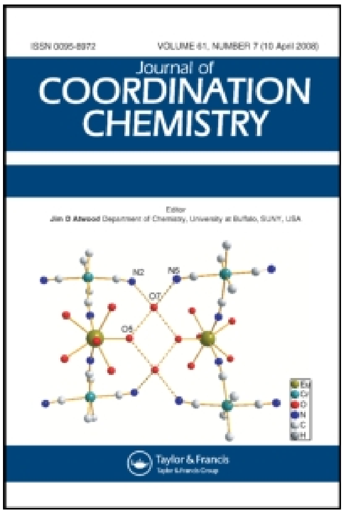

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Synthesis, Magnetism and X-Ray Structure of μl$_4$-Oxo-Hexa-μ$_2$-Chlorotetrakis(Benzimidazole)Copper(II)

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SYNTHESIS, MAGNETISM AND X-RAY STRUCTURE OF μ_4-OXO-HEXA-μ_2-CHLOROTETRAKIS(BENZIMIDAZOLE)COPPER(II)

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The title compound [Cu_4OCl_6(benzim)$_4$], obtained by the dimerization of [Cu_2Cl_3(benzim)$_5$]$^+$ cations with dissociation of six benzimidazole ligands and inclusion of an oxide ion, has been characterized by a single-crystal X-ray diffraction study. It crystallizes with a nonstoichiometric amount of solvent (ethanol) as brown-yellow crystals in space group $P\bar{1}$ with $a = 13.003(2)$, $b = 13.246(2)$, $c = 13.892(5)$ Å, $\alpha = 68.06(1)$, $\beta = 74.27(2)$, $\gamma = 71.43(1)°$ and $Z = 2$. Final discrepancy factors $R = 0.069$ and $R_w = 0.080$ were obtained for 5422 independent reflections and 452 adjustable parameters. The molecule consists of a central oxide ion coordinated tetrahedrally to four copper(II) ions; Cu(II) ions are bridged by six μ_2-chloride ligands above the six edges of the tetrahedron to form a slightly distorted octahedron around the central oxide ion 0(1). Four molecules of benzimidazole complete a distorted trigonal bipyramidal coordination sphere around each copper(II) ion which is displaced (in the direction of the nitrogen atom of benzimidazole) approximately 0.2 Å out of the equatorial plane of the three coordinated chloride ions. A considerable differentiation of Cl–Cu–Cl equatorial angles and Cu–Cl bond lengths indicates the deformation of the trigonal bipyramidal coordination.

Magnetic susceptibility measurements in the temperature range 4.2–295K revealed an antiferromagnetic interaction between the copper(II) ions of the tetramer. The magnetic properties of the complex were interpreted assuming an orbitally nondegenerate $^2A_1$ single ion ground state for the copper ions.

Keywords: Copper(II), tetramer, crystal structure, magnetism

INTRODUCTION

As part of our investigation of the structural and magnetic properties of multinuclear copper(II) complexes we have begun a study of copper(II) halides with benzimidazole. A tetranuclear complex [Cu_4OCl_6(benzim)$_4$] has been obtained by dimerization in ethanol solution of the dimeric cation [Cu_2Cl_3(benzim)$_5$]$^+$ [1] with dissociation of six benzimidazole ligands and inclusion of an oxide ion. We have prepared a tetramer containing a nonstoichiometric amount of ethanol solvent. The tetranuclear complexes of copper(II) of general stoichiometry [$Cu_4OX_6L_{10-n}$]$^{n-4}$, where X represents chloride or bromide ligands and L a Lewis base, contain both μ_4-bridging oxygen and μ_2-bridging halogens between copper ions. They attract attention not only because of their structure, but also in view of their unusual magnetic properties[2] and catalytic activity.[3] We have determined the crystal and molecular structure of a new tetrameric Cu(II) cluster and have studied its magnetic behaviour.

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EXPERIMENTAL

Preparation of the Nonstoichiometric Solvate of [Cu_4OCl_6(benzim)$_4$]

Some 0.20 g of [Cu_2Cl_3(benzim)$_5$]Cl was dissolved in 15 cm^3 of boiling 96% ethanol. After slow evaporation of the green solution at room temperature, pale prismatic crystals were obtained. The crystals were brownish by reflected light and yellow by transmitted light and large enough for use for collection of X-ray diffraction data. Chemical analysis confirmed the formula [Cu_4OCl_6(benzim)$_4$]·0.68C_2H_5OH. *Anal.*: found: C, 35.46; H, 2.85; N, 11.39; Cl, 21.38%. Calculated: C, 35.73; H, 2.85; N, 11.35; Cl, 21.58%.

