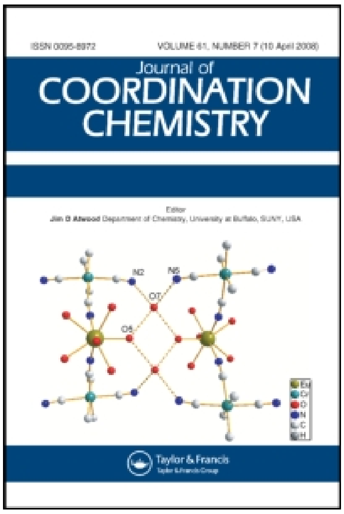

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# STRUCTURAL, MAGNETIC AND SPECTROSCOPIC CHARACTERISATION OF BIS-(BENZIMIDAZOLE) TETRAKIS-(μ-ACETATO)DICOPPER(II)

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# STRUCTURAL, MAGNETIC AND SPECTROSCOPIC CHARACTERISATION OF BIS-(BENZIMIDAZOLE) TETRAKIS-(μ-ACETATO)DICOPPER(II)

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The complex bis-(benzimidazole)tetrakis-(μ-acetato)dicopper(II) has been investigated by spectroscopic and magnetic methods. Variable-temperature (77–290K) magnetic measurements indicate a strong antiferromagnetic interaction between the copper ($Cu^{2+}$) paramagnetic centres. The exchange parameter, J, was found to be −162 $cm^{-1}$, by least-squares fitting to the spin Hamiltonian $\mathcal{H} = -2J\hat{S}_1 \cdot \hat{S}_2$. The EPR spectrum of a polycrystalline sample of the complex revealed triplet state (S = 1) transitions and the D and E zero-field splitting parameters, equal to 0.354 and 0.0032 $cm^{-1}$, respectively.

## INTRODUCTION

Dimeric copper(II) carboxylates and their adducts are very interesting systems for the study of the influence of bridging and axial ligands on magnetic superexchange between pairs of paramagnetic centres of $d^9$ electronic configuration. Studies of the crystal structure of copper acetate monohydrate by X-ray and neutron diffraction methods[1–4] proved it to contain isolated copper(II) pairs, at a distance of about 2.61 Å. Such a distance slightly exceeds the sum of the radii of two copper atoms.[5] The investigations were the basis for further studies of bonding character, physicochemical properties and of magnetic superexchange in the dimers.[6–11]

Binuclear copper(II) acetate and some of its adducts were thoroughly examined. The subject of the present paper is the magnetic and spectroscopic investigation of the new binuclear copper(II) acetate complex with benzimidazole as the axial ligand. This heterocyclic amine has not been previously used in such complexes as the axial ligand.

## EXPERIMENTAL

The data concerning the synthesis, elemental analysis and the three-dimensional X-ray analysis of $[Cu_2(OOCCH_3)_4(C_7H_6N_2)_2]$ was published earlier.[12] Magnetic susceptibility has been measured in the range 77–290K on a Faraday magnetometer, calibrated with mercury tetrathiocyanatocobaltate(II).[13,14] Magnetic susceptibility calculated per copper(II) ion was corrected for diamagnetism using Pascal's constants[15,16] and for temperature independent paramagnetism, equal to $60 \times 10^{-6}$ $cm^3$ $mole^{-1}$. The effective magnetic moment was calculated from the equation $\mu_{eff} = 2.83(\chi_{Cu} \cdot T)^{1/2}$. Exchange integrals, J, and the molar percentage of the monomeric form of the complex were computed on the University of Wroclaw Odra 1305 computer.

The EPR powder spectrum of the complex was measured at room temperature on a Jeol X-band JES-ME-3X spectrometer. Reflectance spectra of undiluted compound have

TABLE I
Magnetic data.[a]

| Temperature (K) | Molar magnetic susceptibility $\chi_M \times 10^6$ cm$^3$ mol$^{-1}$ | Magnetic moment (B.M.) |
|---|---|---|
| 77 | 69 | 0.21 |
| 100 | 197 | 0.40 |
| 150 | 458 | 0.75 |
| 200 | 717 | 1.08 |
| 250 | 780 | 1.25 |
| 290 | 803 | 1.36 |

[a] Some values selected from among 39 experimental points are presented.

been recorded in the range 250-1000 nm on a Beckman UV 5240 spectrophotometer. Infrared spectra were measured in KBr mull on a Perkin-Elmer 621 spectrophotometer in the range 400–4000 cm$^{-1}$.

