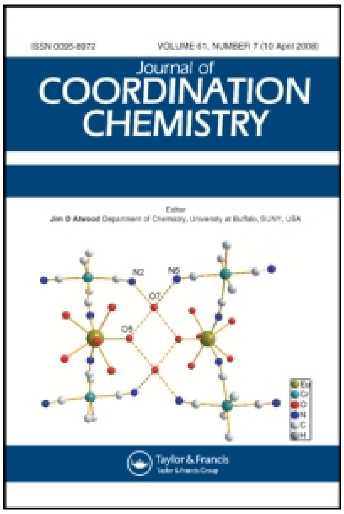

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SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF BIS[3,5-DIMETHYLPYRAZOLE (1-METHOXY,3,5-DIMETHYL PYRAZOLE) COPPER(II) PERCHLORATE]

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SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF BIS[3,5-DIMETHYLPYRAZOLE (1-METHOXY,3,5-DIMETHYL PYRAZOLE) COPPER(II) PERCHLORATE]

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The reaction of anhydrous copper nitrate with 1-hydroxy-methyl-3,5-dimethyl pyrazole in the presence of 3,5-dimethyl pyrazole in methanol gave a deep green colored solution, which upon addition of excess sodium perchlorate afforded dark green crystals of bis[3,5-dimethylpyrazole(1-methoxy,3,5-dimethyl pyrazole) Cu(II) perchlorate] (**1**) upon slow evaporation of the solvent. The structural assignment of (**1**) was made in part by elemental analysis and electronic spectroscopy and was confirmed by single crystal X-ray diffraction studies. The crystal structure reveals that compound (**1**) crystallizes in the monoclinic space group $P2_1/n$ with four molecules in the unit cell of dimensions $a = 8.927(3)$, $b = 19.019(9)$, and $c = 9.794(3)$Å, and $\beta = 112.65(3)°$. The structure has been refined to an R(F) factor of 0.029 based on 2110 observed reflections. The geometry around each Cu(II) center is best described as a square pyramid, with the basal plane occupied by two ligating nitrogen atoms with an average Cu-N distance of 1.961(3)Å and two bridging alkoxide oxygen atoms with Cu-O distances of 1.915(2) and 1.928(2)Å, respectively. The axial position is occupied by an oxygen atom from the perchlorate ion with a Cu-O distance of 2.390(2)Å. The Cu atom lies near the basal plane of a pyramid. The two Cu(II) ions are bridged by two alkoxide groups with a Cu-Cu separation of 3.022(1) Å, and a Cu-O-Cu bond angle of 103.70(1).° Ferromagnetic interaction is found to be operating in this complex, with a room temperature magnetic moment of 2.82 B.M. The electronic absorption spectrum shows a ligand field band at 695 nm ($\varepsilon = 98 M^{-1}cm^{-1}$) which is expected for Cu(II) with tetragonal geometry. There is also an additional peak at 350 nm ($\varepsilon = 2700\ M^{-1}cm^{-1}$) which is associated with the charge transfer band from the bridging alkoxide oxygen to Cu(II).

KEYWORDS: dicopper(II), pyrazole, alkoxo bridge, tetragonal pyramid

INTRODUCTION

The synthesis and characterization of dinuclear Cu(II) complexes with one or more bridging ligands continues to be an area of intense research activity.[1–3] Most of the

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studies center on the magnetic exchange interaction between coupled copper centers, and chemical modelling of the active site of hemocyanin, a binuclear Cu(II) oxygen transport protein in many species of anthropods and mollusks.[2] Interestingly, structural and magnetic relationships (especially involving *bis* (μ-hydroxo), *bis* (μ-alkoxo) and *bis* (μ-chloro) bridged compounds) have shown strong correlations.[1] Both ferromagnetic and anti-ferromagnetic exchange interactions have been observed with the magnitude dependent on the identity of the bridging ligand, the Cu-Cu separation, the bridging angles, the metal-bridge ligand bond length and metal ion stereochemistry. The use of chelating ligands incorporating pyrazole groups has drawn strong interest.[4–7] For example, in $[CuL]_2(OH)_2$ where L is the *tris*(pyrazolyl)borate(-1), a strong anti-ferromagnetic coupling was reported and its peroxo-bridged analogue showed a close spectroscopic match to the active sites in oxyhemocyanin.[4–7] We are particularly interested in 1-hydroxymethyl-3,5-dimethylpyrazole.[8] This planar heteroatomic ligand should allow more control over structural factors that determine magnetic and electronic exchange properties in dinuclear complexes. We present here the synthesis, spectroscopic and structural characterization of a di-alkoxo bridged dicopper complex.

