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Synthesis, Crystal Structure, Spectroscopic Data and Magnetic Properties of the Bis(imidazole-4-acetato)copper(II) Complex

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A novel complex of copper(II) and imidazole-4-acetic acid has been crystallized and investigated by X-ray diffraction, magnetic and spectroscopic (IR, Raman, UV-Vis) methods. The complex of formula $[Cu(ia)_2]$ has crystallographic *Pbca* symmetry. The copper(II) ion is situated in the symmetry centre and chelated by two ligand molecules *via* the oxygen and one of the imidazole ring nitrogen atoms. The compound shows a magnetic moment of 2.03 BM.

Key words: imidazole-4-acetic acid, copper(II) complex, crystal structure, IR, R, UV-Vis spectra, magnetic moment

Research interest in imidazole-4-acetic acid has started in the 1950s, when its biological function was discovered. The acid is a naturally occurring histamine metabolite [1]. It has also been found in the brain as an antagonist of gamma-aminobutyric acid. However, there is still some controversy about its precursors, biosynthesis and breakdown [2]. Since the discussed acid has N, O –coordination centres, its interaction with metal ions is possible. Such interaction may occur in living cells, where selected transition metals are present as biologically important or are accumulated from the polluted environment. The potentiometric and spectroscopic studies [3] have already revealed a bidentate coordination mode of the imidazole-4-acetic acid, forming a six-membered chelate ring, as in the complexes of β-alanine. For copper(II) complexes, the CuL, CuL_2 and oligomeric species have been postulated [3]. To the best of our knowledge, no data have been obtained for these compounds in the solid state. Therefore, we have made an attempt to crystallize the copper–imidazole acid complex in order to confirm the ligand coordination mode and provide some new structural and spectroscopic data, which can be useful in further bioinorganic investigations.

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EXPERIMENTAL

Complex preparation: The imidazole-4-acetic acid hydrochloride and its sodium salt monohydrate were obtained from the Aldrich Chemical Co. The copper(II) salts were of analytical grade. The copper(II) complex was crystallized from water solution containing copper(II) sulphate (2.5×10^{-3} mol/dm^3) and about a ten-fold excess of sodium imidazole-4-acetate, Na(ia). After several days, deep blue crystals were collected, washed with H_2O and dried in air. Use of different copper(II) salts resulted in the same product as above. These observations along with elemental analysis suggest the exclusive coordination of imidazole-4-acetate and the formula $[Cu(ia)_2]$ for the complex.

Instrumental: IR spectra were recorded on Perkin-Elmer FTIR 1600 and FTIR 2000 spectrometers using standard KBr pellet and Nujol mull techniques for middle and far infrared regions, respectively. Raman data were collected on a Nicolet Magna-IR FT spectrometer equipped with Nd YV04 laser excitation. The UV-Vis reflectance spectra were obtained on a CARY 500 scan UV-Vis NIR instrument. Magnetic susceptibility was measured by the Faraday method using a Cahn 1000 balance.

Crystal structure determination: Crystal data together with refinement details are given in Table 1. All measurements on the crystal were performed on a KUMA KM4CCD κ-axis diffractometer with graphite-monochromated MoKα radiation. The crystal was positioned at 65 mm from the KM4CCD camera. The 612 frames were measured at 0.75° intervals with a counting time of 30 sec. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods (program SHELXS97 [4]) and refined by the full-matrix least-squares method on all F^2 data using the SHELXL97 [5] programs. Non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were included from the $\Delta\rho$ maps and refined with isotropic thermal parameters. The final refinement resulted in $R_1 = 0.0275$ and $wR_2 = 0.0742$.

Table 1. Crystal data and structure refinement for $[Cu(ia)_2]$.

