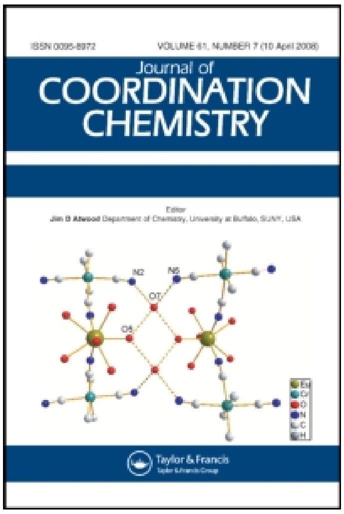

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CRYSTAL STRUCTURE AND SPECTROSCOPIC PROPERTIES OF AQUABIS(IMIDAZOLE-4-ACETATO)COPPER(II)

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Light blue crystals of composition $[Cu(ia)_2(H_2O)]$ (where *ia* denotes the imidazole-4-acetatoanion) were obtained from aqeous solutions of $CuSO_4$ and the sodium salt of the ligand. The complex has been characterized by single-crystal X-ray diffraction as well as by vibrational and electronic spectroscopy. The environment around copper(II) ion may described as *quasi*-square pyramid with carboxylic oxygen and imidazole nitrogen atoms at the corners of the pyramid base and a water molecule at the top. The Cu atom is 0.080(1) Å from the least-squares plane through the four atoms of the pyramid base toward the apical water oxygen atom located 2.365(2) Å from the metal center. The infrared spectrum was interpreted with application of deuterium labeling. The copper *d-d*, ligand-to-metal charge transfer (LMCT) and ligand Π–Π^* transitions were assigned in the reflectance spectrum.

Keywords: Copper(II); Imidazole-4-acetate; X-ray structure; IR; Electronic spectrum

INTRODUCTION

Imidazole-4-acetic acid plays an important role in living systems. Being a catabolite of histidine, it has been found in brain [1] where acts at the GABA receptor [2]. It is also used for the preparation of several specific compounds as protease inhibitors, cystein receptor antagonists or anticancer agents. On the other hand, the acid may interact with transition metal ions forming coordination bonds *via* carboxylic and imidazole groups. Such complexation has been found in solutions containing the ligand and copper(II) salts [3]. In previous work, [4] we reported the crystal structure and spectroscopic data for the bis(imidazole-4-acetato)copper(II) complex. Recently, using the same ligand, we have crystallised another copper(II) complex, whose structure and selected spectroscopic properties are presented here.

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EXPERIMENTAL SECTION

Preparation of the Complex

The sodium salt of imidazole-4-acetic acid Na(ia)$\cdot H_2O$ was purchased from the Aldrich Chemical Co. The title compound was recovered from an aqueous solution containing copper(II) sulphate and the ligand salt in 1 : 2 mol ratio. Crystals suitable for X-ray analysis were obtained from a dilute solution (2.5×10^{-3} molar) of $CuSO_4$. The same complex was produced when copper(II) chloride or perchlorate was used. Preliminary TGA-DTG-DTA studies show that the complex loses one water molecule between 102–200°C ($DTA_{peak} = 166°C$). The results of elemental analysis fit the values calculated for the $Cu(ia)_2 \cdot H_2O$ formula %: C, 36.20; H, 3.65; N, 16.89. Found: C, 36.43; H, 3.77; N, 16.74.

Physical Measurements

Elemental analyses were performed according to the Kumpan (C,H) and Pregl–Dumas (N) methods. For thermal analysis a Derivatograph C (MOM Budapest) was used. Standard KBr pellet and Nujol mull techniques were applied for infrared spectroscopy performed on Perkin–Elmer FTIR 1600 and FTIR 2000 instruments. The reflectance spectrum was obtained using a CARY 500 Scan spectrophotometer.