Collection and Correction of X-ray Diffraction Data

The maximum crystal orthogonal dimensions were 0.5 × 0.2 × 0.2 mm. The unit cell was found to be triclinic and room temperature cell dimensions were obtained from a least-squares fit of 25 reflections on a CAD-4 automated four-circle diffractometer. *Crystal data*: $a = 13.003(2)$, $b = 13.246(2)$, $c = 13.892(5)$ Å: $\alpha = 68.06(1)$, $\beta = 74.27(2)$, $\gamma = 71.43(1)°$; $Z = 2$; $M = 986.8$ for chemical formula $C_{29.36}H_{28.08}N_8O_{1:68}Cl_6Cu_4$; $F(000) = 983.36$; d_m (flotation in CH_3I = benzene solution) = 1.53 g cm^{-3}; $d_c = 1.58$ g cm^{-3}; 24.57 cm^{-1}; space group $P1$. Intensity data with $1 < 2\theta < 50°$ were collected by the θ/ω scan mode using graphite monochromatized MoKα radiation ($\lambda = 0.71069$ Å) and a variable scan rate (1.3–5.5°/min). The intensities of three reflections were monitored after each part of 50 reflections. No significant crystal deterioration was observed. Among more than 7000 independent reflections measured, 5422 had intensities greater than $3\sigma(I)$ and were used for solution and refinement of the structure. The data were corrected for absorption, and Lorentz and polarization effects. Semi-empirical absorption corrections based on a ψ scan of 11 reflections were used. Transmission factors varied from 0.40 to 0.98.

Structure determination and refinement

The structure was solved by direct and Fourier methods using the SHELXS-86 and SHELX-76 programs. Copper, chloride, central oxygen and majority of carbon atoms were found from an E map. The remaining carbons and the oxygen atom of the ethanol molecule were located from a difference Fourier synthesis. Positions of H atoms of benzimidazole ligands were calculated assuming sp^2 configurations for C and N atoms. Further data for absorption effects were introduced by the computer program DIFABS.[4] After the correction, a decrease in R of only 0.2% was observed and experimental localization of hydrogen atoms was not possible. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $w^{-1} = \sigma^2(F) + 0.001F^2$. Refinement was terminated when the maximum shift in any parameter was $<0.2\,\sigma$. The final R was 0.069 and $R_w = (\Sigma w\Delta^2/\Sigma wF_o{}^2)^{1/2} = 0.080$. The highest peak in the final difference map of 1.9 eÅ^{-3} was localized near the nonstoichiometric ethanol molecule at 1.4 Å from the symmetry centre at 0, 1/2, 1/2. The assumption that it corresponds to a nonstoichiometric water molecule was not confirmed in the refinement procedure. Atomic scattering factors were these of SHELX-76.[5] The final positional parameters for the heavy atoms are given in Table I.

TABLE I

Positional parameters (× 10^4) for the nonhydrogen atoms.

	x/a	*y/b*	*z/c*
Cu(1)	3664(1)	7466(1)	9548(1)
Cu(2)	2533(1)	8062(1)	7618(1)
Cu(3)	4639(1)	8884(1)	7322(1)
Cu(4)	2419(1)	9941(1)	8535(1)
Cl(1)	4269(2)	7855(2)	6361(2)
Cl(2)	3759(2)	10802(2)	7172(2)
Cl(3)	5514(2)	7542(2)	8799(2)
Cl(4)	1205(2)	9827(2)	7463(2)
Cl(5)	2545(2)	6488(2)	9258(2)
Cl(6)	2330(2)	8863(2)	10325(2)
O(1)	3313(4)	8593(4)	8250(4)
O(2)	1325(15)	2761(15)	6150(13)
N(1)	4050(6)	6315(6)	10857(6)
N(3)	4480(7)	4605(7)	11992(7)
N(11)	5982(6)	9198(6)	6367(6)
N(13)	7261(6)	9385(7)	4923(6)
N(21)	1435(6)	11299(6)	8836(6)
N(23)	−185(7)	12386(7)	9245(7)
N(31)	1744(7)	7527(7)	6949(6)
N(33)	1356(9)	7009(8)	5803(8)
C(2)	4135(8)	5209(8)	11068(7)
C(4)	4941(10)	5160(10)	13372(9)
C(6)	4709(10)	7168(10)	12817(9)
C(7)	4377(9)	7354(8)	11892(8)
C(8)	4351(7)	6417(8)	11677(7)
C(9)	4609(8)	5347(8)	12430(8)
C(12)	6311(8)	9106(8)	5383(7)
C(14)	8492(8)	10090(10)	5558(10)
C(15)	8544(9)	10346(10)	6406(11)
C(16)	7752(10)	10247(10)	7294(9)
C(17)	6828(9)	9872(9)	7382(8)
C(18)	6775(7)	9602(7)	6519(7)
C(19)	7585(7)	9735(8)	5616(7)
C(22)	360(8)	11401(9)	9097(8)
C(24)	468(11)	14042(9)	9118(10)
C(25)	1445(11)	14391(10)	8874(10)
C(26)	2437(11)	13700(11)	8675(10)
C(27)	2562(9)	12624(10)	8651(10)
C(28)	1605(8)	12273(8)	8841(8)
C(29)	560(8)	12977(8)	9094(8)
C(32)	2089(9)	7279(10)	6083(9)
C(34)	−618(10)	6873(10)	6682(11)
C(35)	−1360(9)	7030(11)	7550(11)
C(36)	−1136(10)	7338(11)	8265(11)
C(37)	−93(9)	7568(10)	8167(9)
C(38)	693(8)	7411(8)	7274(8)
C(39)	408(9)	7080(9)	6569(8)
C(40)	2778(26)	3695(24)	5390(28)

Magnetic susceptibilities of a polycrystalline sample of [Cu_4OCl_6(benzim)$_4$] were measured using the Faraday method over the temperature range 4.2–295K, with a Cahn RG–HV electrobalance. The applied magnetic field was 5.25 kOe. The calibrant used was $HgCo(NCS)_4$, for which the magnetic susceptibility was taken as 16.44×10^{-6} ($cm^3\ g^{-1}$).[6] The correction for diamagnetism of constituent atoms was calculated by use of Pascal's constants[7] and found to be [-247×10^{-6} ($cm^3\ mol^{-1}$) per tetramer molecule. The value 60×10^{-6} ($cm^3\ mol^{-1}$) was used for the t.i.p. of the Cu(II) ion. Magnetism of the sample was found to be field-independent. The effective magnetic moment was calculated from the equation $\mu_{eff} = 2.83(\chi_{Cu}T)^{1/2}$ (B.M.).

