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A new Cu/Zn carboxylato-bridged 1D polymer: Direct synthesis, X-ray structure and magnetic properties

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ABSTRACT

A new complex $[Cu_2Zn(O_2CMe)_6(NH_3)_2]_n$ was isolated as an unexpected product in an open-air synthesis of a mixed-metal compound using zero-valent copper, zinc oxide and ammonium acetate in the presence of 2-diethylaminoethanol in acetonitrile solution. Its structure consists of $Cu_2(O_2CMe)_4$ units situated on crystallographic inversion centres and $Zn(NH_3)_2(O_2CMe)_2$ units on crystallographic 2-fold axes. One O atom of each of the O_2CMe groups is attached *via* Zn bridges to the Cu atoms of the dimeric $Cu_2(O_2CMe)_4$ unit forming a 1D polymer in the *bc* direction. The polymer is not linear, with the dihedral angles between successive Cu–Cu vectors being 48.9°. Within the $Cu_2(O_2CMe)_4$ units the Cu⋯Cu distance is 2.675(2) Å and the angles between the O_2CMe planes are 88.8(5)°. The magnetic properties have been analyzed using the Hamiltonian $\hat{H} = J\hat{S}_1\hat{S}_2$ with $J = 286\ cm^{-1}$ and $g = 2.13$. High-field EPR spectra showed both the exchange-coupled copper pair and non-interacting copper(II) ions. The presence of the latter species was explained as an effect of zinc atoms occupying a fraction of the copper sites.

1. Introduction

Since the crystal structure determination of copper(II) acetate monohydrate [1], the first tetra-carboxylate-bridged copper(II) dimer, numerous adducts of dimeric copper(II) carboxylates have been prepared with a variety of ligands and their structural, magnetic and spectral properties have been reported [2]. Most copper acetate compounds exist as discrete dimers with oxygen or nitrogen donor atoms as apical ligands, while in a few structures the bifunctional oxygen donor ligands extend the dimers into polymeric chains [3–9].

Polynuclear complexes with bridging oxo and carboxylato motifs have been recognized at the active sites of many metalloenzymes [10] and model studies with simple dinuclear metal complexes are becoming increasingly important in understanding biological functions of the bimetallic cores. Polynuclear complexes, particularly mixed-metal systems have gained much interest from various scientific disciplines, including chemistry and biology [11]. Correlations between the structural and magnetic properties in such compounds are important for understanding the magnetic exchange in dinuclear compounds, as well as for the development of models to describe magnetic coupling between metal centers [11].

We have previously reported the synthesis of some trinuclear Cu_2Zn complexes with incomplete cube-like cores consisting of Cu, Zn, X (X = Cl, Br, I, SCN) and O atoms from 2-dimethylaminoethanol formed directly from zero-valent metal powders or metallic copper and zinc oxide [12]. Our systematic study has demonstrated that amino alcohols represent a powerful tool for assembling polynuclear metal complexes in "one pot" reactions using zero-valent metals as starting materials [13]. However, the interaction of metallic copper, zinc oxide and ammonium acetate in the presence of 2-diethylaminoethanol (Et_2HEa) in acetonitrile solution exposed to air, did not result in the desired Cu/Zn/Et_2HEa compound, but afforded the 1D polymer $[Cu_2Zn(O_2CMe)_6(NH_3)_2]_n$ instead.

2. Experimental

2.1. Materials and general methods

Commercially available chemicals were used as received; all experiments were carried out in air. Elemental analyses for metals were performed by atomic absorption spectroscopy. The infrared

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spectrum was recorded in a KBr disc on a UR-10 spectrophotometer in the 4000–400 cm^{-1} region using conventional techniques.

High-frequency EPR spectra at temperatures ranging from ca. 3–290 K were recorded on a home-built spectrometer at the EMR facility of NHMFL [14]. The instrument was a transmission-type device in which microwaves are propagated in cylindrical lightpipes. The microwaves were generated by a phase-locked Virginia Diodes source generating a frequency of 13 ± 1 GHz and producing its harmonics of which the 4th, 8th, 16th, 24th and 32nd were available. A superconducting magnet (Oxford Instruments) capable of reaching a field of 17 T was employed.

