magnetic susceptibility data were obtained as described in a previous paper [18]

Results and discussion

Crystal structure of compound VI

Positional parameters of [Cu(IDA)(5MeImH)]·H_2O are given in Table 2. Bond lengths and angles around the Cu(II) atom are listed in Table 3. A drawing of the complex with the labelling of the atoms are given in Fig. 1 The stereoscopic view of the unit cell (Fig 2) shows that compound **VI** consists of water molecules non-bonded to the metal and zig-zag chains of the complex which extend parallel to the axis b. The atoms N(1), O(1) and O(3) of the same chelating IDA ligand and N(10) of 5MeImH define a slightly distorted square base. The copper(II) atom lies at 0.101 Å from the square base mean plane P(1) toward a fifth donor atom O(4ⁱ) of one adjacent IDA ligand which is related with the former one by the two-fold symmetry screw axis (symmetry code i = 0.5 − x, 0.5 + y, 0.5 − z). The deviations of N donors toward Cu(II) and of O donors in the opposite sense from P(1) are nearly equivalent (mean dev. = 0.07(2) Å). The Cu–O(4ⁱ) bonds are typically longer than the other four coordination bonds. The Cu(II) shows a distorted square base pyramidal environment (type 4 + 1)

TABLE 2 Atomic coordinates and thermal parameters with e.s.d.s in parentheses

Atom	x	y	z	B_{eq}[a] (Å^2)
Cu	0.30661(8)	0.2738(2)	0.11666(8)	2.96(2)
O1	0.3216(4)	0.521(1)	0.0301(4)	3.3(1)
O2	0.2397(5)	0.815(1)	−0.0543(5)	4.5(2)
O3	0.2523(4)	0.027(1)	0.1819(4)	2.8(1)
O4	0.1174(5)	−0.047(1)	0.2321(4)	3.9(2)
O5	0.5820(6)	−0.639(1)	0.3880(5)	5.8(2)
N1	0.1766(6)	0.431(2)	0.1060(7)	6.4(2)
N10	0.4327(5)	0.130(1)	0.1193(4)	2.6(1)
N20	0.5868(5)	0.104(1)	0.1080(5)	3.1(2)
C1	0.2455(7)	0.648(2)	0.0003(6)	3.0(2)
C2	0.1538(6)	0.587(2)	0.0309(6)	2.9(2)
C3	0.1073(6)	0.268(2)	0.1261(6)	3.2(2)
C4	0.1621(7)	0.064(2)	0.1858(6)	2.8(2)
C10	0.5036(6)	0.226(2)	0.0887(6)	3.3(2)

[a] $B_{eq} = (3/4)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\ \gamma)B(1,2) + ac(\cos\ \beta)B(1,3) + bc(\cos\ \alpha)B(2,3)]$.

The Cu–N(10) bond distance (1.926(7)Å) is slightly shorter than the corresponding Cu(II)–N(5MeImH) bond (1.947(3) Å) in the related compound [Cu$_2$(TCC)(5MeImH)$_2$]·2H$_2$O which also has its copper(II) atoms in distorted square pyramidal coordination (type 4+1) [4]. In the new case, the Cu–N(10) bond falls under the range of distances (1.95(1)–1.98(2) Å) reported for Cu–N(ImH) bonds in a variety of Cu(II)-aminodicarboxylate-imidazole and related complexes (refs. 1–4 and refs. therein) As expected, the heterocyclic ring in 5MeImH is strictly planar (observed deviations within the error limits) and its methyl C(21) atom deviates only 0.04(1) Å from the ring mean plane P(2). The Cu(II) atom is 0.201(1) Å out of P(2) which defines a dihedral angle of 7.0° with P(1). No significant d_π–p_π copper(II)→imidazole back-donation contribution is deduced from these data for the σ donor role of the 5MeImH ligand in the studied compound. The noticeable structural evidence is that the coordination of 4MeImH to the Cu(II)–IDA entity actually occurs as 5MeImH. No evidence of the 'adjacent' isomer complex [Cu(IDA)(5MeImH)] is available. In addition, all attempts to obtain a compound with Cu(II)/IDA/4- and/or 5-MeImH equal to 1:1:2 were unsuccessful. Even more, one attempt to isolate the hypothetical compound [Cu(IDA)(ImH)(4/5-MeImH)]·nH$_2$O was carried out, but only an amorphous blue glass was obtained. In clear contrast, we have previously reported the crystal structure of compound **II** which contains the dinuclear complex [Cu(IDA)(ImH)$_2$]$_2$ with two ImH ligands per Cu(II)–IDA entity [1]. In the same sense, we describe in this paper the synthesis of compound **V**, with two 2MeImH ligands per Cu(II)–IDA unit.