EXPERIMENTAL

1-hydroxyl methyl-3,5-dimethyl-pyrazole

This ligand was synthesized following a reported procedure.[8]

[Cu(3,5-dimethylpyrazole)(1methoxy-3,5-dimethyl-pyrazole)(ClO$_4$)]$_2$

To a solution of 0.25 g (2.00 mmol) of *1-hydroxylmethyl-3,5-dimethyl-pyrazole* in 30 mL of methanol was added 0.38 g (2.00 mmol) anhydrous Cu(II) nitrate, followed by addition of 0.19 g (2.0 mmol) of 3,5-dimethyl-pyrazole. The resultant solution was refluxed for 3 h, and cooled to room temperature. Sodium perchlorate (0.5 g, 4 mmol) was added, and stirring continued for an additional thirty min. The solution was filtered and the filtrate was allowed to evaporate slowly to give dark green crsytals 0.5 g (0.65 mmol) 65% yield. *Anal* Calc. for $CuC_{11}H_{17}N_4ClO_5$(%): C, 34.37 H, 4.42 N, 14.58 Found: C, 34.90 H, 4.63 N, 14.81. Visible spectra 350 nm (ε = 2700 cm^{-1} M^{-1}), (LMCT) and 695 nm (ε = 98 cm^{-1}M^{-1}) d-d band. Physical Measurements: C, H, and N analyses were performed by Schwarzkopf Microanalytical Laboratory, NY, U.S.A. The UV/Visible spectrum was measured with a Perkin Elmer Lamda II spectrophotometer in the range of 240–800 nm. The solution paramagnetic susceptibility of 1 was measured by the shift in the proton resonance of *t*-butyl group of the *t*-butanol in methanol using a Varian EM360A NMR spectrometer.

X-ray Structure Determination

A dark green rod (0.10 × 0.15 × 0.50 mm) of (**1**) was placed in oil at the end of a glass fiber and transported to a Nonius CAD-4 diffractometer with graphitemonochromatized Mo Kα (0.71073 Å) radiation. The pertinent crystallographic data are summarised in Table 1. The final unit cell parameters were obtained by least square fit of 25 accurately centered reflections measured in the ranges 17.5° < 2ø < 19.9° and the intensity data were collected at 293(2) K in the range of 2° < 2ø <25°. Three standard reflections monitored every 3600 *s* did not show any significant change in intensity during the data collection. An absorption correction (SHELX-76[9a]) was applied with the minimum and maximum transmission factors of 0.731 and 0.852 respectively. The 4161 total reflections were merged to 2699 independent data (Rint = 0.018), and 2110 with $I>2\sigma(I)$ were used in the structure refinement. The structure solution and refinement were carried out by the direct method (SHELXS-86)[9b] and least-square procedure (SHELXL-93)[9c] [with only one restraint: the N-H bond was restrained to 0.9(1) Å]. The final cycles of refinement converged at $R(F) = 0.029$, $wR(F^2) = 0.061$ based on 2110 observed reflections with $[I>2.0\sigma(I)]$. Anisotropic displacement parameters were applied for all non-hydrogen atoms. For the non-H atoms, the coordinates and equivalent isotropic displacement parameters are given in Table 2. The H atoms were refined with isotropic displacement parameters.

Table 1 Crystallographic and data collection parameters.