EPR spectra were measured with an X-band Radiopan SE/X spectrometer for a powder at room temperature, 77K and 4.2K. Solids sample of Mn(II) in MgO and DPPH were used as references and the magnetic field was calibrated with a nuclear magnetometer (MJ 110R). The reflectance spectrum of the complex diluted in Li_2CO_3 was measured in the range 200–800 nm on a Hitachi 356 spectrometer.

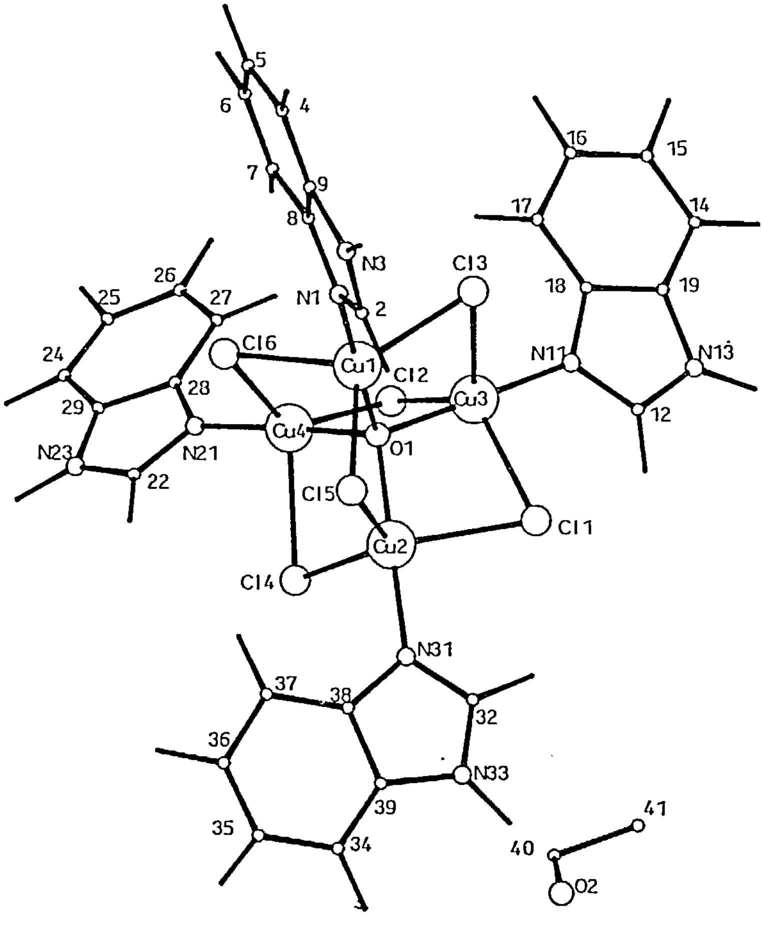

FIGURE 1 View of the molecule Cu_4OCl_6(benzim)$_4$.

TABLE II

Interatomic distances (Å), angles (deg) and esd's.[a]