Magnetic susceptibility data of a powdered sample were measured with a SQUID magnetometer (Quantum Design MPMSXL-5) over the temperature range 1.8–400 K at the magnetic induction of 0.5 T. Corrections for the sample holders were applied. Diamagnetic corrections for the molecule were determined from Pascal's constants [15].

2.2. Synthesis of $[Cu_2Zn(O_2CMe)_6(NH_3)_2]_n$ (**1**)

Copper powder (0.32 g, 5 mmol), ZnO (0.20 g, 2.5 mmol), $NH_4(O_2CMe)$ (1.15 g, 15 mmol), Et_2HEa (2 ml), CH_3CN (20 cm^3) were heated to 50–60 °C and stirred until total dissolution of the Cu^0 and ZnO was observed (35 min). A small portion of an inhomogeneous (under microscopic investigation) product that precipitated immediately after cooling the resulting blue solution was filtered off and subsequently, green–blue microcrystals suitable for X-ray diffraction studies were formed in the remaining solution within one hour. They were collected by filter-suction and dried *in vacuo*.

The compound is soluble in CH_3OH, dmf and in water and is indefinitely stable in air. Recrystallisation from CH_3OH gave single crystals suitable for X-ray diffraction studies.

Yield: 1.23 g, 84.2% (per copper). *Anal.* Calc. for $C_{12}H_{24}Cu_2N_2O_{12}Zn_1$ (M_r = 580.78): C, 24.82; H, 4.17; N, 4.82; Cu, 21.88; Zn, 11.26. Found: C, 24.6; H, 4.2; N, 4.8; Cu, 21.9; Zn, 11.2%. IR (KBr pellet, cm^{-1}): 3310(s), 3230(w), 3210(w), 3170(w), 1628(w), 1575(s C=O), 1465(sh), 1430(s C=O), 1220 (m).

2.3. X-ray structure determination

The crystal data for $[Cu_2Zn(O_2CMe)_6(NH_3)_2]_n$ are summarized in Table 1. Selected bond lengths and angles are shown in Table 2. Crystallographic data for the structure were collected at 150(2) K on a Bruker SMART diffractometer fitted with graphite-monochromated Mo Kα radiation. The structure was refined against F^2 with full-matrix least-squares using the program SHELXL-97 [16]. All H-atoms were added at calculated positions and refined by use of a riding model with isotropic displacement parameters based on those of the parent atom. Anisotropic displacement parameters were employed for all the non-hydrogen atoms. The final residual was rather higher than expected. No disorder was apparent and the use of twin laws did not result in an improvement. The Zn/Cu mixing suggested by the magnetic and EPR data cannot be modeled in the X-ray structure. Although there are voids of 64 $Å^3$ in the unit cell, the use of the program SQUEEZE also failed to result in an improvement.

Table 1
Crystallographic data and relevant data referring to the structure solution and refinement.

Empirical formula	$C_{12}H_{24}Cu_2N_2O_{12}Zn_1$
Formula weight	580.78
T (K)	150(2)
λ (Å)	0.71073
Crystal system	monoclinic
Space group	*C*2/*c*
a (Å)	17.775(6)
b (Å)	16.977(6)
c (Å)	8.190(3)
β (°)	113.723(7)
V ($Å^3$)	2262.6(14)
Z	4
μ (mm^{-1})	2.970
Measured reflections	16 559
Unique reflections	4051
R_{int}	0.085
R ($I > 2\sigma(I)$)	0.111
wR (all data)	0.3859

Table 2
Selected bond distances (Å) and angles (°) for **1**.[a]

Cu–O(11)	1.976(7)	Cu–O(31)	2.047(6)
Cu–O(12)^1	2.014(7)	Zn–O(32)	2.034(6)
Cu–O(21)	1.961(7)	Zn–N(1)	2.003(7)
Cu–O(22)^1	1.965(7)	Cu···Cu	2.675(2)
O(11)–Cu–O(12)^1	166.6(3)	O(22)^1–Cu–O(11)	89.2(4)
O(11)–Cu–O(31)	100.7(3)	O(22)^1–Cu–O(12)^1	88.0(3)
O(12)^1–Cu–O(31)	92.5(3)	O(22)^1–Cu–O(31)	92.7(3)
O(21)–Cu–O(11)	91.2(4)	O(32)–Zn–O(32)^2	90.5(4)
O(21)–Cu–O(12)^1	88.5(3)	N(1)–Zn–O(32)	115.5(3)
O(21)–Cu–O(22)^1	166.2(3)	N(1)–Zn–O(32)^2	111.3(3)
O(21)–Cu–O(31)	100.8(3)	N(1)–Zn–N(1)^2	111.5(4)

[a] Symmetry operations: $^1-x+1/2, -y+1/2, -z+2$, $^2-x, y, -z+3/2$.