TABLE 3 Bond lengths (Å) and angles (°) of compound **VI** with e.s.d.s in parentheses

Copper environment			
Cu–O(1)	1.96(1)	O(1)–Cu–O(3)	164.0(2)
Cu–O(3)	1.98(1)	O(1)–Cu–O(4^i)	101.2(2)
Cu–N(1)	1.99(1)	O(1)–Cu–N(1)	83.0(4)
Cu–N(10)	1.93(1)	O(1)–Cu–N(10)	93.7(3)
Cu–O(4^i)	2.41(1)	O(3)–Cu–O(4^i)	89.0(2)
Cu–Cu^i	5.446(2)	O(3)–Cu–N(1)	84.4(3)
		O(3)–Cu–N(10)	98.7(3)
		O(4^i)–Cu–N(1)	91.7(4)
		O(4^i)–Cu–N(10)	90.3(2)
		N(1)–Cu–N(10)	176.4(4)
IDA			
N(1)–C(2)	1.40(1)	Cu–O(1)–C(1)	114.6(6)
N(1)–C(3)	1.43(1)	Cu–O(3)–C(4)	114.5(5)
C(1)–C(2)	1.51(1)	Cu–N(1)–C(2)	110.9(8)
C(3)–C(4)	1.54(1)	Cu–N(1)–C(3)	109.4(7)
O(1)–C(1)	1.26(2)	C(2)–N(1)–C(3)	124.9(8)
O(2)–C(1)	1.24(1)	O(1)–C(1)–O(2)	124.8(9)
O(3)–C(4)	1.29(1)	O(1)–C(1)–C(2)	117.3(9)
O(4)–C(4)	1.22(1)	O(2)–C(1)–C(2)	117.9(8)
		N(1)–C(2)–C(1)	111.5(7)
		N(1)–C(3)–C(4)	111.6(7)
		O(3)–C(4)–O(4)	126.4(8)
		O(3)–C(4)–C(3)	115.4(8)
		O(4)–C(4)–C(3)	118.2(8)
		C(4^i)–O(4^i)–Cu	125.4(5)
5MeImH			
N(10)–C(10)	1.31(1)	Cu–N(10)–C(10)	125.0(6)
N(10)–C(30)	1.40(1)	Cu–N(10)–C(30)	130.7(6)
N(20)–C(10)	1.32(1)	C(10)–N(10)–C(30)	103.9(7)
N(20)–C(20)	1.38(1)	C(10)–N(10)–C(20)	106.9(8)
C(20)–C(21)	1.50(1)	N(10)–C(10)–C(20)	113.5(9)
C(20)–C(30)	1.34(1)	N(20)–C(20)–C(21)	120.8(8)
		N(20)–C(20)–C(30)	106.4(7)
		C(21)–C(20)–C(30)	132.7(9)
		N(10)–C(30)–C(20)	109.2(8)

Symmetry code i 0.5−x, 0.5+y, 0.5−z

A second structural feature of compound **VI** is the near coplanarity of the two five-membered Cu(II)–IDA chelate rings sharing the Cu–N(amino) bond. The dihedral angle between the ring mean planes is $\phi = 13.6°$ in this case. The same 'opening' IDA conformation has been reported in the crystallographic studies of [Cu(IDA)(ImH)(CH$_3$OH)]·0.37H$_2$O (**II**′ with $\phi = 15.5°$) – obtained by recrystallization of compound **II** from hot methanol [2] – and [Cu$_2$(IDA)$_2$(4,4′-bipy)] [19], which has a half of the 4,4′-bipyridine ligand per Cu–IDA unit. These two complexes, in common with compound **VI**, also have a Cu–N(heterocycle) bond of <2.00(1) Å. In clear contrast, compounds [Cu(IDA)(ImH)$_2$]$_2$·2H$_2$O (**III**) [1] (with $\phi = 83°$) and [Cu(IDA)(2,2′-bipy)]·6H$_2$O [20] – with two Cu(II)–N heterocycle bonds in *cis* positions – have the tridentate IDA ligand forming two nearly perpendicular chelate rings and Cu–N(IDA) bonds of >2.00(1) Å. We have argued that the nearly coplanar Cu–IDA chelate rings in the Cu–