Copper-copper contacts:			
Cu(1)-Cu(2)	3.129(2)	Cu(2)-Cu(3)	3.132(2)
Cu(1)-Cu(3)	3.122(2)	Cu(2)-Cu(4)	3.142(2)
Cu(1)-Cu(4)	3.124(2)	Cu(3)-Cu(4)	3.112(2)
		mean: 3.127 ± 0.010[b]	
Cu_4OCl_6 core:			
Cu(1)-Cl(3)	2.366(3)	Cu(3)-Cl(1)	2.448(4)
Cu(1)-Cl(5)	2.422(4)	Cu(3)-Cl(2)	2.385(3)
Cu(1)-Cl(6)	2.456(3)	Cu(3)-Cl(3)	2.432(3)
Cu(2)-Cl(1)	2.459(3)	Cu(4)-Cl(2)	2.405(3)
Cu(2)-Cl(4)	2.398(3)	Cu(4)-Cl(4)	2.515(4)
Cu(2)-Cl(5)	2.447(3)	Cu(4)-Cl(6)	2.352(3)
		mean: 2.424 ± 0.046	
Cl(5)-Cu(1)-Cl(6)	104.5(1)	Cl(1)-Cu(3)-Cl(3)	108.9(1)
Cl(3)-Cu(1)-Cl(6)	123.8(1)	Cl(1)-Cu(3)-Cl(2)	123.8(1)
Cl(3)-Cu(1)-Cl(5)	129.1(1)	Cl(2)-Cu(3)-Cl(3)	124.6(1)
Cl(1)-Cu(2)-Cl(5)	113.1(1)	Cl(2)-Cu(4)-Cl(4)	101.3(1)
Cl(1)-Cu(2)-Cl(4)	122.3(1)	Cl(4)-Cu(4)-Cl(6)	119.9(1)
Cl(4)-Cu(2)-Cl(5)	122.4(1)	Cl(2)-Cu(4)-Cl(6)	136.0(1)
		mean: 119.1 ± 10.2	
Cu(1)-O(1)	1.921(5)	Cu(3)-O(1)	1.905(5)
Cu(2)-O(1)	1.922(7)	Cu(4)-O(1)	1.911(5)
		mean: 1.915 ± 0.008	
Cu(1)-O(1)-Cu(2)	109.1(3)	Cu(2)-O(1)-Cu(3)	109.8(3)
Cu(1)-O(1)-Cu(3)	109.4(3)	Cu(2)-O(1)-Cu(4)	110.1(3)
Cu(1)-O(1)-Cu(4)	109.2(3)	Cu(3)-O(1)-Cu(4)	109.3(3)
		mean: 109.5 ± 0.4	
Cl(6)-Cu(1)-O(1)	82.9(2)	Cl(3)-Cu(3)-O(1)	83.9(2)
Cl(3)-Cu(1)-O(1)	85.4(2)	Cl(1)-Cu(3)-O(1)	84.7(2)
Cl(5)-Cu(1)-O(1)	85.5(2)	Cl(2)-Cu(3)-O(1)	84.7(2)
Cl(1)-Cu(2)-O(1)	84.0(2)	Cl(4)-Cu(4)-O(1)	83.1(2)
Cl(5)-Cu(2)-O(1)	84.8(2)	Cl(2)-Cu(4)-O(1)	84.0(2)
Cl(4)-Cu(2)-O(1)	86.1(2)	Cl(6)-Cu(4)-O(1)	86.0(2)
		mean: 84.6 ± 1.1	
Copper-nitrogen bond distances and angles:			
Cu(1)-N(1)	1.954(7)	Cu(3)-N(11)	1.943(7)
Cu(2)-N(31)	1.973(2)	Cu(4)-N(21)	1.963(8)
		mean: 1.958 ± 0.014	
Cl(3)-Cu(1)-N(1)	93.5(3)	Cl(2)-Cu(3)-N(11)	94.7(3)
Cl(5)-Cu(1)-N(1)	95.0(3)	Cl(1)-Cu(3)-N(11)	95.4(3)
Cl(6)-Cu(1)-N(1)	97.9(2)	Cl(3)-Cu(3)-N(11)	96.7(3)
Cl(5)-Cu(2)-N(31)	95.9(1)	Cl(6)-Cu(4)-N(21)	93.6(2)
Cl(4)-Cu(2)-N(31)	93.9(1)	Cl(4)-Cu(4)-N(21)	94.7(3)
Cl(1)-Cu(2)-N(31)	95.3(1)	Cl(2)-Cu(4)-N(21)	98.2(3)
		mean: 95.4 ± 1.6	
O(1)-Cu(1)-N(1)	178.9(3)	O(1)-Cu(2)-N(31)	179.2(2)
O(1)-Cu(3)-N(11)	179.3(3)	O(1)-Cu(4)-N(21)	177.1(3)
		mean: 178.6 ± 1.0	

TABLE II (*cont.*)