Empirical formula	$C_{10}H_{10}N_4O_4Cu$
Formula weight	313.76
Temperature	90(2) K
Wavelength	0.71073 Å
Crystal system	orthorhombic
Space group	*Pbca*
Unit cell dimensions	$a = 9.827(2)$ Å
	$b = 8.515(2)$ Å
	$c = 13.290(3)$ Å
Volume	1112.1(4) Å^3
Z	4
Density (calculated)	1.874 Mg/m^3
Absorption coefficient	1.982 mm^{-1}
F(000)	636
Crystal size	0.12 × 0.12 × 0.15 mm
Theta range for data collection	3.70 to 28.70 deg.
Index ranges	$-13 <= h <= 12, -10 <= k <= 11, -11 <= l <= 17$
Reflections collected/unique	7030/1362 [R(int) = 0.0328]

Table 1 (continuation)

Refinement method	Full-matrix least-squares on F^2
Data [$I > 2\text{sigma}(I)$]/parameters	1253/109
Goodness-of-fit on F^2	1.092
Final R indices [$I > 2\text{sigma}(I)$]	$R_1 = 0.0275$, $wR_2 = 0.0742$
R indices (all data)	$R_1 = 0.0304$, $wR_2 = 0.0764$
Extinction coefficient	0.0091(14)
Largest difference peak and hole	0.804 and –0.783 e. Å^{-3}

RESULTS AND DISCUSSION

Description of the structure: An ORTEP [6] view of the molecular arrangement of the [Cu(ia)$_2$] complex is shown in Fig. 1, whereas selected bond lengths and angles are presented in Table 2. The molecule of the complex is formed by two organic ligands bonded to the copper(II) ion through their carboxyl groups and N1 atoms of the imidazole rings. A symmetry centre, located at the metal atom, relates the ligand molecules. The central atom and coordinating O1, N1, O1^a and N1^a atoms form an ideal plane. The similar values of the Cu–O1 and Cu–N1 bond lengths equal respectively 1.978(1) and 1.950(1) Å, together with the almost perpendicular orientation of the coordination bonds (N1–Cu–O1 angle is equal to 91.1(1)°) enables us to describe the basic copper coordination shell as very close to square-planar. The crystal structure consists primarily of discrete [Cu(ia)$_2$] molecules. The non-coordinating oxygen atoms from adjacent molecules have weak interaction with the metal through the axial position; the Cu–O2^b distance equals 2.782(1) Å. Metal–ligand bond lengths are comparable with respective values reported in the literature. For example, the coordination Cu–O1 bond length is slightly longer than respective distances for copper(II) complexes with substituted pyridine-2-carboxylic acid (1.935(5) Å) [7] and shorter than in [Cu(β-alanine)$_2$]·4H_2O (2.015(3) Å) [8]. The Cu–N1 distance is: between values observed for copper(II) complexes with imidazole (2.004(7) Å) [9] and 3,5-pyrazoledicarboxylic acid (1.907(4) Å) [10] or Schiff base derivatives containing imidazole and β-alanine groups (from 1.937(6) to 1.952(4) Å) [11]. The mean plane of the six-membered chelate ring is defined by the equation: $5.833(7)X + 6.741(5)Y + 1.927(8)Z = 0.375(2)$ with the angle to the O1–Cu–N1 plane equal to 15.9(1)°. Four atoms: O1, N1, C3 and C5 are only slightly displaced from the mean plane (no more than 0.025 Å), whereas the Cu and C4 deviate by –0.375(2) and –0.588(2) Å, respectively. Taking into account that the C3–C4–C5 plane forms an angle of 44.5(1)° to the O1–C5–C3–N1 plane, the chelate ring may be described as unsymmetrical boat. The C–C bond lengths of the chelate ring are quite similar to respective distances in the free ligand (1.485(4) and 1.517(4) Å) [12]. The carboxyl group is planar; the sum of angles around the C5 atom equals 180°. The C–O2 (uncoordinated) bond length is comparable to those in the ligand (1.249(3) and 1.252(3) Å), whereas the second, C–O1 (coordinated to metal) is 0.028 Å longer. Similar difference was found in the