3. Results and discussion

3.1. Synthesis

The reaction of copper powder with zinc oxide, ammonium acetate and Et_2HEa in a CH_3CN solution exposed to air, using a molar ratio of Cu:ZnO:$NH_4(O_2CMe)$ = 2:1:6 gave blue-green microcrystals that showed analytical data accounting for the presence of Cu(II) and Zn(II) in a 2:1 stoichiometry. IR absorption frequency of carboxylate appear at 1575 cm^{-1} for $\nu_{as}(CO_2)$ and 1430 cm^{-1} for $\nu_s(CO_2)$. The difference $\Delta = \nu_{as}(CO_2) - \nu_s(CO_2)$ suggests a chelating-bridging coordination of the acetate ligands [17]. In the region 3310–3170 cm^{-1} several distinctive bands due to N–H stretching were observed. A distinctive band at 1250 cm^{-1} is assigned to N–H stretching of the NH_3 molecules.

3.2. Structural analysis

The structure consists of $Cu_2(O_2CMe)_4$ units situated on crystallographic inversion centres and $Zn(NH_3)_2(O_2CMe)_2$ units on crystallographic 2-fold axes. One O atom of each O_2CMe group on the latter unit bridges to the Cu atoms of the dimeric $Cu_2(O_2CMe)_4$ entity forming a 1D polymer in the *bc* direction. The polymer is not linear with the dihedral angles between successive Cu···Cu vectors being 48.9°. A view of a portion of the polymeric chain is shown in Fig. 1. The geometry around the copper atom is square-pyramidal, with four oxygen atoms from the bridging syn–syn acetate groups at distances of 1.961(7)–2.014(7) Å and the fifth oxygen atom, O(31), in the syn-anti bridging acetate group at 2.047(6) Å (Table 2). The Cu···Cu distance within the $Cu_2(O_2CMe)_4$ units is 2.675(2) Å with the angles between the O_2CMe planes being 88.8(5)°. The Cu···Cu length is in the range of those found for other known tetra-μ-carboxylatodicopper(II) complexes according to a search of structures from the CSD (version 5.31, November 2009).

The coordination sphere of Zn consists of a pair of nitrogen atoms from the two ammonia molecules at a distance of 2.003(7) Å and a pair of oxygen atoms from the acetate groups at

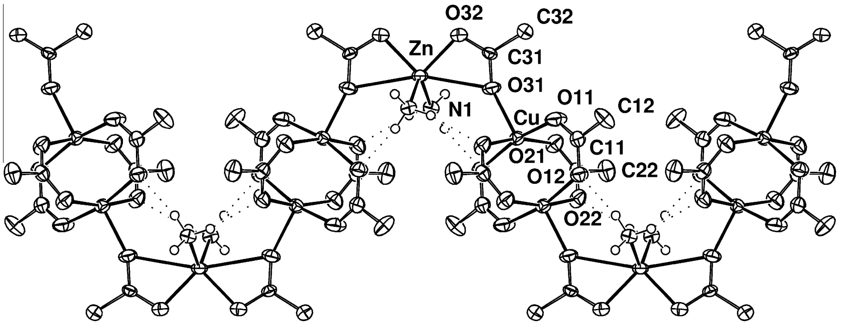

Fig. 1. View of the 1D chain structure of **1**. Ellipsoids have been drawn at the 50% probability level with CH_3 hydrogen atoms omitted for clarity.

Table 3
Hydrogen-bonding geometry (Å, °) for **1**.[a]

D–H···A	D–H	H···A	D···A	D–H···A
N(1)–H(1A)···O(32)[1]	0.91	2.20	3.098(10)	169.9
N(1)–H(1B)···O(22)[2]	0.91	2.14	3.015(10)	160.7
N(1)–H(1C)···O(12)[3]	0.91	2.20	3.084(10)	164.8

[a] Symmetry operations: [1]$x,-y+1,z-1/2$, [2]$x-1/2,-y+1/2,z-1/2$, [3]$-x+1/2,-y+1/2,-z+2$.

a longer distance of 2.034(6) Å. The O/N–Zn–O/N angles lie in the range 90.5(4)–115.5(3)°, showing the strong distortion of the ZnN_2O_2 tetrahedron (Table 2).