Formula	$C_{11}H_{17}N_4Cl\ O_5Cu$
FW	384.28
Density (calculated)	1.663 Mg m^{-3}
Crystal system	Monoclinic
Space group	*P2₁/n*
a, Å	8.927(3)
b, Å	19.019(9)
c, Å	9.794(3)
β, °	112.65(3)
V, Å^3	1534.6(10)
Z	4
Scan type and range	ω-scan, 1.10 + 0.35*tan (θ)°
Aperture setting	3.00 + 0.35*tan (θ) mm
Scan speed	2 to 8 deg min^{-1}
Abs. coeff, mm^{-1}	1.625
Index ranges	$-8 \le h \le 10$, $0 \le k \le 22$, $-11 \le l \le 10$
θ range for data collection	2 to 25°
No. reflections	4318
Independent reflections	2699 [R(int) = 0.018]
Obsd. reflctns, $I>2.0\sigma(I)$	2110
Data/parameters	2699/267
Refinement Method	Full-matrix least-squares on F^2
Final R(F)[a], wR (F^2)[b] $[I>2.0\sigma(I)]$	0.029, 0.061
Final R(F)[a], wR (F^2)[b] [all data]	0.050, 0.065
wR(F^2)[b]	0.061
Goodness of Fit on F^2 (all data)	1.045
Largest diff. peak and hole	0.30 and −0.28 e.Å^{-3}
Radiation (type, wavelength)	Mokα 0.71073 Å
Crystal size	0.50 × 0.16 × 0.10 mm

[a] $R(F) = \Sigma\|F_o| - |F_c\|/\Sigma|F_o = 0.029$, $wR(F^2)^b = \{\Sigma[w(F_o^2\text{-}Fc^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2/} = 0.061$ $w = 1/[\sigma^2(F_o^2) + 0.0464{*}P^2 + 6.1065{*}P]$, where $P = [0.33333{*}MAX(0,F_o^2) + 0.66667{*}F_c^2]$

Table 2 Atomic coordinates (× 10^5 for Cu and Cl atoms, × 10^4 for all other atoms) and equivalent isotropic displacement parameters (Å^2 × 10^4 for all atoms) for (1). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	*x*	*y*	*z*	U(eq)
Cu	511(4)	4141(2)	-12977(3)	239(1)
Cl	32180(9)	-7720(4)	-4908(7)	286(2)
O(1)	1996(3)	-1303(1)	-885(2)	416(6)
O(2)	4472(3)	-973(1)	-991(3)	433(6)
O(3)	3894(3)	-682(1)	1082(2)	528(7)
O(4)	2519(2)	-115(1)	-1202(2)	291(4)
O(5)	-902(2)	-408(1)	-838(2)	288(4)
N(1)	-2319(3)	-408(1)	-3353(2)	273(5)
N(2)	-1379(3)	160(1)	-3328(2)	262(5)
N(3)	913(3)	1327(1)	-1561(2)	260(5)
N(4)	2474(3)	1427(1)	-1414(3)	286(6)
C(1)	-2104(4)	-756(2)	-1935(3)	367(8)
C(2)	-3317(4)	-572(2)	-4749(3)	298(7)
C(3)	-3002(4)	-93(2)	-5655(3)	309(7)
C(4)	-1785(3)	351(2)	-4744(3)	268(6)
C(5)	-4442(5)	-1181(2)	-5074(4)	422(8)
C(6)	-994(4)	951(2)	-5174(4)	333(7)
C(7)	2756(4)	2086(2)	-1733(3)	273(6)
C(8)	1294(4)	2432(2)	-2133(3)	293(7)
C(9)	186(4)	1948(2)	-2004(3)	276(6)
C(10)	4386(4)	2328(2)	-1616(4)	357(8)
C(11)	-1578(4)	2037(2)	-2294(5)	414(8)

RESULTS AND DISCUSSION

Spectroscopy

Spectral data for this dicopper complex are consistent with a square pyramidal geometry about each of the Cu(II) centers and may be taken as evidence that no geometrical change occurs going from the solid state to solution (*vide infra*). Electronic spectra of (**1**) show a broad peak at λ = 695 nm (ε = 98 $M^{-1}cm^{-1}$) which is in agreement with a tetragonally-based coordination geometry.[10] In addition, a very strong peak centered at λ = 350 nm (ε = 2700 $M^{-1}cm^{-1}$) is present and is assigned to the charge transfer mediated absorption from the bridging methoxide to Cu(II). Similar uv/visible peak positions have been observed in other alkoxo dicopper complexes.[11]

