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Synthesis and molecular structure of monomeric copper(II) acetates with 2-methylimidazole and 1,2-dimethylimidazole

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Abstract

The complexes *cis*-bis(acetato)bis(2-methylimidazole)copper(II) (**1**), and *cis*-bis(acetato)bis(1,2-dimethylimidazole)copper(II) (**2**) have been prepared by the reaction of the appropriate imidazole derivative with copper(II) tetraacetate. The complexes have been characterized by analytical, magnetic, spectroscopic and crystallographic methods. Complex **1** crystallizes in the orthorhombic space group $P2_12_12_1$ and has unit cell dimensions of $a = 7.5380(10)$, $b = 7.7100(10)$, $c = 26.310(5)$ Å. Complex **2** crystallizes in the monoclinic space group $P2/c$ and has unit cell dimensions of $a = 15.574(2)$, $b = 7.9520(10)$, $c = 14.752(2)$ Å.

Introduction

Adducts of dimeric copper(II) tetracarboxylates are well documented and reviews of their preparation, magnetic and spectral properties have been reported [1]. The number of monomeric copper(II) complexes containing non-halogenated carboxylate ligands and other basic ligands is quite limited [2–7]. However, there have been several studies designed to investigate the factors that influence monomer formation over dimer formation in copper(II) carboxylate adducts [1b, 4–8]. In general it has been found that by increasing the acidity of the carboxylate groups and/or the basicity of the other ligands, the tendency towards formation of monomeric adducts increases [4–7]. Those monomeric copper(II) carboxylate adducts with monodentate nitrogen donor ligands for which structural data are available, exist as bis-adducts with a *trans* square-planar CuN_2O_2 chromophore [3, 4, 6].

Complexes of copper(II) with carboxylate and imidazole ligands have been studied as models for copper proteins that contain both functionalities in the side chain [9]. In addition, some of these copper(II) ternary complexes were found to have a variety of pharmacological effects such as antitumour [10] and superoxide dismutase activities [8]. For instance, the bis(acetato)bis(imidazole)copper(II) complex was recently found to have antitumour activity [10], and copper(II) aspirinate with imidazoles have been reported to have superoxide dismutase activities [8].

The interaction of the dimeric copper(II) acetate with imidazole and with *N*-methylimidazole had been studied previously [3, 11]. While the product of the reaction of the tetraacetate with imidazole is monomeric [3], that obtained with *N*-methylimidazole is dimeric [11]. X-ray analysis of bis(acetato)bis(imidazole)copper(II) demonstrated that this complex contains the CuN_2O_2 chromophore in a *trans* square-planar arrangement [3]. To date there have been no analogous monomeric *cis* adducts reported. The structure of the *N*-methylimidazole adduct, as shown by X-ray analysis, is that of a binuclear complex in which two acetate ligands act as monodentate bridging ligands and each copper atom has a distorted square pyramidal environment [11]. The nature of the products that result from the reaction of $Cu_2(\mu\text{-}O_2CCH_3)_4$ with basic ligands are due, at least in part, to the electronic properties of the added bases,

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though the correlations between these properties and the resulting structures have not been fully assessed. This article reports the synthesis, spectroscopic and X-ray structural characterization of *cis*-bis(acetato)bis(2-methylimidazole)copper(II), $Cu(OAc)_2(2mIm)_2$, and *cis*-bis(acetato)bis(1,2-dimethylimidazole)copper(II), $Cu(OAc)_2(12mIm)_2$.

Experimental

Preparation of $Cu(OAc)_2(2mIm)_2$ (1)

One gram of anhydrous copper(II) acetate was added to a solution of 2 g of 2-methylimidazole in 20 ml of chloroform and 5 ml of methanol. The mixture was stirred for 45 min at about 60 °C. The blue solution was filtered over anhydrous diethyl ether and the mixture was stirred until a light blue precipitate formed. The complex was filtered under reduced pressure, washed several times with chloroform and anhydrous diethyl ether and air dried. Recrystallization from hot methanol produces light blue crystals. *Anal.* Calc. for ($CuC_{12}H_{18}N_4O_4$): C, 41.65; H, 5.21; N, 16.2; Cu, 18.38. Found: C, 41.58; H, 5.20; N, 16.10; Cu, 18.30%.