The acetate groups coordinate to the metals as symmetric bidentate ligands bridging two copper centres [O(22),O(12)], or as ligands bound to the zinc atom [O(32)] with additional slightly weaker bridging to the Cu atom [O(31)]. The polymer is further stabilized by hydrogen bonds between two of the NH_3 hydrogen atoms and the acetate O atoms as shown by the N(1)···O(22) $\{x-1/2,-y+1/2,z-1/2\}$, N(1)···O(12) $\{-x+1/2,-y+1/2,-z+2\}$distances and N–H···O angles (Table 3, Fig. 1). Additional association in the lattice occurs through the hydrogen bonding of the N–H···O type involving NH_3 molecules and the acetate oxygen O(32) linking the various polymeric strands (Table 3).

3.3. EPR studies

Spin Hamiltonian in the usual form was used to interpret the triplet-state EPR spectra (Fig. 2):

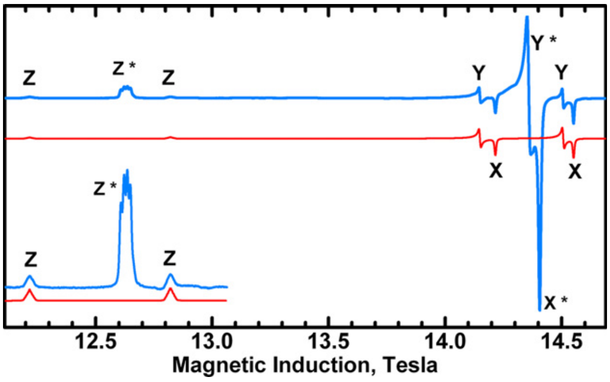

Fig. 2. Blue traces: EPR spectra recorded at 416 GHz and at 80 K. Red traces: triplet-state spectrum simulated with $g_x = 2.065$, $g_y = 2.073$, $g_z = 2.372$, $D = -0.334\ cm^{-1}$, $E = -0.0035\ cm^{-1}$, $A_z(Cu) = 0.0074\ cm^{-1}$. The molecular orientations for the dimer signals are marked with X, Y and Z. Resonances due to the uncoupled copper(II) ions are marked with X*, Y* and Z*. (For interpretation of the references in color in this figure legend, the reader is referred to the web version of this article.)

$$\boldsymbol{H} = \mu_B B \cdot \boldsymbol{g} \cdot \boldsymbol{S} + D\{\boldsymbol{S}_z^2 - S(S+1)/3\} + E(\boldsymbol{S}_x^2 - \boldsymbol{S}_y^2) \qquad (1)$$

A pattern characteristic for dimeric carboxylato-bridged copper 'paddlewheel' complexes was observed with $g_x = 2.065$, $g_y = 2.073$, $g_z = 2.372$, $D = -0.334\ cm^{-1}$, $E = -0.0035\ cm^{-1}$, $A_z(Cu) = 0.0074\ cm^{-1}$ at 80 K. A strong spectrum of uncoupled Cu(II) species was also present with $g_x = 2.062$, $g_y = 2.069$, $g_z = 2.352$ and $A_z(Cu) = 0.0148\ cm^{-1}$. The parameters are only slightly different at 280 K: dimer: $g_x = 2.070$, $g_y = 2.077$, $g_z = 2.378$, $D = -0.338\ cm^{-1}$, $E = -0.0037\ cm^{-1}$; monomer: $g_x = 2.067$, $g_y = 2.072$, $g_z = 2.359$.

The similarity of the *g* parameters of the 'monomeric' impurity to those of the 'paddlewheel' unit suggests that some fraction of the 'paddlewheel' units contain one Cu and one Zn atom instead of two copper atoms. Such mixed pair formation has been observed before in our direct syntheses [18]. Doping symmetric binuclear complexes, such as copper propionate with Zn^{2+} in order to obtain a heterobinuclear system with uncoupled copper ions is also a known procedure [19].