Benzimidazole ligands:			
N(1)-C(2)	1.355(13)	N(11)-C(12)	1.357(13)
C(2)-N(3)	1.343(13)	C(12)-N(13)	1.326(13)
N(3)-C(9)	1.404(18)	N(13)-C(19)	1.413(16)
C(9)-C(4)	1.399(19)	C(19)-C(14)	1.376(17)
C(4)-C(5)	1.345(23)	C(14)-C(15)	1.365(24)
C(5)-C(6)	1.436(15)	C(15)-C(16)	1.370(16)
C(6)-C(7)	1.377(19)	C(16)-C(17)	1.399(20)
C(7)-C(8)	1.393(18)	C(17)-C(18)	1.397(18)
C(8)-C(9)	1.413(12)	C(18)-C(19)	1.397(11)
C(8)-N(1)	1.364(15)	C(18)-N(11)	1.396(15)
N(21)-C(22)	1.321(13)	N(31)-C(32)	1.289(12)
C(22)-N(23)	1.334(14)	C(32)-N(33)	1.308(14)
N(23)-C(29)	1.360(16)	N(33)-C(39)	1.397(16)
C(24)-C(29)	1.390(18)	C(34)-C(39)	1.404(18)
C(24)-C(25)	1.402(22)	C(34)-C(35)	1.363(22)
C(25)-C(26)	1.350(17)	C(35)-C(36)	1.332(17)
C(26)-C(27)	1.394(21)	C(36)-C(37)	1.443(19)
C(27)-C(28)	1.389(18)	C(37)-C(38)	1.414(18)
C(28)-C(29)	1.422(12)	C(38)-C(39)	1.382(13)
C(28)-N(21)	1.380(15)	C(38)-N(31)	1.357(15)
N(1)-C(2)-N(3)	110.8(9)	N(11)-C(12)-N(13)	111.8(9)
C(2)-N(3)-C(9)	108.2(9)	C(12)-N(13)-C(19)	108.0(8)
N(3)-C(9)-C(8)	104.8(9)	N(13)-C(19)-C(18)	105.4(8)
C(9)-C(8)-N(1)	109.2(9)	C(19)-C(18)-N(11)	108.7(8)
C(8)-N(1)-C(2)	107.0(8)	C(18)-N(11)-C(12)	106.0(8)
C(5)-C(4)-C(9)	116.7(12)	C(15)-C(14)-C(19)	117.0(11)
C(4)-C(5)-C(6)	120.7(12)	C(14)-C(15)-C(17)	123.0(12)
C(5)-C(6)-C(7)	122.6(12)	C(15)-C(16)-C(17)	121.3(11)
C(6)-C(7)-C(8)	117.2(10)	C(16)-C(17)-C(18)	116.0(10)
C(7)-C(8)-C(9)	119.0(9)	C(17)-C(18)-C(19)	121.3(9)
C(8)-C(9)-C(4)	123.7(10)	C(18)-C(19)-C(14)	121.4(10)
N(21)-C(22)-N(23)	112.4(10)	N(31)-C(32)-N(33)	113.7(11)
C(22)-N(23)-C(29)	108.3(9)	C(32)-N(33)-C(39)	107.1(9)
N(23)-C(29)-C(28)	105.4(8)	N(33)-C(39)-C(38)	103.6(10)
C(29)-C(28)-N(21)	107.8(9)	C(39)-C(38)-N(31)	110.0(9)
C(28)-N(21)-C(22)	106.1(9)	C(38)-N(31)-C(32)	105.6(9)
C(25)-C(24)-C(29)	117.2(13)	C(35)-C(34)-C(39)	115.6(9)
C(24)-C(25)-C(26)	121.3(13)	C(34)-C(35)-C(36)	123.1(13)
C(25)-C(26)-C(27)	123.0(14)	C(35)-C(36)-C(37)	122.6(13)
C(26)-C(27)-C(28)	117.0(12)	C(36)-C(37)-C(38)	115.5(11)
C(27)-C(28)-C(29)	120.3(10)	C(37)-C(38)-C(39)	118.8(11)
C(28)-C(29)-C(24)	121.0(11)	C(38)-C(39)-C(34)	124.3(11)
Solvate molecule:			
O(2)-C(41)	1.42(4)	O(2)-C(41)-C(40)	111.4(3)
C(40)-C(41)	1.46(4)		

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[a] Esd's are shown in parentheses. [b] The errors associated with the mean values were calculated from $\sigma = [(\Sigma(\bar{x}-x_i)^2)/(N-1)]^{1/2}$, where $\bar{x}$ is the mean, x_i is the value of the i'th observation and N is the number of observations.

RESULTS AND DISCUSSION

The geometry of the [Cu_4OCl_6benzim)$_4$] complex is shown in Figure 1 with the labelling system used in the discussion. Selected bond lengths and bond angles are presented in Table II. The molecule consists of a tetrahedron of copper(II) atoms at the centre of which a μ_4-oxide ion is situated, and above each of the six edges of which a μ_2 chloride ion is located. The structure is completed by four benzimidazole ligands bonded one to each Cu atom by a nitrogen atom. The Cu–O–Cu angles and Cu–O bonds vary between 109.1(3)–110.1(3) and 1.905(5)–1.922(7) Å with average values of 109.5 ± 0.4° and 1.915 ± 0.008 Å, the latter being somewhat longer than in other similar molecules.[8] Examples of an oxide ion forming four σ bonds to surrounding atoms are relatively rare. Except for Cu(II) clusters, such coordination of the oxide ion has been found by X-ray diffraction studies in basic beryllium and zinc acetates [$Be_4O(CH_3COO)_6$][9] and [$ZnO(CH_3COO)_6$],[10] and in the magnesium complex [$Mg_4OBr_6(Et_2O)_4$].[11] The present structure is a case in which all atoms of the complex are crystallographically independent. It is thus not surprising to find that the core of the molecule in the present structure is distorted from ideal T_d symmetry. The distortion can be described in terms of the coordination geometry of the Cu atom. Similar as it is to other Cu(II) clusters of the [$Cu_4OX_{10-n}L_n$]$^{n-4}$ type (X = Cl, L = Cl;[12–15] X = Cl, L = $OPPh_3$;[16–17] X = Cl, L = N-methylimidazole;[18] X = Cl, L = $OPEt_3$;[19] X = Cl, L = piperidine[20] X = Cl, L = 3-quinuclidinone;[21] X = Br, L = Morpholine;[22] X = Cl, L = dimethlylformamide[8]), the geometry of the Cu atoms is trigonal bipyramidal with O and N atoms in axial positions and Cl atoms in the equatorial plane. Two of the four Cu atoms have geometries in which one of the equatorial Cu–Cl distances is considerably longer (2.515(4) and 2.456(3) Å) than the other two. In addition, the equatorial Cl–Cu–Cl angles opposite the longer Cu–Cl bonds are greater than 129°. The coordination geometry of these two Cu atoms can thus be described as being trigonal bipyramidal but distorted towards a tetragonal pyramid in which the Cl atom of the long Cu–Cl bond would occupy the apical position. The persistent feature of the C_3 symmetry deformation of the Cu(II) polyhedrons is the distinct shortening of one equatorial Cu–Cl bond from 2.352(3) to 2.398(3) Å and reduction of the opposite Cl–Cu–Cl angle from 101.3(1) to 113.1(1)°. The observed deformation indicates the correlation of the equatorial Cu–Cl bond-length and the opposite Cl–Cu–Cl angle. Figure 2 illustrates the observed dependence for four Cu(II) coordination polyhedra in the present structure. In our opinion the reason for the observed deformation of the core of the molecule is the influence of axial benzimidazole ligands on the bridge Cl atoms. Table III and Figure 3 give intramolecular Cl...H contacts. The H atoms of C(2)–H, C(22)–H and C(32)–H groups of individual imidazole rings approach the Cl(1), Cl(4) and Cl(5) atoms at distances of from 2.66 to 2.93 A, which indicate weak C–H...Cl hydrogen bonds. This type of bond is often observed between a halogen atom and the C(2)–H group of an imidazole ring.[1,23] The elongation of the bridge Cu–Cl bonds for Cl(1), Cl(4) and Cl(5) atoms is caused by the observed intramolecular C–H...Cl interactions. The lengths of the six Cu–Cl bonds vary between 2.398(3) and 2.515(4) Å with the average value 2.448 ± 0.039 Å. The lengths of the Cu–Cl bonds formed by Cl(2), Cl(3) and Cl(6) atoms, not involved in hydrogen bonds, vary between 2.352(3)–2.456(3) Å with the average 2.399 ± 0.040 Å. As in other complexes of this type, each of the copper(II) ions is displaced from the equatorial plane of three Cl atoms towards N atoms by values ranging in individual polyhedra from 0.211(2) to 0.235(2)° with the average 0.225 ± 0.009 Å. Angles at the bridging chloride atoms are all acute, with individual values from 79.3(1) to 81.2(1)° and an average of 80.3 ± 0.8°.