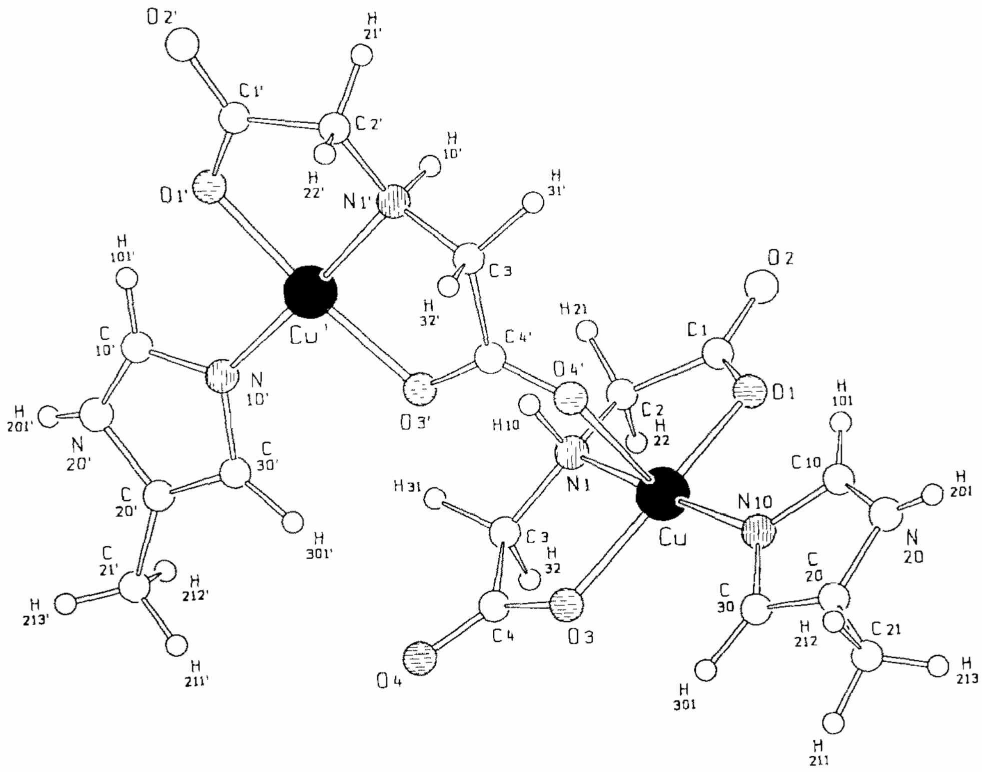

Fig 1 Illustration of the structure of the asymmetric entity [Cu(IDA)(5MeImH)] H_2O