X-ray Crystallography

All data were collected on a KUMA KM4CCD κ-axis diffaractometer with graphite-monochromated MoK radiation. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods employing the SHELXS97 program [5]. SHELXL97 [6] was applied for data refinement by full-matrix least-squares methods. Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included from the $\Delta\rho$ maps and refined with isotropic thermal parameters. Final refinement resulted in $R_1 = 0.0268$, $wR_2 = 0.0702$. Other refinement details and crystal data are summarized in Table I. Coordinates of non-hydrogen atoms are listed in Table II. Molecular graphics were prepared using ORTEP-3 [7].

RESULTS AND DISCUSSION

Crystal Structure

Two imidazole-4-acetato ligands are bound with the copper(II) ion in bidentate mode *via* the unprotonated nitrogen atom of the imidazole ring and an oxygen atom of the carboxyl group. The copper(II) surrounds are completed by an oxygen atom of the water molecule located at the axial position. The structural arrangement and atom numbering system used are shown in Fig. 1. Cu–O and Cu–N bonds as well as angles between them (Table III) show that the metal environment may be described as slightly distorted square-based pyramid. Such stereochemistry is characteristic of five-coordinated copper(II) and has been found in many complexes of this metal. In addition, a weak interaction between the metal atom and a non-coordinating carboxyl oxygen atom of a neighbouring molecule should be noted. This oxygen

TABLE I Crystal data and structure refinement details for [Cu(ia)$_2$(H$_2$O)]

Empirical formula	$C_{10}H_{12}N_4O_5Cu$
Formula weight	331.78
Temperature	100(1) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1$
Unit cell dimensions	$a = 8.374(2)$ Å
	$b = 6.891(2)$ Å
	$c = 10.691(2)$ Å
	$\beta = 100.28(3)$ deg.
Volume	607.0(2) Å^3
Z	2
Density (calculated)	1.815 Mg/m^3
Absorption coefficient	1.826 mm^{-1}
$F(000)$	338
Crystal size	0.10 × 0.12 × 0.15 mm
Theta range for data collection	3.85 to 28.62 deg.
Index ranges	$-10 <= h <= 8$, $-9 <= k <= 9$, $-13 <= l <= 13$
Reflections collected/unique	4047/2478 [R(int) = 0.0374]
Refinement method	Full-matrix least-squares on F^2
Data [$I > 2\sigma(I)$]/parameters	2365/229
Goodness-of-fit on F^2	1.060
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0268$, $wR2 = 0.0702$
R indices (all data)	$R1 = 0.0283$, $wR2 = 0.0708$
Extinction coefficient	0.007(3)
Largest difference/peak and hole	0.499 and −0.549 Å^{-3}

TABLE II Atomic coordinates and displacement parameters of non-hydrogen atoms for [Cu(ia)$_2$(H$_2$O)]

Atom	*x/a*	*y/b*	*z/c*	*U*(eq)
Cu	0.29456(3)	0.2400	0.3115(2)	0.0094(1)
O(11)	0.4933(2)	0.1660(3)	0.4315(2)	0.0120(4)
O(12)	0.6610(2)	0.1117(3)	0.6125(2)	0.0129(4)
O(21)	0.0983(2)	0.3379(3)	0.1992(2)	0.0148(4)
O(22)	−0.0714(2)	0.4118(4)	0.0233(2)	0.0200(5)
N(11)	0.1666(3)	0.1959(3)	0.4445(2)	0.0114(5)
N(12)	−0.0366(3)	0.1346(4)	0.5425(2)	0.0128(5)
N(21)	0.4279(3)	0.3018(4)	0.1845(2)	0.0099(4)
N(22)	0.6390(3)	0.3643(4)	0.0966(2)	0.0132(5)
C(11)	0.5249(3)	0.1632(4)	0.5522(2)	0.0098(5)
C(12)	0.3992(3)	0.2309(6)	0.6295(2)	0.0105(4)
C(13)	0.2257(3)	0.1890(4)	0.5742(2)	0.0109(5)
C(14)	0.0090(3)	0.1618(4)	0.4299(3)	0.0117(5)
C(15)	0.0999(3)	0.1508(4)	0.6351(3)	0.0123(5)
C(21)	0.0693(3)	0.3733(4)	0.0813(2)	0.0116(5)
C(22)	0.1988(3)	0.3688(5)	−0.0003(3)	0.0190(6)
C(23)	0.3732(3)	0.3623(4)	0.0611(2)	0.0108(5)
C(24)	0.5890(3)	0.3044(4)	0.2016(3)	0.0131(5)
C(25)	0.5041(3)	0.4013(5)	0.0058(3)	0.0135(5)
O(5)	0.2414(3)	−0.0727(4)	0.2227(2)	0.0235(5)