Description of the Structure

The dimeric $[Cu(3\text{-}5dimethylpyrazole)(\mu_2\text{-}1\text{-}OCH_2\text{-}3,5\text{-}dimethylpyrazole)(ClO_4)]_2$ unit and atomic numbering scheme is shown in Figure 1. The structure consists of a dicopper complex with two bridging methoxide groups. The five-coordinate environment about each copper atom is best described as tetragonal pyramidal. Occupying the apex of the pyramid is one of the oxygen atoms of the perchlorate, and the four basal positions are comprised of one nitrogen atom from the 3,5-dimethyl pyrazole and a nitrogen and two bridging methoxide oxygen atoms from the 1-methoxy-3,5-dimethylpyrazole ligand. The latter yields a five-membered chelate ring, with the Cu atom. The halves of the dinuclear unit are related by

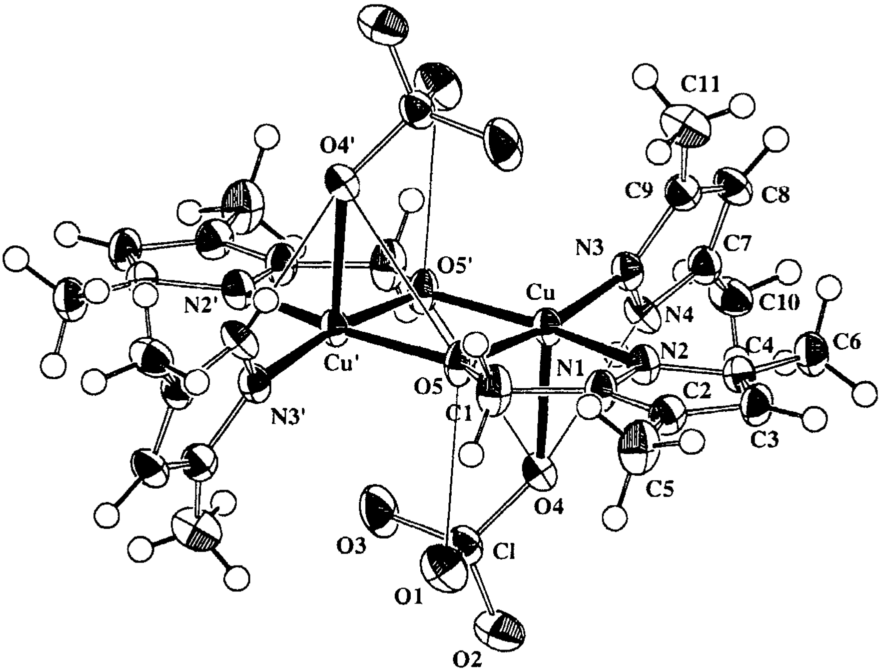

Figure 1 The molecular structure and labelling scheme of [Cu(3,5-dimethylpyrazole) (μ_2-1-OCH_2-3,5-dimethylpyrazole) $(ClO_4)]_2$ **1**, with thermal ellipsoids drawn at the 50% probability level.

crystallographic inversion symmetry, the dimeric plane composed of Cu, Cu′, O(5),O(5)′,N(2), N(3),N(2)′ and N(3)′ is also essentially planar. The geometry in this compound is not unusual as it is also observed in $[Cu(DMAEP)OH]_2[ClO_4]_2$,[12a] where DMAEP = 2-(2-dimethylaminoethyl)pyridine, $[Cu(EAEP)OH]_2[ClO_4]_2$[12b] where EAEP is 2-(2-ethylaminoethyl)pyridine and both nitrate[12c] and sulphate[12d] salts of $[Cu(bipy)OH]_2^{2+}$. The bond distances and angles presented in Table 3 are consistent with those in similar complexes.[12a–d] The Cu-Cu' separation being 3.022(1) Å and the Cu-O(5) and Cu-O(5)' bond lengths being 1.915(2), and 1.931(2) Å. The bond angles of Cu-O(5)-Cu' and O(5)-Cu-O(1)' of 103.6(1) and 76.43(9)°, respectively, are in range with those found in previously investigated di-μ-alkoxo copper(II) complexes.[12a,b,c,d,13–18] The bond length between the copper center and the perchlorate oxygen atom Cu-O(4) of 2.390(2) Å is considerably shorter than at in $[Cu(DMAEP)OH]_2$[12a] where Cu-O(2) is 2.721(4) Å. The geometry of the perchlorate group is essentially tetrahedral with Cl-O bond lengths ranging from 1.426(3) to 1.449(2) Å and the O-Cl-O bond angles of 108.3(1) to 109.8(2)°. The dihedral angle between the mean planes of the 3,5-dimethylpyrazole and the 1-methoxy-3,5 dimethylpyrazole in the coordination sphere is 70(1)°. There is extensive inter- and intra-molecular hydrogen bonding involving the pyrazole NH and the oxygen atoms of the perchlorate and the alkoxide. The shortest interatomic contact distance involves O(5) of 1-OCH_2-3,5 dimethyl pyrazole and H(4)N of the adjacent pyrazole at 2.48 Å (see Figure 2). The inter- and intra-molecular distances less than or equal to the sum of the associated van der Waals radii are