Preparation of $Cu(OAc)_2(12mIm)_2$ (2)

To a suspension of 0.5 g anhydrous copper(II) acetate in 10 cm^3 of methanol, 4 cm^3 of freshly distilled 1,2-dimethylimidazole was added. The blue mixture was stirred for 1 h at about 50 °C filtered into anhydrous diethyl ether and stirred until a light blue precipitate formed. The complex was filtered under reduced pressure and washed several times with anhydrous diethyl ether. Recrystallization from hot methanol and a few drops of the neat ligand produces light blue crystals. *Anal.* Calc. for ($CuC_{14}H_{22}N_4O_4$): C, 44.95; H, 5.89; N, 14.98; Cu, 17.00. Found: C, 44.73; H, 5.88; N, 14.99; Cu, 16.92%.

Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Copper was determined volumetrically.

Physical measurements

Room temperature (298 K) magnetic susceptibility measurements of powdered samples were determined by the Gouy method, with $HgCo(NCS)_4$ as calibrant, and corrected for diamagnetism with the appropriate Pascal constants. The effective magnetic moment was calculated from the expression: $\mu_{eff} = 2.84(\chi_M T)^{1/2}$. Electronic spectra of methanol solutions were obtained on a Bauch and Lomb spectronic 2000. Nujol mulls sealed between polyethylene sheets were used to obtain IR spectra of the complexes in the 4000 to 450 cm^{-1} region with an FTS-7 Bio-Rad SPC 3200 Fourier transform infrared spectrometer. The ESR spectra of powdered and methanol/toluene solutions were taken at different temperatures with a Varian E-4 X-band spectrometer equipped with a variable temperature unit and 100 KHz field modulation. Diphenylpicrylhydrazide (DPPH, $g = 2.0036$) was used as the calibrating field marker.

X-ray data collection

Blue parallelepipeds of **1** and **2** were covered with Paratone N, a heavy colorless oil obtained from Exxon Corporation (USA), and mounted on a glass fiber attached to a copper pin on the goniometer head and placed in the path of a cold nitrogen stream on a Siemens R3mV diffractometer. The diffractometer was equipped with a highly oriented graphite crystal monochromator. The crystal temperature was maintained by a Siemens LT-2 low-temperature attachment. For each crystal the setting angles of random intense reflections ($25 < 2\theta < 45°$) were used to determine unit cell constants and the orientation matrix by least-squares fit. Data collection was performed by the ω scan method for **1** and the 2θ–θ scan method for **2**. The total number of reflections collected and the unique reflections were 2075 and 2049 for **1** and 2480 and 2186 for **2**. The intensities of 3 standard reflections were measured every 97 reflections and no significant decay was observed. The intensities were corrected for Lorentz and polarization effects but not for absorption. Sets of 1831 and 1585 reflections with $F > 4\sigma F$ were used in the structure solution and refinement for **1** and **2**, respectively. Other crystal and structure analysis data are given in Table 1.

Structure solution and refinement

The structures of **1** and **2** were solved by direct methods and successive difference Fourier syntheses with the aid of the SHELXTL PLUS structure solution software [12]. The refinements were performed by full-matrix least-squares methods with the quantity $\Sigma w(F_0 - F_c)^2$ minimized. Hydrogen atoms were located in their idealized positions (C–H = 0.96 Å) and were not refined but were allowed to ride along with their bonded atoms during refinement. The weighting scheme used was $w^{-1} = \sigma^2(F) + AF^2$, where $A = 0.001$ for **1** and 0.0002 for **2**. The largest peak in the final difference map was 1.35 e $Å^{-3}$ for **1** and 0.61 e $Å^{-3}$ for **2**. In each case the peak was in the vicinity of the metal atom.