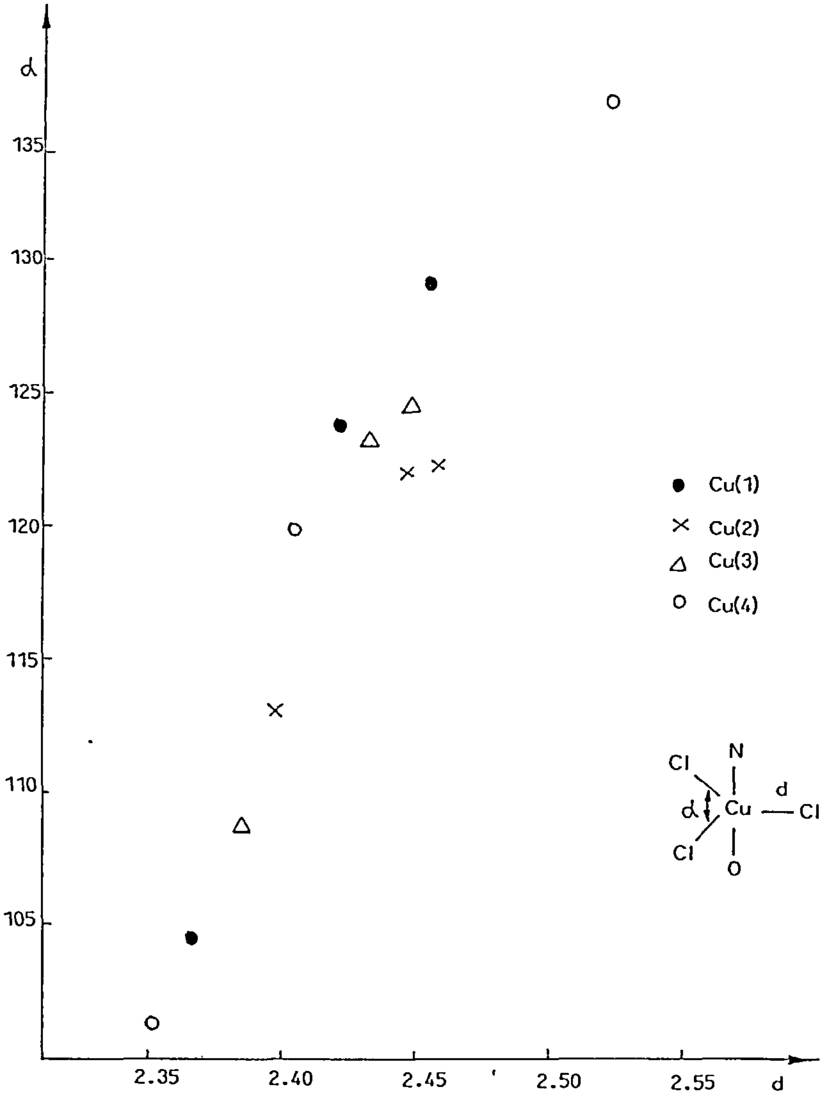

FIGURE 2 The correlation of Cu–Cl bond length and opposite Cl–Cu–Cl bond angle in the $CuCl_3ON$ polyhedra.