Table 3 Bond lengths [A] and angles [°] for (I).

Cu-O(5)	1.915(2)	Cu-O(5)^{a}	1.931(2)
Cu-N(2)	1.965(2)	Cu-N(3)	1.956(2)
Cu-O(4)	2.390(2)	Cu-Cu^{a}	3.022(1)
Cl-O(1)	1.426(2)	Cl-O(2)	1.436(2)
Cl-O(3)	1.432(2)	Cl-O(4)	1.449(2)
O(5)-Cu^{a}	1.931(2)		
N(1)-C(1)	1.483(4)	O(5)-C(1)	1.362(4)
N(1)-N(2)	1.363(3)	N(3)-N(4)	1.358(3)
N(1)-C(2)	1.350(3)	N(3)-C(9)	1.336(4)
N(2)-C(4)	1.341(3)	N(4)-C(7)	1.338(4)
C(2)-C(3)	1.375(4)	C(7)-C(8)	1.378(4)
C(2)-C(5)	1.484(4)	C(7)-C(10)	1.1488(4)
C(3)-C(4)	1.393(4)	C(8)-C(9)	1.393(4)
C(4)-C(6)	1.486(4)	C(9)-C(11)	1.498(5)
O(5)-Cu-O(5)^{a}	76.43(9)	O(5)^{a}-Cu-N(3)	97.91(9)
O(5)-Cu-N(2)	82.11(9)	N(3)-Cu-N(2)	102.72(10)
O(5)-Cu-N(3)	171.39(9)	O(5)^{a}-Cu-N(2)	157.80(9)
O(5)-Cu-O(4)	97.67(8)	O(5)^{a}-Cu-O(4)	88.99(8)
N(3)-Cu-O(4)	88.62(9)	N(2)-Cu-O(4)	99.55(9)
Cu-O(5)-Cu^{a}	103.6(1)		
C(1)-O(5)-Cu	119.9(2)	C(1)-O(5)-Cu^{a}	135.5(2)
O(1)-Cl-O(2)	109.6(1)	O(1)-Cl-O(3)	109.8(2)
O(1)-Cl-O(4)	109.7(1)	O(2)-Cl-O(3)	109.7(2)
O(2)-Cl-O-(4)	108.3(1)	O(3)-Cl-O(4)	109.8(1)
Cl-O(4)-Cu	127.0(1)		
C(2)-N(1)-C(1)	130.0(2)		
N(2)-N(1)-C(1)	118.7(2)		
C(2)-N(1)-N(2)	111.3(2)	C(7)-N(4)-N(3)	112.6(3)
C(4)-N(2)-N(1)	106	C(9)-N(3)-N(4)	105.1
C(4)-N(2)-Cu	142.3(2)	C(9)-N(3)-Cu	131.3(2)
N(1)-N(2)-Cu	111.6(2)	N(4)-N(3)-Cu	123.3(2)
O(5)-C(1)-N(1)	107.5(2)		
N(1)-C(2)-C(3)	106.3(3)		
N(4)-C(7)-C(8)	105.7(3)		
N(1)-C(2)-C(5)	121.7(3)	N(4)-C(7)-C(10)	122.6(3)
C(3)-C(2)-C(5)	132.0(3)	C(8)-C(7)-C(10)	131.7(3)
C(2)-C(3)-C(4)	107.0(3)	C(7)-C(8)-C(9)	106.6(3)
N(2)-C(4)-C(3)	109.4(2)	N(3)-C(9)-C(8)	109.9(3)
N(2)-C(4)-C(6)	122.1(3)	N(3)-C(9)-C(11)	120.3(3)
C(3)-C(4)-C(6)	128.5(3)	C(8)-C(9)-C(11)	129.8(3)

Symmetry transformations used to generate equivalent atoms: ^{a}-*x*,-*y*,-*z*.