The EPR parameters of the dimeric unit are very similar to those of copper acetate monohydrate ($g_x = 2.0545$, $g_y = 2.0792$, $g_z = 2.3637$, $D = -0.335\ cm^{-1}$, $E = -0.0103\ cm^{-1}$). Although positive *D* in such systems has been reported in the literature, [3] the negative sign of *D* in copper acetate monohydrate and copper acetate pyrazinate was proven by single-crystal high-field EPR [20] and more recently also in binuclear copper perfluorocarboxylates [21] and there is no reason to expect it to be positive in any dimeric copper carboxylates.

We assume therefore that the zero-field splitting parameter D is negative also in the present complex. The magnetic dipole–dipole contribution to *D* can be calculated from

$$D_{\rm dip} = -(2g_z^2 + (g_x^2 + g_y^2)/2)\mu_B^2/2r^3_{\text{Cu-Cu}} \qquad (2)$$

resulting in $D_{dip} = -0.176\ cm^{-1}$. Accordingly, the anisotropic exchange-related contribution equals $D_{ex} = -0.159\ cm^{-1}$. The theory of this contribution has been discussed in many papers [22].

3.4. Magnetic susceptibility

Since in EPR signals of uncoupled Cu(II) were observed, it should be possible to calculate the magnetic susceptibility as a sum of an antiferromagnetic component contaminated by a substantial amount of a paramagnetic component. Assuming as above that some fraction "*f*" of the paddlewheel units contains ZnCu pairs instead of CuCu pairs, the total susceptibility of the sample can be expressed as

$$\chi_{\rm total} = f\chi_{\rm CuZn} + (1-f)\chi_{\rm CuCu} \qquad (3)$$

The susceptibility of the CuZn pairs is may be calculated from the Curie law

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$$\chi_{\mathrm{CuZn}} = Ng^2\mu_B^2/3kT(1/2)(3/2) + \mathrm{TIP} \tag{4}$$

although at the lowest temperatures it is better to use

$$\chi_{\mathrm{CuZn}} = (Ng\mu_B/2B)(x - 1/x)/(x + 1/x) + \mathrm{TIP} \tag{4a}$$

where $x = exp(g\mu_B B/2kT)$ and B is the magnetic induction of the magnetometer (5000 G).

The Curie's lawbreaks down at the lowest temperatures since the Zeeman splitting (~0.47 cm^{-1} at 5000 G) is comparable to kT (1.4 cm^{-1} at 2 K).

The susceptibility due to the CuCu pairs can be calculated from the Bleaney–Bowers expression

$$\chi_{\mathrm{CuCu}} = (Ng^2\mu_B^2/3kT)\cdot 6exp(-J/kT)/(1+3exp(-J/kT)) + 2\mathrm{TIP} \tag{5}$$

The formula above refers to two copper ions. The susceptibility calculated using Eq. (5) with $J = 300\ \mathrm{cm}^{-1}$, $g = 2.16$ and TIP = 60×10^{-6} cgs units, as in copper acetate monohydrate, is presented as blue dots in Fig. 3. Since g for the monomeric copper is known from EPR, it should be possible to subtract the monomer contribution and recover the pure dimer susceptibility by using