Three of the four benzimidazole ligands are perfectly planar; in the fourth the maximum displacements, D, of the atoms from the mean plane are less than $3\sigma(D)$. Analogous bond lengths and angles of the coordinated benzimidazole molecules show full agreement. The coordination of the imidazole ring, for the greater part than is usual, equalizes the lengths of C(2)–N(1) and C(2)–N(3) bonds but leaves the N(1)–C(2)–N(3) angles typical of the noncoordinated molecule.[24] The average value for the four C(2)–N(1) bonds is 1.331 ± 0.032 Å, of C(2)–N(3) bonds 1.328 ± 0.015 Å; the average value of N(1)–C(2)–N(3) angles is 112.2 ± 1.2°. The intramolecular hydrogen bonds are not observed.

TABLE III
Intermolecular Cl...H contact data.

Donor–H^a	Donor...Acceptor^a	H...Acceptor^a	Donor–H...Acceptor^b
C(2)–H(2)	C(2)...Cl(5)	H(2)...Cl(5)	C(2)–H(2)...Cl(5)
1.07	3.298(10)	2.75	111
C(12)–H(12)	C(12)...Cl(1)	H(12)...Cl(1)	C(12)–H(12)...Cl(1)
1.08	3.286(11)	2.67	116
C(22)–H(22)	C(22)...Cl(4)	H(22)...Cl(4)	C(22)–H(22)...Cl(4)
1.10	3.381(13)	2.93	105
C(27)–H(27)	C(27)...Cl(2)	H(27)...Cl(2)	C(27)–H(27)...Cl(2)
1.11	3.471(15)	2.78	121
C(32)–H(32)	C(32)...Cl(1)	H(32)...Cl(1)	C(32)–H(32)...Cl(1)
1.12	3.310(12)	2.65	117

^{a} Å. ^{b} Degrees.

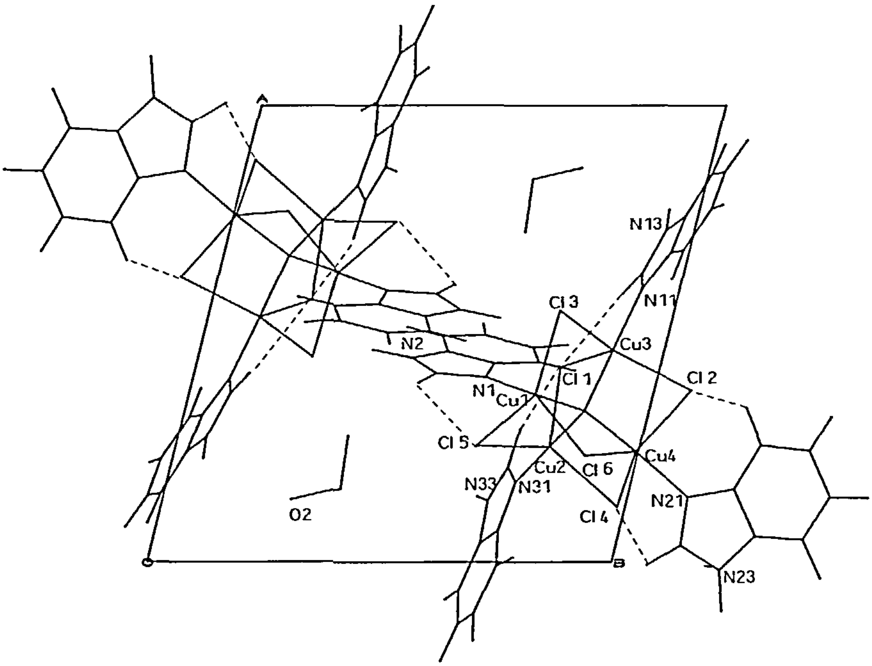

FIGURE 3 Molecular packing showing shortened intermolecular contacts.

The electronic spectrum (reflectance) of the complex in the solid phase consists of a band centred at *ca* 13 300 cm^{-1}, two shoulders at 23 800 and 27 800 cm^{-1} and a very strong band at 36 900 cm^{-1} with shoulder at *ca* 40 000 cm^{-1}. The broad band at 13 300 cm^{-1} is attributed to d–d transitions of copper(II) in the trigonal bipyramidal ligand field; the shoulders at 23 800 and 27 800 cm^{-1} are due to overlapping of bands corresponding to ligand-to-metal charge-transfer transitions and a ligand band. The band at 36 900 cm^{-1} should be assigned to transitions in the benzimidazole ligand.

The variable-temperature (4.2–295K) magnetic susceptibility measurements of the tetramer sample indicated a magnetic susceptibility increase with cooling, together with a simultaneous systematic decrease of the magnetic moment from 1.78 B.M. at 295K to 0.82 B.M. at 4.2K. The magnetic behaviour is shown in Figure 4 in the form of the variation χ_{Cu}^{-1} and μ_{eff} *versus* T. The magnetic properties of a series of tetramers of a general formula $[Cu_4OX_6L_4]$ (where X = Cl, Br; L = Cl, Br, Ph_3PO, C_5H_5N, C_5H_5NO, tetramethylurea, DMSO or 3-quinuclidinone) have been scrutinized.[25–33] The magnetic moment *vs* T pattern allowed the classification of these complexes into two groups, those which exhibit increasing μ_{eff} with decreasing temperature, and a maximum followed by rapid decrease as the temperature is further lowered, and those for which μ_{eff} continuously decreases with the lowering temperature. The continuous decrease observed with lowering temperature for $[Cu_4OCl_6(benzim)_4]$ parallels that of $[(CH_3)_4N]_4(Cu_4OCl_{10})$,[29] $[(CH_3)_4N]_4(Cu_4OCl_6Br_4)$[25] and $[Cu_4OCl_6](Ph_3PO)_4$.[26]