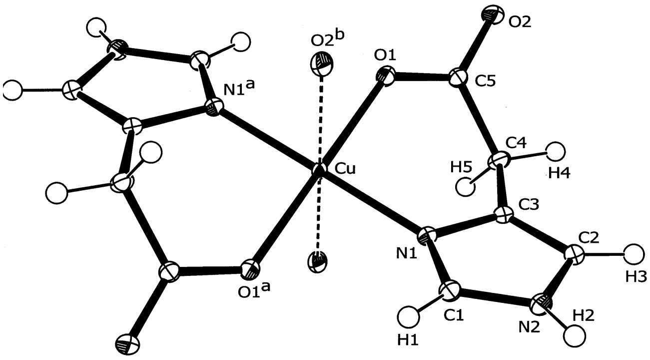

Figure 1. View of the [Cu(ia)$_2$] molecule together with weakly interacting oxygen atoms.

mentioned Cu(II)-β-alanine complex structure [8]. The imidazole ring bond lengths and angles are within the values typical for this system (Table 2). The attached C4 atom is positioned close to the imidazole plane; the values of the respective torsion angles are higher than 178°. Besides van der Waals interactions, the crystal structure is stabilized by hydrogen bonding, in which the O2 atom acts as an acceptor (A) of hydrogen, whereas the non-coordinating imidazole N2 atom is a donor (D). The respective D–H and H····A distances were found to be 0.85(3) and 1.94(3) Å, respectively. The D–H····A angle is 174(2)° and the D····A distance equals 2.79(2) Å.

Table 2. Selected bond lengths [Å] and angles [deg] for [Cu(ia)$_2$].

Distances			
		C3–N1–Cu	122.5(1)
Cu–N1	1.950(1)	O1–C5–O2	123.1(1)
Cu–O1	1.978(1)	O2–C5–C4	119.1(1)
Cu–O2^b	2.782(1)	C1–N1–C3	106.8(1)
O1–C5	1.276(2)	C2–C3–N1	108.5(1)
O2–C5	1.248(2)	C3–C2–N2	106.0(1)
N1–C1	1.328(2)	C1–N2–C2	108.3(1)
N1–C3	1.386(2)	N1–C1–N2	110.3(1)
N2–C1	1.229(2)	Torsion angles	
N2–C2	1.379(2)	N1–Cu–O1–C5	23.6(1)
C2–C3	1.367(2)	N1^a–Cu–O1–C5	–156.5(1)
C3–C4	1.490(2)	O1–Cu–N1–C1	141.8(1)
C4–C5	1.520(2)	O1–Cu–N1–C3	–16.5(1)
Bond angles		Cu–N1–C1–N2	–161.1(1)
N1–Cu–O1	91.1(1)	C2–N2–C1–N1	0.3(2)
N1^a–Cu–O1	88.9(1)	C1–N2–C2–C3	–0.4(2)

Table 2 (continuation)

O1–Cu–O2^b	83.7(1)	N2–C2–C3–N1	0.4(2)
O1^a–Cu–O2^b	96.3(1)	N2–C2–C3–C4	–178.9(2)
N1–Cu–O2^b	97.3(1)	C1–N1–C3–C2	–0.2(2)
N1^a–Cu–O2^b	82.3(1)	Cu–N1–C3–C4	–18.6(2)
C5–O1–Cu	129.5(1)	N1–C3–C4–C5	56.5(2)
O1–C5–C4	117.7(1)	Cu–O1–C5–O2	–174.6(1)
C3–C4–C5	112.3(1)	Cu–O1–C5–C4	6.5(2)
N1–C3–C4	120.7(1)	C3–C4–C5–O1	–49.2(2)

Symmetry transformations used to generate equivalent atoms:
a: –x, –y, –z; b: –x + 1/2, y + 1/2, z; c: x – 1/2, –y – 1/2, –z.