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

atom (O12a) is located 2.693(2) Å from the metal center at an approximately axial position, opposite to the water molecule (Table III). Equatorial copper–oxygen bond lengths are similar to those reported for copper(II) complexes with 3,5-pryazole-dicarboxylic acid [8] (1.955(3) Å) or β-alanine [9] (1.960(4) Å). The Cu–N bond is

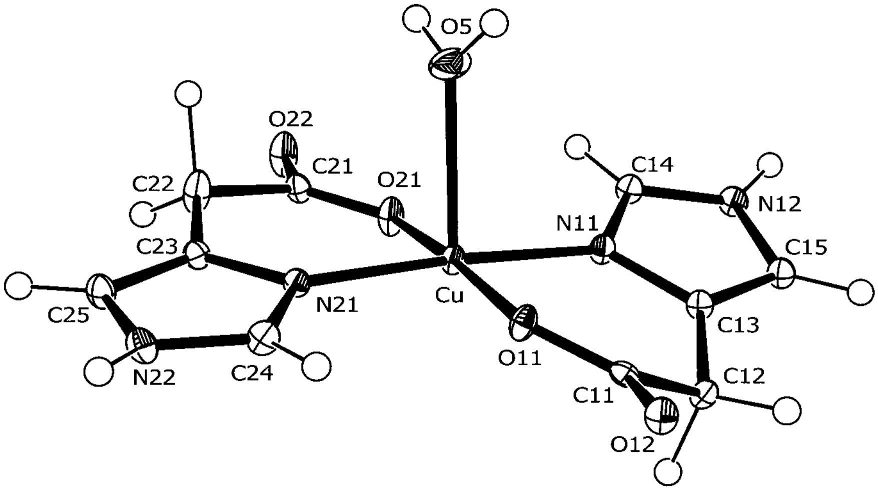

FIGURE 1 ORTEP plot of the title compound showing 50% probability displacement ellipsoids and the atom numbering scheme.

slightly shorter than that observed for the dihistaminecopper(II) complex [10] (1.985(9) Å). The axial copper(II)–water distance is usually longer than equatorial ones because of the Jahn–Teller effect. Cu-O5 2.365(2) Å is within the range of observed values [11,13].

The basal coordinating atoms are close to the equatorial plane

$$0.791(6)X + 6.442(4)Y + 3.419(8)Z = 2.925(3).$$

O11 and O21 atoms deviate about 0.011(1) Å from this plane, whereas the N11 and N21 atoms are located at similar distances but on the opposite side of the plane. The copper(II) atom is displaced out of the plane by 0.080(1) Å towards the axial direction and the chelate rings are not planar. Four atoms, O11, N11, C11 and C13, derivate between 0.0024(11) and 0.0028(13) Å from the best plane

$$0.615(8)X + 6.871(4)Y + 0.046(19)Z = 1.467(10).$$

and remaining Cu and C12 atoms are 0.378(4) and 0.395(5) Å out of the plane. Such displacements give dihedral angles formed by the Cu–O11–N11 and C11–C12–C13 planes with the O11–N11–C11–C13 plane of 15.8(1) and 29.7(3)°, respectively. Thus, the conformation of the ring may be described as boat-shaped. Both chelate rings are arranged in opposite ways as shown in Fig. 1. However, it should be pointed out that this arrangement is not centrosymmetric with respect to the metal atom. For example, the second chelate ring is more flattened with respective dihedral angles of 9.6(1) and 13.8(3)°.