The asymmetric unit for **1** contains a single molecule. The asymmetric unit of **2** contains halves of two molecules since the copper atom in each molecule lies on the crystallographic two-fold axis.

TABLE 1. Crystal data for *cis*-Cu(OAc)$_2$(2mIm)$_2$ (**1**) and *cis*-Cu(OAc)$_2$(12mIm)$_2$ (**2**)[a]

Molecular formula	$C_{12}H_{18}CuN_4O_4$ (**1**)	$C_{14}H_{22}CuN_4O_4$ (**2**)
Formula weight	345.8	373.9
Space group	$P2_12_12_1$	$P2/c$
Z	4	4
a (Å)	7.5380(10)	15.574(2)
b (Å)	7.7100(10)	7.9520(10)
c (Å)	26.310(5)	14.752(2)
β (°)	90	114.720(10)
V (Å^3)	1529.1(5)	1659.6(3)
D_{calc} (g/cm^3)	1.502	1.496
Crystal size (mm)	0.25×0.65×0.70	0.15×0.22×0.60
Radiation type; wavelength (Å)	Mo; 0.71073	
Temperature (K)	153	
2θ Range (°)	3.5–55	3.5–45
Absorption coefficient (cm^{-1})	14.5	13.4
No. parameters	191	210
Index ranges	$0 \leq h \leq 10$	$0 \leq h \leq 17$
	$0 \leq k \leq 11$	$0 \leq k \leq 10$
	$0 \leq l \leq 35$	$-18 \leq l \leq 18$
R (%)	5.66	4.62
R_w (%)	6.74	4.92
GOF	1.69	1.99
Largest shift/e.s.d., final cycle	0.001	0.003
Largest peak (e/Å^{-3})	1.35	0.61
Independent reflections	2049	2186
Observed reflections	1831	1585

[a] 2mIm = 2-methylimidazole, 12mIm = 1,2-dimethylimidazole.

Results and discussion

Magnetic and spectroscopic results

Room-temperature solid-state magnetic moments for the two bis-adducts, **1** and **2** of 1.90 and 1.85 BM, respectively, are consistent with the presence of one unpaired electron in monomeric copper(II) complexes.

The electronic spectra for **1** and **2** in methanol solutions exhibit low energy absorption bands at 685 nm ($\epsilon_M = 60$) for **1** and 675 nm ($\epsilon_M = 64$) for **2**. These bands are assigned to the copper(II) d–d transition. The spectra lack the charge transfer band near 370 nm that is characteristic of dimeric copper(II) carboxylate adducts [1b, 2, 14]. The spectra of the two adducts are of the general type found for tetragonally distorted copper(II) complexes containing a Cu-N_2O_2...O_2 chromophore [1b, 5, 13, 15, 16].

The IR absorption bands for the acetate antisymmetric carboxyl vibration for the two complexes are not resolved, but they overlap with the imidazole bands to give intense and broad absorption bands centered at 1570 and 1565 cm^{-1} for the 1,2-dimethylimidazole and 2-methylimidazole complexes, respectively. The symmetric carboxyl stretching frequency, ν_s(COO), for both complexes occurs at 1415 cm^{-1}. The position of this frequency and the small separation between it and ν_{as}(COO) are consistent with a carboxylate group that acts as an unsymmetrical bidentate ligand [17]. This is borne out by the solid-state structures (*vida infra*).