$$\chi_{\mathrm{dimer}} = (\chi_{total} - f\chi_{\mathrm{CuZn}})/(1-f) \tag{6}$$

Thus, by choosing a proper f value in Eq. (6) it should be possible to obtain from the experimental susceptibility (black dots) a curve similar to that represented by blue dots, this reaching a constant value of 2TIP (120×10^{-6} cgs units) below ca. 40 K. However, this does not appear to be the case. When $f = 0.22$ is taken, the curve shown by the red dots is obtained, which is similar to the copper acetate monohydrate susceptibility, but is raised by an approximately constant amount. Different susceptibility curves were measured for various sample preparations, showing different fractions of monomeric Cu(II), but always exhibiting a problem like that shown in Fig. 3, albeit of varying strength. No such difficulties have ever been observed in this laboratory for other complexes and it must be concluded that the effect is real and the magnetic susceptibility indeed cannot be expressed as a sum due to the Cu–Cu and Cu–Zn pairs. Moreover, with the f value as high as 0.2, excess of zinc should be found in elemental analysis. Since it is not observed, one has to assume that some copper substitutes zinc at the $Zn(NH_3)_2(O_2CMe)_2$ sites leading to the formation of pentanuclear fragments (CuCu)Cu(CuCu) instead of (CuCu)Zn(CuCu). No uncoupled copper was observed by EPR on that site, where much lower g components would be expected than those found above for both the CuZn and CuCu paddlewheel units. Thus, if copper substitutes zinc at the $Zn(NH_3)_2(O_2CMe)_2$ sites but is not seen in EPR as monomeric Cu^{2+}, then it must interact with two neighboring copper paddlewheel units. The magnetic properties of such species are impossible to predict, and in addition it seems to be EPR-silent. In principle, various configurations of the disordered fragment dimer-monomer–dimer can be considered. If the probability of zinc entering the paddlewheel unit is 0.2, as follows from the magnetic data, and the probability of copper being present at the zinc site is also 0.2, then the probability of the 'normal' configuration (CuCu)Zn(CuCu) is 0.512 while the probabilities of (CuZn)Zn(CuCu), (CuCu)Cu(CuCu) and (CuZn)Cu(ZnCu) are 0.128, 0.128 and 0.002, respectively. Only the last configuration ensures that the Cu at Zn site would not interact with the Cu atoms bound in paddlewheel units, which may explain why no spectrum of 'free' copper at the Zn site was observed. We have attempted to estimate the relative amounts of the dimeric and monomeric species seen in EPR. The spectrum of the dimer overlaps completely the spectrum of monomer and it appears that the only way of estimating the intensities is simulation of each of them followed by double integration of the simulated spectra. Such procedure was performed for spectra recorded at 292 and at 80 K as described in the Supplementary material and allowed estimation of the exchange integral $J = 295\ \mathrm{cm}^{-1}$ and of the ratio of the monomeric to dimeric species seen in EPR. That ratio was found to be 0.1, while 0.2 was derived from the magnetic susceptibilities. Our interpretation is that indeed species exist in the system which contribute to the magnetic susceptibility but are not seen in EPR. It is thus clear that copper and zinc can replace each other at their expected sites and the direct synthesis appears to be less selective here than it was observed is our previous studies.

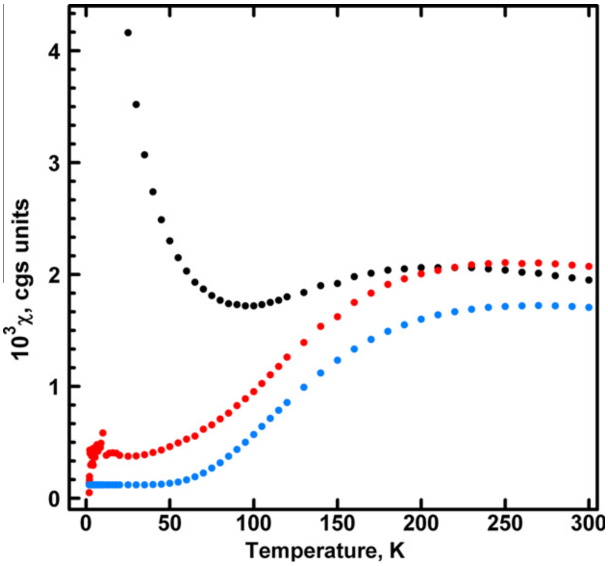

Fig. 3. Magnetic susceptibility of **1**. Black circles: raw experimental data. Red circles: experimental data converted by using formula (6) with $f = 0.22$. Blue circles: calculated from Eq. (5) with $J = 286\ \mathrm{cm}^{-1}$, $g = 2.133$, TIP = 120 cgs emu. (For interpretation of the references in color in this figure legend, the reader is referred to the web version of this article.)

4. Conclusions

A standard 'direct synthesis' procedure did not result in an expected polynuclear heterometallic compound but afforded a 1D polymer consisting of alternating 'paddlewheel' copper acetate dimers and $Zn(NH_3)_2(O_2CMe)_2$ units. A high fraction of uncoupled copper(II) ions observed both in the EPR spectra and in magnetic susceptibility was explained by postulating that zinc(II) can substitute one of the copper(II) ions in the dimeric units, thereby freeing another Cu(II) ion from the exchange interactions.

Acknowledgments

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Appendix A. Supplementary material

CCDC 764842 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.03.040.

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