The chelate ring carbon–carbon bond lengths are very close (maximum difference 0.01 Å) to respective values of the ligand in the zwitterionic form [14]. The adjacent imidazole ring forms a dihedral angle of 15.1(1)° with the O11–N11–C11–C13

TABLE III Selected bond lengths [Å] and angles [°] for [Cu(ia)$_2$(H$_2$O)]

Distances	
Cu–N11	1.950(2)
Cu–N21	1.953(2)
Cu–O21	1.974(2)
Cu–O11	1.978(2)
Cu–O5	2.365(2)
Cu–O12a	2.693(2)
O11–C11	1.269(3)
O12–C11	1.256(3)
O21–C21	1.264(3)
O22–C21	1.258(3)
N11–C14	1.322(3)
N11–C13	1.388(3)
N12-C14	1.339(3)
N12–C15	1.377(3)
C13–C15	1.359(4)
N21–C24	1.329(3)
N21–C23	1.381(3)
N22–C24	1.332(4)
N22–C25	1.376(4)
C23–C25	1.362(4)
C11–C12	1.523(3)
C12–C13	1.495(3)
C21–C22	1.508(4)
C22–C23	1.491(4)
Bond angles	
N11–Cu–O11	89.7(1)
N21–Cu–O21	91.1(1)
C11–O11–Cu	131.4(2)
C21–O21–Cu	132.6(2)
O11–C11–C12	120.5(2)
O21–C21–C22	122.9(2)
C11–C12–C13	116.3(2)
C21–C22–C23	119.6(2)
N11–C13–C12	122.4(2)
N21–C23–C22	124.2(2)
C13–N11–Cu	126.1(2)
C23–N21–Cu	126.6(2)
N11–Cu–N21	175.9(1)
O11–Cu–O21	174.1(1)
N11–Cu–O21	89.5(1)
N21–Cu–O11	89.3(1)
N11–Cu–O5	93.6(1)
N21–Cu–O5	90.5(1)
O11–Cu–O5	95.8(1)
O21–Cu–O5	89.5(1)
N11–Cu–O12a	89.6(1)
N21-Cu-O12a	86.4(1)
O11–Cu–O12a	89.7(1)
O21–Cu–O12a	85.1(1)
O11–C11–O12	122.1(2)
O22–C21–O21	121.9(2)
O12–C11–C12	117.3(2)
C22–C21–C22	115.2(2)
O5–Cu–O12a	173.6(2)
H–O5–H	101(4)
Torsion angles	
N11–Cu–O11–C11	−21.5(3)
N21–Cu–O21–C21	16.6(3)
Cu–O11–C11–C12	−2.1(4)
Cu–O21–C21–C22	8.2(4)
O11–C11–C12–C13	34.7(4)
O21–C21–C22–C23	−12.8(5)
O11–Cu–O21–C21	−73.9
O21–Cu–O11–C11	59.8(10)
C11–C12–C13–C15	148.1(3)
C21–C22–C23–C25	−163.9(3)
Cu–O11–C11-O12	−179.6(2)
Cu–O21–C21-O22	170.6(2)
O5–Cu–O11–C11	−115.1(2)

Symmetry transformation used to generate equivalent atoms: $1-x$, $0.5+y$, $1-z$.

plane (9.1(1)° for the second *ia* ligand). In general, both equatorial ligands show approximately a mutually inverse orientation.

In the crystal structure, the molecules are linked in a two-dimensional manner by hydrogen bonds. Each water molecule in engaged in H-bonding with two neighbouring molecules *via* their non-coordinating oxygen atoms. These atoms also form a second hydrogen bond with imidazole N–H groups of other molecules. Thus, five different molecules are joined in a hydrogen bonding system of the following type