The ESR parameters, g and A, for the solution and solid-state spectra of **1** and **2** are given in Table 2. The room-temperature solution spectra are isotropic and consist of the four equally-spaced lines expected for the copper(II) ion. The frozen-solution spectra of the 2-methylimidazole and 1,2-dimethylimidazole complexes are shown in Fig. 1(A) and (B), respectively. The spectra exhibit resolved structures with $g_\parallel > g_\perp$ and are consistent with a tetragonally elongated structure [16]. The $g_\perp$ region of the spectra exhibits a ^{14}N super-hyperfine structure consisting of five lines. This structure is attributed to the presence of two nitrogen atoms in the plane of the copper(II) ion. The spectral parameters for the complexes are comparable to those of previously reported complexes that have the CuN_2O_2 chromophore or the tetragonally elongated chromophore CuN_2O_2...O_2 [5, 8, 10, 13, 15–17]. The solid-state ESR spectrum of complex **1** is anisotropic and contains $g_\parallel$ and $g_\perp$ components, while that of complex **2** contains an asymmetric signal centered near 3100 G. The lack of copper(II) hyperfine coupling in these complexes is likely due to dipole–dipole interactions between copper atoms of neighboring molecules.

TABLE 2. ESR data

Compound	State (temperature)	g_0	$g_\parallel$	$g_\perp$	$10^4\times A_0(\mathrm{Cu})^a$	$10^4\times A_\parallel(\mathrm{Cu})$	$10^4\times A_\perp(\mathrm{N})$
$\mathrm{Cu(OAc)_2(2mIm)_2}$ (**1**)	powder[b]	2.123	2.230	2.070			
	solution (r.t.)	2.120			55		
	solution[b] (113 K)	2.128	2.279	2.053		154	15
$\mathrm{Cu(OAc)_2(12mIm)_2}$ (**2**)	powder	2.126 (only one peak)					
	solution (r.t.)	2.134			60		
	solution (113 K)	2.120	2.259	2.050		164	14

[a] All hyperfine coupling constants are in cm^{-1}. [b] g_0 values for powdered and frozen samples are calculated from the equation $g_0 = 1/3(g_\parallel + 2g_\perp)$.

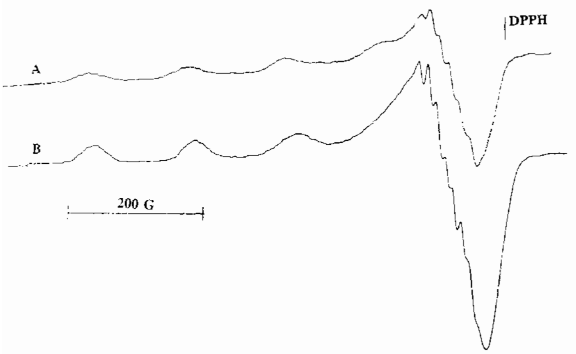

Fig. 1. X-band frozen-solution ESR spectra of **1** and **2**.

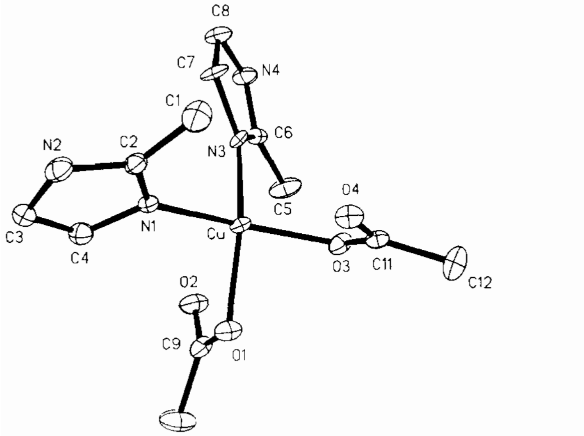

Fig. 2. The molecular structure of **1** showing the atom labelling scheme. Atoms are represented by thermal ellipsoids at the 50% level.