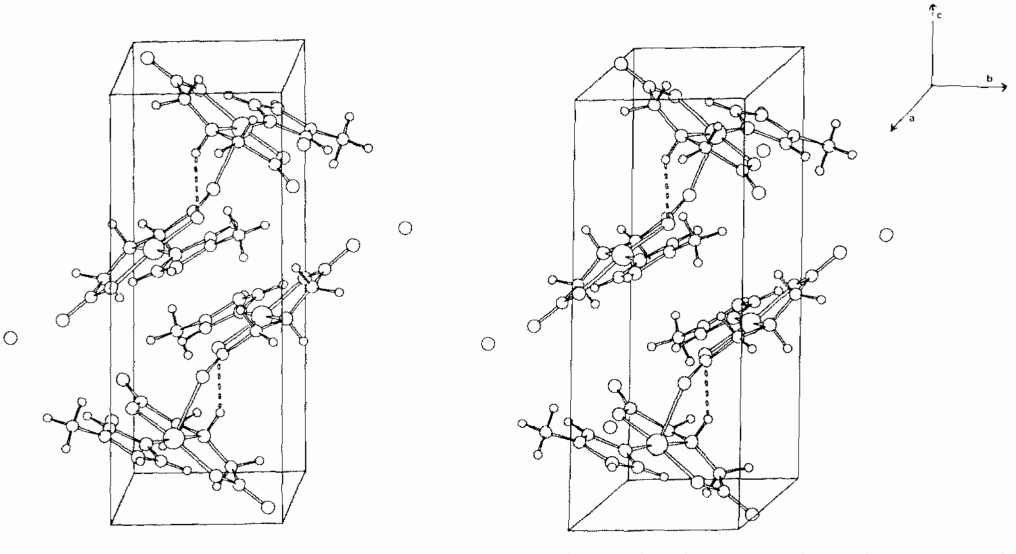

Fig 2 Stereo view of the unit cell showing some hydrogen bonds looking down the *a* axis with the *c* axis vertical and *b* axis horizontal

IDA–N(heterocycle) complexes arise from the preference of the first incoming N-heterocyclic ligand for the *trans*-coordination position to the N(IDA) donor atom which induces a rather short Cu–N(IDA) bond, whereas the nearly perpendicular Cu–IDA chelate ring is imposed by the *cis*-coordination of two N heterocyclic donors in plane with the Cu–N(IDA) bond, which results in a rather long bond.

Properties of compounds IV–VI

The hydrated forms of compounds **IV–VI** have low thermal stabilities, in comparison with the reported results for compounds **II** and **III** with unsubstituted ImH (Table 4). The complete loss of uncoordinated water for the complexes with known structure (**III**, $2H_2O$ at 403–430 K; **VI**, H_2O at 348–413 K) strongly suggest that the other compounds contain non-bonded water molecules (**I**, $2H_2O$ at 373–418 K; **IVa**, 2.5 H_2O at 338–363 K; **IVb**, $1/2H_2O$ at 390–415 K; **V**, $2H_2O$ at 358–393 K). All these dehydration processes occur with the corresponding endothermic effect in the DTA diagram, as expected for hydrogen bonded water molecules contributing to the crystal packing. Analogous examples were reported for L-aspartato derivatives, [Cu(L-Asp)(ImH)]·$2H_2O$, of known crystal structure, and [Cu(L-Asp)(2MeImH)]·H_2O [21] which loses its water molecule in the 308–403 K range.

The IR spectra of compounds **II–VI** have also in common the expected bands for the stretching (ν) and bonding (δ) modes of the N–H groups (imidazole ligands and IDA) and carboxylate groups (IDA) as well as of the water ($\nu \sim 34500$, δ 1640±10 cm^{-1}). The N–H heterocyclic absorbs at 3200–3280 (ν) and 1550±10 (δ) cm^{-1}. The N–H (IDA) shows its bands at lower wave numbers, 3100–3150 (ν) and 1500–1530 (δ) cm^{-1} The ν_{as} band of the carboxylate IDA groups 1595–1615 cm^{-1} are overlapped by the $\delta(H_2O)$ mode, but one or two bands (or shoulders) of $\nu_{as}(COO)$ are recorded in the range 1375–1400 cm^{-1}. A comparison of these spectra with the IR spectrum of the diaqua parent compound **I** shows the absence of the absorption bands ν(N–H) and δ(N–H) of the imidazole ring in the latter case. In this sense the reported IR spectral data have diagnostic value in the routine study of synthesized products.

TABLE 4 TG and DTA data for the loss of water in Cu(II) complexes with iminodiacetato (IDA) and imidazole or a methyl derivative (2MeImH or 5MeImH) as secondary ligand

Compound	TG			DTA	
	Weight loss (%)		T range (K)	Endo effect T (K)	Remark
	Exp	(calc.)			
II	10.05	(9.46)	373–418	400	$-2H_2O$ [2]
III[a] (dimer)	5.17	(4.76)	403–430	418	$-2H_2O$ [1]
IVa	13.61	(13 3)	338–363	348	-2 $5H_2O$
IVb	2 74	(2.4)	390–415	410	-0 $5H_2O$
V(dimer)	9 12	(7 95)	358–393	385	$-4H_2O$
VI[a]	6 11	(5 21)	348–413	400	$-H_2O$

[a]Crystal structure known with H_2O non-bonded to the copper(II) atom.