$$\mathrm{N12}\overset{0{\cdot}89}{\text{———}}\mathrm{H}\overset{1{\cdot}93}{\text{- - - -}}\mathrm{O12}\overset{2{\cdot}06}{\text{- - - -}}\mathrm{H}\overset{0{\cdot}81}{\text{———}}\mathrm{O5}\overset{0{\cdot}76}{\text{———}}\mathrm{H}\overset{2{\cdot}03}{\text{- - - -}}\mathrm{O22}\overset{1{\cdot}93}{\text{- - - -}}\mathrm{H}\overset{0{\cdot}78}{\text{———}}\mathrm{N22}$$

where interatomic distances are in Å and standard deviations vary between 0.04 and 0.05 Å. As a result of the above intermolecular bonding, the equatorial atoms are organised into layers as shown in Fig. 2. Since each water molecule interacts with a neighbouring layer, the copper–water coordination bond is the main linkage between the layers.

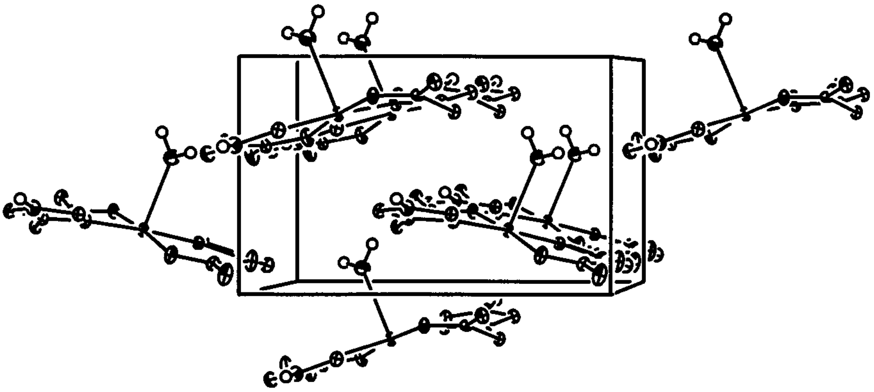

FIGURE 2 Crystal packing viewed normal to the (100) plane. Hydrogen atoms bonded to carbon have been excluded for clarity.

Infrared Spectroscopy

A selection of fundamental IR transitions observed for the $[Cu(ia)_2(H_2O)]$ complex, is presented in Table IV. Nine skeletal modes of the imidazole ring were located and assigned by comparison with imidazole [15], 4-methyloimidazole [16], the Cu-imidazole complexes [17] and histamine [18]. Frequencies of the coordinated carboxylate group are found in regions reported in the literature for other copper-carboxylato complexes [19]. Methylene group vibrations have been identified in characteristic regions reported elsewhere. Special attention has been focused on vibrations of the H_2O and NH groups involved in hydrogen bonding interactions. In order to distinguish the respective transitions, the IR spectrum of the deuterated (ND, D_2O) complex was measured. For comparison, IR data for the similarly deuterated ligand salt have also been listed in Table IV.

The formation of the intermolecular hydrogen bond between imidazole NH, carboxylate and water groups is reflected in the infrared spectra. Upon complex deuteration, several bands observed between 3100 and 2600 cm^{-1} are shifted to the 2400–2000 cm^{-1} region. Bands observed there have been assigned mainly to vibrations of hydrogen bonds formed by the water group with neighbouring oxygen atoms and absorptions due to the $N-H\cdots O$ system. The stretching O–H vibrations of the H_2O group are clearly seen as two bands at 3460 and 3380 cm^{-1} shifted to 2583 and 2486 cm^{-1} after deuteration. The position of the NH stretching vibration is not so evident. As it depends on intermolecular interactions, this mode is proposed in a wide infrared region between 3300 and 2600 wavenumbers [15,17,18]. For copper–imidazole [17] and copper – histamine [20] complexes, bands at 3275, 3193, 3108 and 3040 cm^{-1} were attributed to the mode. In the present work broad bands at 3095 and 3025 cm^{-1} are affected by deuteration and may result from vibrations with significant contribution of the $\nu(N–H)$ mode. The bending $\delta(H_2O)$ mode is observed at 1643 cm^{-1} in the spectrum of the sodium salt of the ligand where the lattice water is present. In the complex spectrum, the respective band is hidden under broad and intense absorptions between 1650 and 1510 cm^{-1} due to carboxylate and imidazole group vibrations. Assuming the $\delta(H_2O)$ frequency as being about 1600 cm^{-1}, the $\delta(D_2O)$ mode may be assigned to a new band observed for the deuterated complex at 1191 cm^{-1}, which