O(1)–O(5) = 3.11 Å, O(4)–O(5)(–x, –y, –z) = 3.05 Å, O(4)–N(3) = 3.05 Å, O(4)–N(4) = 2.94 Å, and O(2)–N(4)(1–x, –y, –z) = 2.96 Å. The extensive inter- and intra-molecular hydrogen bonding contributes to the overall stability of this complex in the solid state. The effective magnetic moment of **1** in solution at 295K is 2.82 μ_B.[19] This observed value at 295K is comparable to the magnetic moment value of 2.64 μ_B at 200K reported for ferromagnetically coupled binuclear $[Cu_2(O)(H_2O)(O_2CMe)(bpy)_2](ClO_4)_2$[18] in which the two Cu centers are square pyramid and the Cu-Cu bond length is 3.035(2) Å and the Cu-O-Cu angle was 103.8(2)°. Although dinuclear Cu(II) complexes usually display antiferromagnetic exchange interactions, ferromagnetic systems are by no means rare.[14–18] Complex 1 is a new member of this latter group. The exchange interactions within

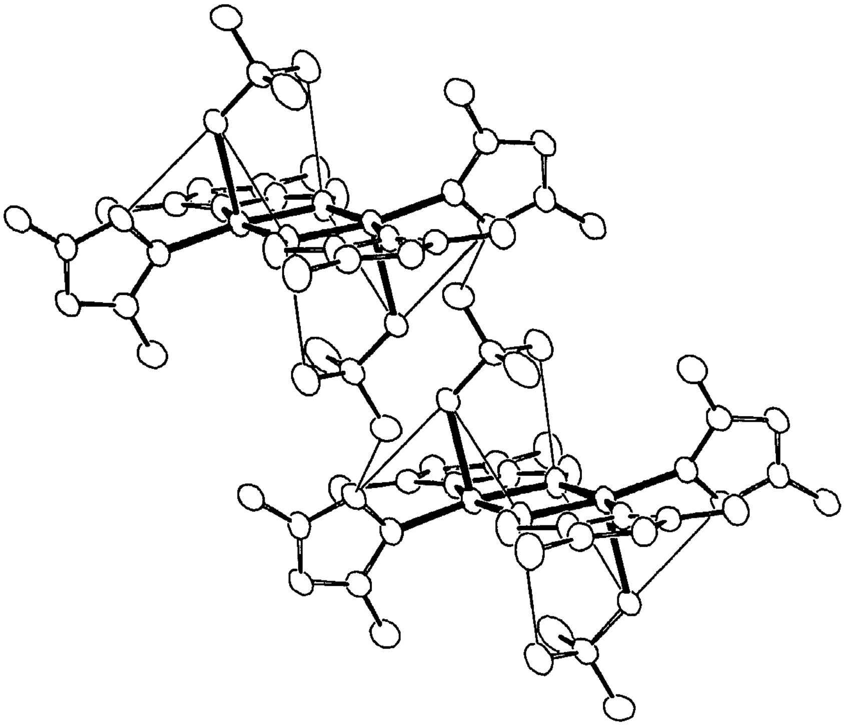

Figure 2 Hydrogen bonding (thin lines) in the crystal structure of [Cu(3,5-dimethylpyrazole)(μ_2-1-OCH$_2$-3,5-dimethylpyrazole)(ClO$_4$)]$_2$ **1**, which connects the dimer along the crystallographic *a*-axis ("needle" axis of the crystal).

bis(μ-hydroxo) Cu(II) systems have been well investigated,[18] and the magnitude and sign of the interaction have been found to be sensitive to a number of factors including the Cu-O-Cu angle. The bridging angle of 103.6(1)°, a relatively small value may be contributing to the observed magnetism.

Supplementary material

Tables of H atom coordinates (Table S-1), anisotropic displacement parameters (Table S-II), the torsion angles (Table S-III) and observed and calculated structure factor amplitudes (Table S-IV) are available from the authors on request.

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