Table 5 shows the diffuse reflectance spectra and magnetic data for compounds **II–VI**. It is well known that the shape and $\bar{\nu}_{max}$ values of the d–d band in electronic spectra of the Cu(II) ion in its complexes can only be compared in very related compounds and should be made with caution [22]. On this basis, we found that compounds **II**, **IVa** and **VI** have a similar $\bar{\nu}_{max}$ electronic spectrum and μ_{eff} value for Cu(II). These values agree well with distorted octahedral or square pyramidal Cu(II) coordination. The 'reverse' type ESR spectrum of **II** with the lowest $g_{\parallel}$ value significantly >2.03 – also as reported for [Cu(L-Asp)(ImH)]·$2H_2O$ but not for [Cu(L-Asp)(2MeImH)]·H_2O [21] – would be attributed to a distorted octahedral Cu(II) coordination with $d_{x^2-y^2}$ ground state and total misalignment of the local molecular axes which is referred to an antiferrodistorsive ordering [22]. This assumption is supported by the crystal structure reported for [Cu(IDA)(ImH)(CH_3OH)]·$0.37H_2O$, and the suggestion was made that the compound **II** could have a similar structure but with H_2O instead of coordinated methanol [2]. The rhombic ESR spectrum of compound **IVa** would correspond to a rhombic octahedral or square pyramidal Cu(II) coordination. The data for compound **VI** in Table 5 are in agreement with its crystal structure where the shortest Cu–Cu' distance (5.446(2) Å) corresponds to two adjacent intrachain complex units.

Compounds **II** and **V** having two imidazole ligands per Cu(II) atom also have analogous electronic and magnetic properties. However, the μ_{eff} value of Cu(II) in compound **V** is not under the spin only value (1.73 BM), as observed for **II**. The ESR spectra of both compounds also show a very weak signal at half field. The available data suggest a dinuclear structure for **V**

TABLE 5. Spectral and magnetic data for mixed-ligand Cu(II) complexes with IDA and secondary imidazole ligands

Compound	Electronic spectra $\bar{\nu}_{max}$ (cm^{-1})	ESR spectra[a] g values	μ_{eff} Cu(II)[b] (BM)	Ref.
II	14180	$g_{\parallel}$ 2 06 $g_{\perp}$ 2 18	1 75	2
III (dimer)	17275(sh) 16500	$g_{\parallel}$ 2.23 $g_{\perp}$ 2 03	1 65	1
IVb	14600	g_1 2 08 g_2 2 14 g_3 2 27	1 71	
V (dimer)	17700(sh) 15650	$g_{\parallel}$ 2 20 $g_{\perp}$ 2 05	1 76	
VI	14750	$g_{\parallel}$ 2 19 $g_{\perp}$ 2.08	1 76	

[a]Recorded at 298 and 77 K. [b]All these compounds follow the Curie-Weiss law (77–298 K).

analogous to that reported for **III** with a (4+1)+1 Cu(II) environment, but with a longer sixth distance which leads to a weaker magnetic interaction between the neighbouring Cu(II) atoms.

Conclusions

Unfortunately the structural details of compounds **IV** and **V** with 2MeImH remain unknown, as they would add light on the steric factor of the methyl group in the ligand role of the imidazole for the copper(II)–iminodiacetate unit. In compound **II** the planes of the two ImH ligands linked to the same Cu(II) atom define an angle of 66.0° because of the steric hindrance (and other crystal requirements) [1]. The isolation of compound **V** suggests that the 2-methyl substituent does not introduce any noticeable change in the imidazole ligating behaviour toward Cu(II). Thus, the restricted coordinating ability of 4MeImH toward the Cu–IDA unit seems to be due to its 'tautomeric' possibility, that is absent in the ImH and 2MeImH cases.

Supplementary material

Hydrogen atomic coordinates and thermal parameters of compound **IV**, torsion angles, mean planes and dihedral angles between the planes containing the Cu(IDA) chelate rings in complexes **III** and **IV** as well as TG-DTA diagrams, IR, diffuse reflectance and ESR spectra and plots of $1/\chi_{\mathrm{mol}}$ vs. T (K) for compounds **IVa–VI** are available from the authors on request Further details of the structure determination have been deposited as Supplementary Publication No. CDS-57690. Copies may be obtained through the Fachinformationszentrum Karlsruhe, D-7514 Eggenstien-Leopoldshafen 2, Germany.

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