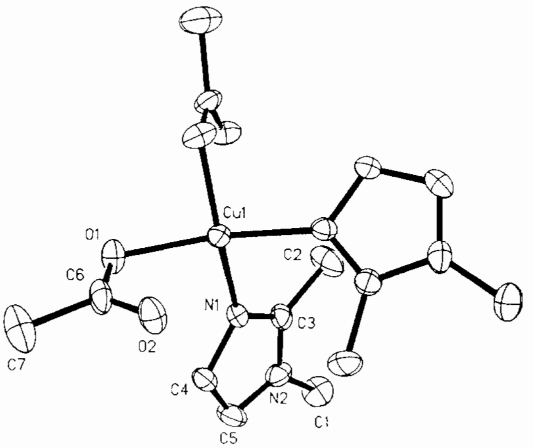

Fig. 3. The molecular structure of **2** showing the atom labelling scheme. Atoms are represented by thermal ellipsoids at the 50% level.

Structures of $\mathrm{Cu(OAc)_2(2mIm)_2}$ (1) and $\mathrm{Cu(OAc)_2(12mIm)_2}$ (2)

The solid-state structures of **1** and **2** are shown in Figs. 2 and 3, respectively. Positional coordinates for **1** and **2** are given in Tables 3 and 4. The Cu atoms occupy approximate square planar environments that consist of two imidazole nitrogen atoms and two carboxylate oxygen atoms in a *cis* disposition with weak interactions between the Cu atoms and the remaining two more distant acetate oxygen atoms. When one considers the weak carboxylate interactions, the geometry about the Cu is that of a severely distorted octahedron. Selected bond distances and angles are given in Table 5 for **1** and Table 6 for **2**. The Cu–O distances for the nearest oxygen atoms are 2.00 ± 0.02 Å for both **1** and **2**. These distances are in close agreement with those previously determined for similar Cu(II) coordination [3]. The weakly interacting acetate oxygen atoms are in the order of 2.50 ± 0.05 Å from the Cu atom. These distances are significantly shorter than those of similar weakly interacting carboxylate oxygen atoms in the imidazole

TABLE 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for **1**

	x	y	z	U_{eq}
Cu	1321(1)	8998(1)	8791(1)	14(1)
O(1)	3622(6)	7678(6)	8868(2)	21(1)
O(3)	2695(5)	11182(6)	8776(2)	20(1)
O(4)	2028(6)	10763(6)	9584(2)	22(1)
O(2)	2856(6)	7684(7)	8064(2)	25(1)
N(1)	7(7)	6932(7)	9030(2)	14(1)
N(2)	−1409(8)	5061(7)	9509(2)	21(2)
C(2)	−930(8)	6725(8)	9459(2)	17(2)
N(3)	−749(7)	10071(7)	8456(2)	15(1)
C(9)	3878(9)	7213(9)	8413(2)	21(2)
N(4)	−2373(7)	11397(7)	7875(2)	21(2)
C(11)	2858(8)	11574(8)	9252(2)	19(2)
C(8)	−3529(8)	10767(9)	8240(2)	23(2)
C(6)	−718(8)	10941(10)	8018(2)	18(2)
C(4)	89(9)	5309(8)	8813(3)	20(2)
C(1)	−1373(11)	8106(9)	9828(2)	27(2)
C(3)	−783(9)	4140(10)	9103(3)	23(2)
C(5)	879(9)	11447(10)	7710(3)	29(2)
C(10)	5421(10)	6064(12)	8292(3)	34(2)
C(7)	−2539(9)	9977(10)	8595(3)	22(2)
C(12)	4075(10)	13024(10)	9375(3)	31(2)