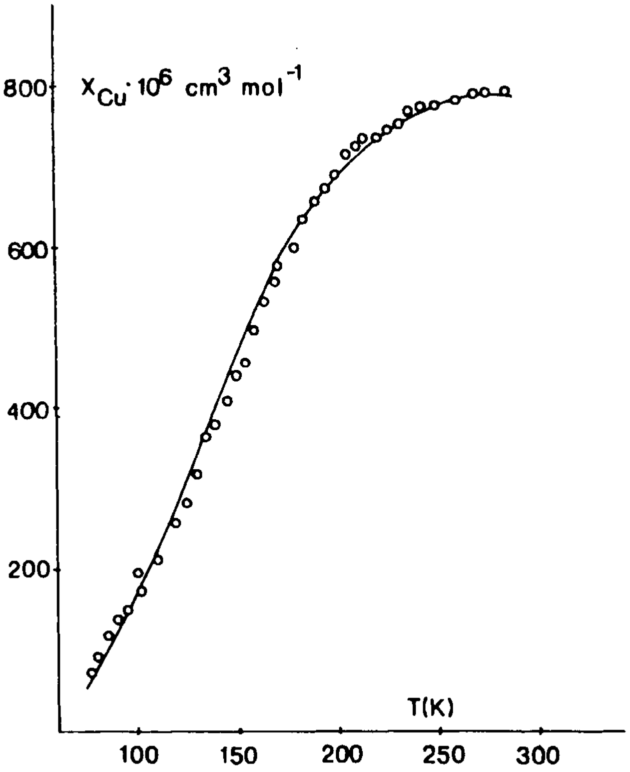

FIGURE 1 Theoretical and experimental magnetic susceptibilities for $[\mathrm{Cu_2(OOCCH_3)_4(C_7H_6N_2')_2}]$ calculated per Cu ion. The solid line has been calculated with J = $-162$ cm$^{-1}$ and x = 0.11%. The experimental data are shown by open circles.

## RESULTS AND DISCUSSION

The magnetic susceptibility of bis-(benzimidazole)tetrakis-($\mu$-acetato)dicopper(II) measured in the range 77-290K was found to decrease systematically with falling temperature from 803 x $10^{-6}$ cm$^3$ mole$^{-1}$ to 69 x $10^{-6}$ cm$^3$ mole$^{-1}$, at 290K and 77K, respectively. An analogous relation is evidenced by the change of the effective magnetic moment which for the same temperatures decreases from 1.36 to 0.21 B.M. Such a change in the magnetic susceptibility (Fig. 1, Table 1) is characteristic of copper(II) dimers, formed by the coupling of two Cu(II) centres *via* four bridging carboxyl anions.[17]

Bis-(benzimidazole)tetrakis-($\mu$-acetato)dicopper(II) crystallizes in the orthorhombic system with space group Pbca.[12] Two copper ions are linked by four carboxylate bridges to form a dimer; the axial coordination sites are occupied by benzimidazole ligands. The copper atom is thus surrounded by four oxygen atoms (average Cu-O distance = 1.977 Å) and a nitrogen atom (average Cu-N distance = 2.145 Å) which forms a square pyramidal coordination sphere (Fig. 2). The copper-copper distance is 2.663 Å and is distinctly greater than in other acetate dimers (Table 2).

For determination of the exchange integrals for pair of interacting paramagnetic centres the corrected experimental magnetic susceptibilities were fitted to the modified Bleaney-Bowers expression[17] by a non-linear least-squares method.

$$\chi_{Cu}^{corr} = \frac{Ng_{av}^2\beta^2}{3kT}\left[1 + 1/3\left(e^{-2J/kT}\right)\right]^{-1}(1-x) + \frac{Ng_{imp}^2\beta^2}{4kT}\, x \qquad (1)$$

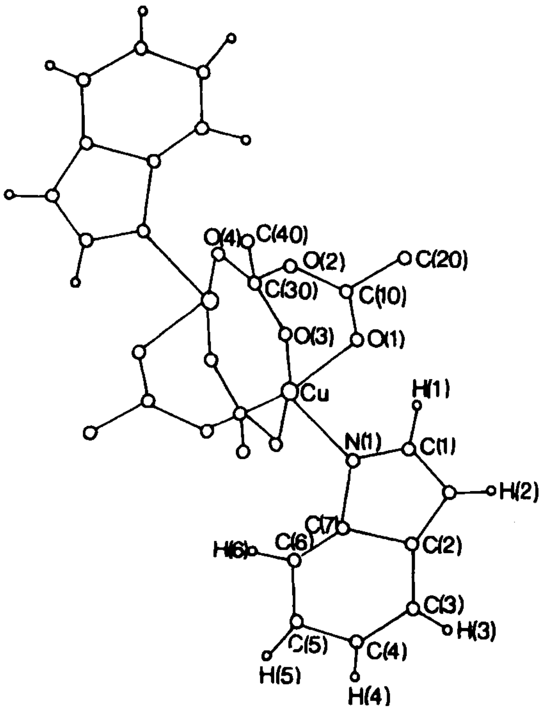

FIGURE 2 The binuclear molecule viewed along the z axis. Relevant bond lengths (Å) are: Cu-O (1), 1.983 (4), Cu-O (3), 1.971 (4); Cu-N (1), 2.145 (5); Cu-Cu', 2.663 (1).