TABLE IV Selected infrared bands [cm^{-1}] for [$Cu(ia)_2(H_2O)$] and the sodium salt of the ligand

[$Cu(ia)_2(H_2O)$]		*$Na(ia)\cdot H_2O$*		*Assignment**
H	*D*	*H*	*D*	
3460		~ 3400		$\nu_a(H_2O)$
3380				$\nu_s(H_2O)$
3154	3153, 3145	3115, 3093	3124, 3099	ν(C–H)
3095, 3025		3020		ν(NH)
2972	2971	2986	2995	$\nu_a(CH_2)$
2890	2890	2850	2840	$\nu_s(CH_2)$
2840, 2660		2747, 2643		$\nu(N-H\cdots O\cdots H_2O)$
	2583		2590	$\nu_a(D_2O)$
	2486		2540	$\nu_s(D_2O)$
	2240, 2140		2340	$\nu(N-D\cdots O\cdots D_2O)$
		1643		$\delta(H_2O)$
1585	1565	1600	1600	$\nu_a(CO_2)$
1565	1565	1578	1581	R_1
1505	1504	1497	1496	R_2
1493	1491	1480	1481	R_3
1432, 1426	1431, 1426	1421	1412	$\delta(CH_2)$
1405,1398	1400	1395	1387	$\nu_s(CO_2)$
1333	1333	1353	1353	$\rho_w(CH_2)$
1304	1301	1301	1294	R_4
1274	1251	1257	1255	δ(CH)
1235	1228	1230	1228	$R_5 + \nu(CC)$
1208, 1197		1161, 1147		δ(NH)
	1191		1246	$\delta(D_2O)$
1175	1178	1183	1181	$\rho_t(CH_2)$
1093	1071	1107	1097	δ(CH)
1040	1054	999	990	$\nu(C\text{-}CO_2)$
	976		946, 955	δ(ND)
950, 945	946	951, 946	938	R_6
923	905	926	917	R_7
884		726, 756		γ(NH)
833	839	854, 831	834	$\rho_r(CH_2)$
804	803	818, 794	815	γ(CH)
728	727	700	697	δ(C=O)
	691		~ 600	γ(ND)
668	668	668, 660	664	R_8
633	632	642, 631	637	R_9
621	621	584, 423	563, 421	δ(NCCC)
552				H_2O lib.
	~ 450			D_2O lib.
395	392			ν(CuO), $\nu(CuOH_2)$
	375_{sh}			$\nu(CuOD_2)$
330, 317	329, 313	342, 304	345, 300	δ(NCCC)
287	281			ν(Cu-N)

*ν – stretching, δ – in-plane bending, γ – out-of-plane bending, ρ_w – wagging, ρ_t – twisting, ρ_r – rocking, R – imidazole ring vibrations, sh – shoulder, lib. – librational mode.

gives a $\delta(H_2O)/\delta(D_2O)$ ratio equal to 1.34. Two deformation modes of the NH group, in-plane δ(NH) and out-of-plane γ(NH) are attributed respectively to bands at 1209, 1197 and 884 cm^{-1}. Upon deuteration, these bands shift to 976 and 691 cm^{-1}. The positions of the in-plane bands can be compared with respective values found in the spectra of imidazole and 2,4,5-tribromoimidazole [15] at 1244 and 1282 cm^{-1}. For deuterated compounds the respective transition appear at 914 and 947 cm^{-1}. Similar comparison can be made for out-of-plane vibration, but this mode is more sensitive to intermolecular interactions and its energy varies, for example, from 958 cm^{-1} for imidazole to 828 cm^{-1} for 2,4,5-tribromoimidazole [15].