Infrared and Raman spectra: For the centrosymmetric complex studied here, the "mutual exclusion rule" applies and only antisymmetric vibrations are infrared active. In order to collect the wavenumbers of respective symmetric modes, the Raman spectrum has been measured. Both spectra are presented in Fig. 2 as additional "finger print" characterization of the complex. For most vibrations, the wavenumbers of symmetric and antisymmetric modes (related to molecule inversion symmetry) are very similar and therefore such distinction will be frequently omitted in band assignments given here. The broad and complicated absorption between 3200 and 2600 cm^{-1} confirms the hydrogen bonding postulated in X-ray analysis. The ν(NH) vibrations were assigned to the 3088 cm^{-1} band, which shifts to 2410 cm^{-1} after complex N-deuteration. Two imidazole ring ν(CH) [13,14] and two side chain ν(CH_2) modes [15] are much better seen in the Raman spectrum at 3144, 3128 cm^{-1} and 3034, 2898 cm^{-1}, respectively. These wavenumbers are affected no more than 10 cm^{-1} by N-deuteration. The 1700 cm^{-1} band in the ligand hydrochloride is due to antisymmetric (local symmetry) ν(CO_2) vibrations. Upon neutralization, this band shifts to 1600 cm^{-1} absorption observed in the Na(ia)·H_2O spectrum. The metal chelation causes further shift to 1584 cm^{-1}. Similar tendency has been observed for the symmetric carboxyl stretching frequencies. This mode appears in the [Cu(ia)$_2$] spectrum as the intense broad band centred at about 1380 cm^{-1}. The energy separation between both carboxyl stretching frequencies is about 200 cm^{-1}, which confirms the monodentate coordination of the carboxylate group [16]. Among nine skeletal vibrations of the imidazole ring, those observed in the infrared spectrum at 1509, 1492, 907 and 678 cm^{-1} and described for pure imidazole as R_2, R_3, R_7, and R_8 [17], are the most sensitive to metal coordination. Inspection of the IR and Raman spectra below 600 cm^{-1} shows that the frequency separation between antisymmetric and symmetric modes (related to the molecule symmetry centre) is the largest for the infrared bands at 400 and 296 cm^{-1}; their Raman counterparts are located at 381 and 258 cm^{-1}. Such an effect is observed when two oscillating molecular fragments have a common atom. This is the case for copper–oxygen and copper–nitrogen vibrations. Moreover, four bands mentioned are not present in the spectra of the ligand sodium salt. Taking into account that metal–ligand stretching vibrations are usually coupled with other coordination sphere and chelate ring modes, we only propose that there is a significant contribution of the ν_a(Cu–O) vibration to the 400 cm^{-1} infrared absorption, whereas the 296 cm^{-1} band is mostly of the ν_a(Cu–N) character [18,19].

Electronic transitions: The complex formation is very well confirmed by electronic spectroscopy. Comparing the reflectance spectra of the ligand sodium salt and [Cu(ia)$_2$], at least three new intense transitions at about 37000, 28000 and 15000 cm^{-1} are observed (Fig. 3). More precise band positions of [Cu(ia)$_2$] spectrum were found by variable digital filtration [20,21]. The results obtained are listed in Table 3 together with proposed band assignments. All expected *d*-*d* transitions are located within the broad absorption around 15000 cm^{-1}. The digital filtration resolved this band into two components at 14400 and 16000 cm^{-1}, but this number of transitions is still too small for square planar symmetry [22], which may be ascribed to the present complex. Therefore, the more detailed interpretation of the *d*-*d* transitions is not possible at present. The coordination mode of the ligand suggests that the following ligand to metal charge transfer (LMCT) transitions should be expected: n(imidazole) → Cu(II), π(imidazole) → Cu(II) and σ(O-carboxylate) → Cu(II). It has been observed for copper(II)–imidazole complexes that the n(imidazole) → Cu(II) transition usually overlaps with the π-π* (imidazole) mode, giving an absorption at about 45000 cm^{-1} [9]. A similar assignment is proposed here for the highest energy absorption at 43800 cm^{-1} [23]. Two remaining occupied imidazole orbitals (π_1, π_2) are involved in π(imidazole) → Cu(II) transitions, assigned to bands at 27900 and 34500 cm^{-1}. These band positions correspond well to those observed for Cu(II) complexes with substituted imidazole [9,24]. The CD studies of several Cu(II) complexes with aminoacids [25] revealed that the σ(O-carboxylate) → Cu(II) LMCT absorbs between 35000–39000 cm^{-1}. In the spectrum of [Cu(ia)$_2$], this region is covered by a