TABLE 4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for **2**

	x	y	z	U_{eq}
Cu(1)	0	7283(1)	2500	21(1)
O(1)	−800(3)	9036(5)	1575(3)	32(2)
N(2)	−638(4)	3400(6)	454(4)	29(2)
O(2)	−1567(3)	8078(6)	2441(3)	33(2)
N(1)	−507(3)	5570(6)	1416(3)	22(2)
C(4)	−1436(4)	5436(8)	726(5)	29(3)
C(2)	975(4)	3929(9)	1796(5)	42(3)
C(3)	−55(4)	4319(8)	1228(4)	25(3)
C(5)	−1523(4)	4094(8)	138(5)	34(3)
C(6)	−1510(5)	9035(8)	1793(5)	30(3)
C(7)	−2321(5)	10200(9)	1214(5)	49(4)
C(1)	−398(5)	1889(8)	49(5)	39(3)
Cu(2)	5000	7482(1)	2500	22(1)
O(11)	5824(3)	9279(5)	2347(3)	29(2)
N(12)	5580(3)	3583(6)	971(3)	23(2)
O(12)	6563(3)	8251(6)	3879(3)	31(2)
N(11)	5477(3)	5778(6)	1823(3)	21(2)
C(13)	5034(4)	4434(8)	1312(4)	22(3)
C(11)	5346(4)	2020(8)	398(4)	29(3)
C(16)	6505(4)	9282(8)	3214(5)	24(3)
C(15)	6439(4)	4416(8)	1301(5)	29(3)
C(12)	4053(4)	3909(9)	1113(5)	36(3)
C(14)	6371(4)	5762(8)	1821(5)	26(3)
C(17)	7277(4)	10584(8)	3423(5)	31(3)

TABLE 5. Selected bond lengths (Å) and bond angles (°) for **1**

Bond lengths (Å)			
Cu–O(1)	2.021(5)	Cu–O(3)	1.978(4)
Cu–N(1)	1.978(5)	Cu–N(3)	1.974(5)
O(1)–C(9)	1.265(8)	O(3)–C(11)	1.295(8)
O(4)–C(11)	1.242(8)	O(2)–C(9)	1.253(8)
Cu...O(2)	2.455	Cu...O(4)	2.546
Bond angles (°)			
O(1)–Cu–O(3)	88.9(2)	O(1)–Cu–N(1)	89.6(2)
O(3)–Cu–N(1)	162.6(2)	O(1)–Cu–N(3)	159.1(2)
O(3)–Cu–N(3)	92.7(2)	N(1)–Cu–N(3)	94.8(2)
O(1)–C(9)–O(2)	121.2(6)	O(3)–C(11)–O(4)	121.0(6)

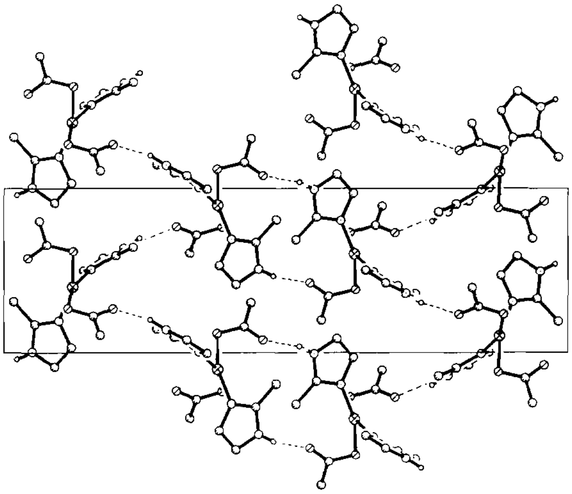

Fig. 4. Projection plot of bis(2-methylimidazole)bis(acetato)copper(II) (**1**) viewed down the *a* axis showing the positions of the hydrogen bonds.

complex *trans*-Cu(OAc)$_2$(Im)$_2$ [3]. The distances between the carboxyl carbon and the coordinated acetate oxygen atoms in the square plane is longer by *c*. 0.02–0.04 Å than that between the carboxyl carbon and the weakly interacting acetate oxygen atom for both **1** and **2**. This is consistent with the expected trend of the shorter the Cu–O bond the longer the associated C–O bond. Though there is no obvious explanation, except maybe crystal packing requirements, the interaction of the weakly coordinated acetate oxygen is stronger for the *cis*-2-methylimidazole and *cis*-1,2-dimethylimidazole copper acetate complexes than for the analogous *trans* imidazole complex.