In addition to the fundamental transitions discussed above, the coordinated water shows several librational modes [21] observed below 1000 cm^{-1}. In the spectrum of the title complex, the region between 600 and 500 cm^{-1} is covered by broad absorption with a maximum at 552 cm^{-1}. After deuterium substitution, only two weak bands remain in this region, with simultaneous absorption increase at bout 450 cm^{-1}. Such changes may be due to water librational modes similar to those observed for tetraaquacopper(II) complex [21] at 887, 855 and 535 cm^{-1}. In the present work some intensity lowering between 750 and 810 cm^{-1} was also observed after deuteration, which may result from another weak librational transition.

Deuterium substitution has also been used for detection of the copper– water stretching vibration. For the $[Cu(H_2O)_4]^{2+}$ cation, where the Cu–O distance [22] equals 2.3 Å, such vibrations [21] were observed at 440 cm^{-1}. In $[Cu(ia)_2(H_2O)]$ the Cu–OH$_2$ bond length is 2.365(2) Å and the respective stretching vibration may be expected at a similar frequency. The only change observed in this region after deuteration is a new shoulder at about 375 cm^{-1}, positioned close to the 392 cm^{-1} band. This has been attributed to the ν(Cu–O) vibration involving the carboxyl oxygen atom and the shoulder to the ν(Cu–OD$_2$) mode. Taking into account the fact that deuterium substitution lowers ν(Cu–OH$_2$) by about 20 cm^{-1}, the 395 cm^{-1} band in the natural complex spectrum may be an overlap of both modes.

Electronic Transitions

The reflectance spectrum of the complex shows a single band centered at about 16000 cm^{-1} and intense absorption starting from 25000 cm^{-1} and composed of two maxima at about 40000 and 47500 cm^{-1} with three shoulders. More precise positions of the transitions have been found by digital filtration [23] of the spectrum and are summarized in Table V. The band assignment proposed is based on literature data concerning copper(II) complexes with imidazole, [24,25] trimethylimidazole [26] and aminoacids [27]. Assignment of the 43900 cm^{-1} absorption to the Π–Π* imidazole ring transition corresponds well with observations made for Na(ia)·H$_2$O, where the most intense band was found at 43200 cm^{-1}. However, in the complex spectrum, the transition may overlap with the n(imidazole) → Cu(II) absorption, as has been postulated in the literature [26]. In general, the transition energies are close to those observed for $[Cu(ia)_2]$ [4]. The most noticeable difference is the additional band at 47500 cm^{-1} observed for $[Cu(ia)_2(H_2O)]$. The above comparisons suggest

TABLE V Electronic transitions of $[Cu(ia)_2(H_2O)]$

ν[cm^{-1}] (λ[*nm*])	*Assignment*
47500 (210)	(H$_2$O) → Cu(II) LMCT
43900 (228)	Π → Π* (imidazole) n(imidazole) → Cu(II) LMCT
40000 (250)	σ(O-carboxylate) → Cu(II) LMCT
34800 (287)	Π(imidazole) → Cu(II) LMCT
28800 (347)	Π(imidazole) → Cu(II) LMCT
15800 (633)	d–d

that the band at 47500 cm^{-1} may be due to a water–copper(II) charge transfer transition. Employing the well known formula

$$\nu_{\mathrm{LMCT}} = 30000[\chi_{\mathrm{opt}}(\mathrm{L}) - \chi_{\mathrm{opt}}(\mathrm{M})]$$

where χ_{op} denotes the optical electronegativities, the approximate energy of the transition may be evaluated [28]. According to Jørgensen [29], $\chi_{\mathrm{opt}}(\mathrm{H_2O})$ equals 3.5 whereas $\chi_{\mathrm{opt}}(\mathrm{Cu})$ for higher energy *d* orbitals varies between 1.9 and 2.1. These values give a $(\mathrm{H_2O}) \rightarrow \mathrm{Cu(II)}$ LMCT energy between 48000 and 42000 cm^{-1} and the observed 47500 cm^{-1} transition falls in this region.

Supplementary Data

Supplementary data are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition number CCDC 160144.

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