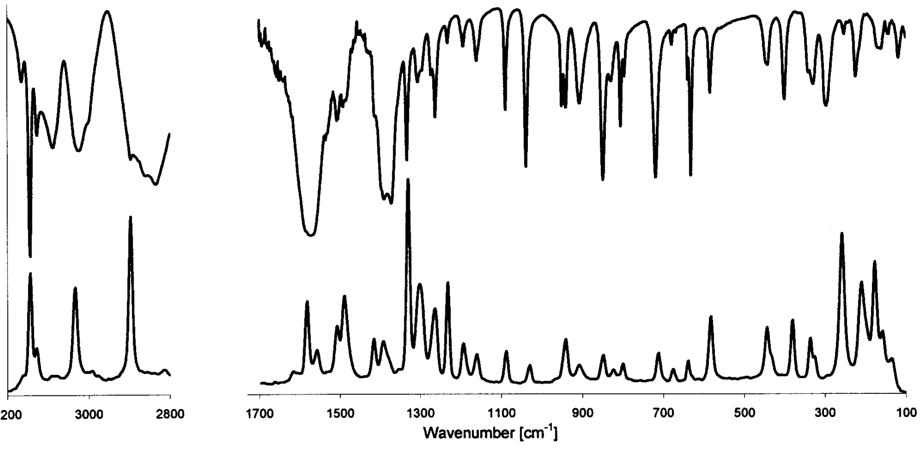

Figure 2. Infrared (top) and Raman (bottom) spectra of the [Cu(ia)$_2$] complex.

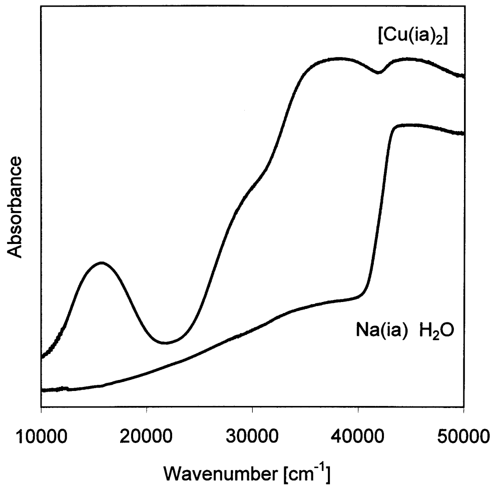

Figure 3. Reflectance spectra of [Cu(ia)$_2$] complex and ligand sodium salt.

broad and intense absorption for which two maxima at 34500 and 39300 cm^{-1} were found by digital filtration. Excluding the maximum already assigned at 34500 cm^{-1}, the last wavenumber has been attributed to the σ(O-carboxylate) → Cu(II) LMCT mode.

Table 3. Band positions and assignments for reflectance spectrum of [Cu(ia)$_2$].

Band positions [cm^{-1} (nm)]		Assignment	Ref.
Original spectrum	Filtered spectrum		
44000 (227)	43800 (228)	π → π* (imidazole)	[9]
		n (imidazole) → Cu(II) LMCT	[23]
	39300 (254)	σ (O-carboxylate) → Cu(II) LMCT	[24,25]
37000 (270)	34500 (290)	π (imidazole) → Cu(II) LMCT	[9,24]
28000 (357)	27900 (358)	π (imidazole) → Cu(II) LMCT	[9,24]
	16000 (625)		
15000 (666)		d → d	[22]
	14400 (694)		

Magnetic moment: The results of magnetic susceptibility measured between 5 and 80 K indicate that simple Curie law is obeyed for [Cu(ia)$_2$]. For the obtained data, the diamagnetic corrections, estimated as 1.7×10^{-4} cm^3 mol^{-1} from Pascal's constants, were employed. The C constant was found to be 0.510 K cm^3 mol^{-1}, which gives the magnetic moment μ of 2.03 BM. This is a typical value observed for monomeric Cu(II) complexes in the range 1.9–2.2 BM [26,27].

Supplementary data are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ UK on request, quoting the deposition number CCDC 158728.

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