For complex **1** the deviations from the least-squares plane O(1)–O(3)–N(1)–N(3) are ΔCu = +0.0366, ΔO1 = −0.3342, ΔO3 = +0.3289, ΔN1 = +0.3206, ΔN3 = −0.3152 Å. In the case of complex **2** the deviations from the O(1)–N(1)–O(1A)–N(1A) least-squares plane (where O(1A) and N(1A) were generated by symmetry) are ΔCu = 0.000, ΔO(1) = −0.3013, ΔN(1) = +0.2909, ΔO(1A) = +0.3013, ΔN(1A) = −0.2909 Å. These deviations result in torsional angles between the O(1)–Cu–O(3)

TABLE 6. Selected bond lengths (Å) and bond angles (°) for **2**[a]

Bond lengths (Å)			
Cu(1)–O(1)	1.984(4)	Cu(1)–N(1)	1.995(5)
O(1)–C(6)	1.274(10)	O(2)–C(6)	1.254(9)
Cu(1)...O(2)	2.487		
*Cu(2)–O(11)	1.995(5)	*Cu(2)–N(11)	2.002(6)
*O(11)–C(16)	1.275(6)	*O(12)–C(16)	2.252(8)
*Cu(2)..O(12)	2.509		
Bond angles (°)			
O(1)–Cu(1)–N(1)	90.3(2)	O(1)–Cu(1)–O(1A)	90.7(2)
N(1)–Cu(1)–O(1A)	162.8(2)	O(1)–Cu(1)–N(1A)	162.8(2)
N(1)–Cu(1)–N(1A)	93.9(3)	O(1)–C(6)–O(2)	122.5(6)
O(1)–C(6)–C(7)	117.8(6)	O(2)–C(6)–C(7)	119.6(7)
*O(11)–Cu(2)–N(11)	92.2(2)	*O(11)–Cu(2)–O(11A)	88.5(3)
*N(11)–Cu(2)–O(11A)	158.7(2)	*O(11)–Cu(2)–N(11A)	158.7(2)
*N(11)–Cu(2)–N(11A)	94.8(3)	*O(11)–C(16)–O(12)	122.8(6)
*O(11)–C(16)–C(17)	117.5(6)	*O(12)–C(16)–C(17)	119.7(5)

[a] The starred entries are for the second molecule in the asymmetric unit.

and N(1)–Cu–N(3) planes for **1** and the O(1)–Cu–O(1A) and N(1)–Cu–N(1A) planes for **2** of 26.5 and 29.4°, respectively.

The lattice of **1** consists of discrete molecules connected via hydrogen bonds from the protonated 2-methylimidazole nitrogen atom to the weakly coordinated carboxylate oxygen atom of a neighboring molecule. The intermolecular hydrogen bonding leads to the three-dimensional network shown in Fig. 4. The separation of donor atoms for the N–H...O hydrogen bonding interactions involving O(2) is 2.688 Å and that involving O(4) is 2.737 Å. These distances compare favorably with the 2.787 Å reported for the hydrogen bonds found in *trans*-bis(acetato)-bis(imidazole)copper(II) [3]. The N–H...O angles are 162.2 and 161.5°, respectively.

Conclusions

The results of this study are consistent with those of previous ones in showing that there is a preference for monomer formation over dimer formation in copper(II) carboxylate adducts with basic ligands such as imidazoles than with less basic ligands [3–7, 18]. To our knowledge, this is the first report of the crystal structures of monomeric copper(II) acetate and other carboxylate adducts where the monodentate nitrogen bases coordinate in a *cis* configuration. Further studies designed to elucidate the factors that control the formation of *cis* and *trans* adducts of copper(II) carboxylates are underway. The pharmacological effects of these new complexes are also being investigated.

Supplementary material

Complete tables of bond lengths and angles, hydrogen atom coordinates, anisotropic thermal parameters, and observed and calculated structure factors for **1** and **2** are available from the authors on request.

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