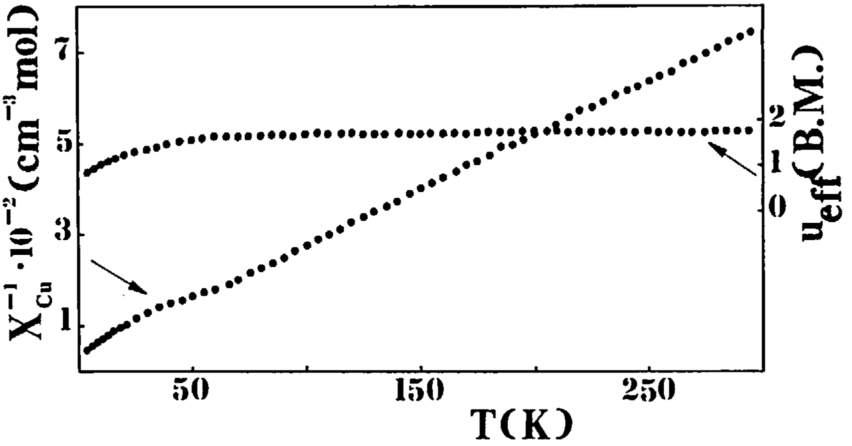

FIGURE 4 Plots of the reciprocal magnetic susceptibility (χ_{Cu}^{-1}) and magnetic moment *vs* T for $[Cu_4OCl_6(benzim)_4]$.

The μ_{eff} = f(T) form is different to a few other tetramers of formula $[Cu_4OCl_6L_4]$ (L = neutral ligand). The reason could be due to the donor–acceptor effect exercised by the axial imidazole ligand. Undoubtedly, imidazole influences the superexchange interaction in the Cu–Cl–Cu system because of the formation of intramolecular C–H … Cl hydrogen bonds between the halogen atom and the C(2)–H group of the imidazole ring.

Interpretation of the magnetic data for $[Cu_4OCl_6(benzim)_4]$ was made assuming an orbitally nondegenerate single Cu(II) ion ground state $^2A_1$, isotropic exchange interaction and neglecting the spin-orbitally induced contributions.[25,26,29]

Lines[29] consequently notes the exchange Hamiltonian of a copper-pair as $H_{ij} = -Js_i.s_j$ with spin quantum number s = 1/2 and hence the complete spin Hamiltonian for tetramer will be,

$$H = J(s_1.s_2 + s_1.s_3 + s_1.s_4 + s_2.s_4 + s_3.s_4) - g\beta(s_1 + s_2 + s_3 + s_4)H \quad (1)$$

and in the condensed form,

$$H = -1/2J(S^2 - 3) - g\beta HS^z \qquad (2)$$

where z defines the direction of applied magnetic field, H. Furthermore,

$$<S> = <S^z> = 2\,g\beta HF(T)/kT \qquad (3)$$

where

$$F(T) = \frac{5 + 3\exp(-2J/kT)}{5 + 9\exp(-2J/kT) + 2\exp(-3J/kT)} \qquad (4)$$

and the effective magnetic moment per copper(II) centre is given in (*5*).

$$\mu^2_{\text{eff}} = 3\,g^2\beta^2F(T)/2 \qquad (5)$$

The EPR spectrum of the tetramer at room temperature, 77K and at 4.2K shows no signals in the X-band. For this reason, a spectroscopic splitting factor of g = 2.13 was used as a constant in the fitting process, as calculated from the magnetic data. The best fit value for parameter J (singlet–triplet separation value) 11–14.3 cm^{-1} for

$$R = \sum_{i=1}^{66} \left\{\left(\mu_i^{\text{exptl}}\right)^2 - \left(\mu_i^{\text{calcd}}\right)^2\right]^2 = 1.86.$$

The J value indicates that $[Cu_4OCl_6(\text{benzim})_4]$ represents an effective antiferromagnetic system, when the ground state is an orbital singlet. Magnetic data are given in Tables IV and V.

TABLE IV
Selected magnetic data.[a]

T(K)	$\chi_{Cu} \times 10^6$ ($\text{cm}^3\,\text{mol}^{-1}$)	μ_{eff} (B.M.)
4.2	19900	0.82
10	13200	1.03
20	9220	1.22
30	7500	1.34
50	6030	1.55
100	3560	1.69
150	2470	1.72
200	1900	1.75
250	1560	1.77
295	1340	1.78

[a] Selected from 66 experimental points.

TABLE V

Magnetic parameters.

Temperature range (K)	Curie constant, C ($cm^3 mol^{-1} K$)	Weiss constant, θ $-\Theta$ (K)	R[a]
4.2–25	0.295	−12.2	$4.22.10^{-6}$
100–295	0.418	−18.7	$6.71.10^{-9}$

[a] $R = \sum_{i=1}^{n} \left(\chi_{Cu}^{exptl} - \chi_{Cu}^{calcd} \right)^2.$

SUPPLEMENTARY DATA

Full lists of thermal parameters, H atom positions and observed and calculated structure factors are available from J.M.

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