TABLE II
Cu-Cu distances (A) in dimeric copper acetate adducts.

| Axial ligand | Cu-Cu (A) | Reference |
|---|---|---|
| Benzimidazole | 2.663 | This work |
| Pyridine | 2.645 | 18 (monoclinic) |
| Thiocyanate | 2.643 | 19 |
| Quinoline | 2.642 | 20 |
| Pyridine | 2.630 | 21 (orthorhombic) |
| Water | 2.616 | 1-3 |
| Methanol | 2.597 | 22 |
| Pyrazine | 2.584 | 23 (300K) |
| Acetic acid | 2.582 | 22 |
| Pyrazine | 2.576 | 23 (100K) |

where $\chi^{corr}$ is the molar magnetic susceptibility calculated per copper(II) ion, J is the exchange integral in the Heisenberg-Dirac-Van Vleck Hamiltonian $\mathcal{H} = -2J\hat{S}_1 \cdot \hat{S}_2$, x is the molar percentage of monomeric form of the complex and the other symbols having their usual meaning. The spectroscopic splitting parameter, $g_{av}$, obtained from the EPR spectra was used as a constant in the process of fitting the data. The minimization of the sum of the squares of the deviation

$$\mathrm{ERR} = \sum_{i=1}^{n} (\chi^{calc} - \chi^{exp})^2$$

was used to determine the best fit.

Bis-(benzimidazole)tetrakis-($\mu$-acetato)dicopper(II) is typical copper dimer in which antiferromagnetically coupled pairs of copper(II) ions lie in the S=0 ground state, with an S=1 level at an energy $|2J|$ above this. Satisfactory least-squares fits to the experimental results were obtained for a single-triplet separation of $-324$ cm$^{-1}$. Percent monomeric impurities was 0.11% and ERR $1.126 \times 10^{-7}$.

The singlet-triplet separation value of bis-(benzimidazole)tetrakis-($\mu$-acetato)dicopper (II) ($|2J| = 324$ cm$^{-1}$) exceeds by 38 cm$^{-1}$ that found for hydrated copper(II) acetate,[6] which is indicative of a stronger superexchange interaction in this dimer.

The EPR powder spectrum of the complex exhibits the absorption typical for the triplet state of axial symmetry and could be interpreted in terms of the effective spin Hamiltonian (*2*)

$$\mathcal{H} = g\beta H\hat{S} + D\hat{S}_z^2 + E(\hat{S}_x^2 - \hat{S}_y^2) - 2/3D \qquad (2)$$

where D and E are the zero-field splitting parameters (axial and rhombic respectively) and x, y and z refer to a principal-axis coordinate system fixed with respect to the Cu-Cu vector. The line components of a triplet appear at 605G($H_{z1}$), 4580G ($H_{\perp 2}$) and 5950G($H_{z2}$). An additional line, very weak, appears at 3180G and is related to the presence of a small monomeric impurity in the dimer (0.11%). Zero-field splitting parameters D and E equal 0.354 cm$^{-1}$ and 0.0032 cm$^{-1}$ respectively (Table 3) and are characteristic of dimeric copper(II) carboxylates.[25-28]

The infrared spectrum of the dimer shows the characteristic bands due to acetate bridges in the range 1400-1650 cm$^{-1}$. For sodium acetate the $\nu_s(COO^-)$ and $\nu_{as}(COO^-)$ stretching vibrations are related to the bands at 1414 cm$^{-1}$ and 1578 cm$^{-1}$, respectively.[29] The spectrum of the bis-(benzimidazole)tetrakis-($\mu$-acetato)dicopper(II) exhibits very

TABLE III
EPR parameters.

| Spectroscopic splitting factor | | | | Zero-field splitting parameter | |
|---|---|---|---|---|---|
| $g_\parallel$ | $g_\perp$ | $g_{av}^{a}$ | $g_{imp}$ | D(cm$^{-1}$) | E(cm$^{-1}$) |
| 2.384 | 2.110 | 2.205 | 2.072 | 0.354 | 0.0032 |

[a] $g_{av} = 1/3(g_\parallel^2 + 2g_\perp^2)$.

intensive bands in the same region at 1413, 1430, 1609 and 1630 cm$^{-1}$. The eigen vibration of benzimidazole (1409 cm$^{-1}$) and the $\delta_{CH_3}$ vibration of the acetate anion at 1430 cm$^{-1}$ are also observed in this region. In the range 1600-1650 cm$^{-1}$, besides the $\nu_{as}(COO^-)$ vibration, only the very weak absorption at 1622 cm$^{-1}$ of free benzimidazole[30] may be present. The bands at about 3230 and 3420 cm$^{-1}$ correspond to the symmetric and asymmetric N-H vibrations of benzimidazole.

Reflectance spectra in the range 250-1000 nm revealed two absorption bands at ~ 365 and 740 nm (the so-called Bands I and II).[7] These bands are characteristic for copper(II) dimers with carboxylic bridges. Band I is closely associated with the Cu-O-C-O-Cu bridge system and corresponds to the $np_\pi \rightarrow \sigma^*(x^2-y^2)$ transition.[31] Its energy is practically constant for various carboxylate acids. Band II, corresponding to the $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$ transition, exhibits the evident dependence upon the axial ligand donor strength.[32-34] For bis-(benzimidazole)tetrakis-(μ-acetato)dicopper(II), the benzimidazole axial ligand is responsible for the considerable energy lowering of that transition, with respect to the majority of carboxylate dimers.

## ACKNOWLEDGEMENT

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