Symmetric and asymmetric trinuclear cores in novel μ-alkoxo-bridged mixed-metal $Cu^{II}{}_2Zn^{II}$ complexes: synthesis from zerovalent copper and zinc oxide, structure and magnetism

Elena A. Vinogradova,[a] Olga Yu. Vassilyeva,*[a] Volodymyr N. Kokozay,[a] Philip J. Squattrito,[b] Jan Reedijk,[c] Gerard A. Van Albada,[c] Wolfgang Linert,[d] Satish K. Tiwary[e] and Paul R. Raithby[f]

[a] *Department of Inorganic Chemistry, National Taras Shevchenko University, Volodimirska st. 64, Kyiv 01033, Ukraine. E-mail: vassilyeva@chem.univ.kiev.ua; Fax: +380 44 296 2467*
[b] *Department of Chemistry, Central Michigan University, Mt. Pleasant, MI 48859, USA*
[c] *Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, PO Box 9502, 2300 RA Leiden, The Netherlands*
[d] *Institute of Inorganic Chemistry, Vienna University of Technology, Getreidemarkt 9/153, A-1060 Vienna, Austria*
[e] *Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh, UK EH9 3JJ*
[f] *Department of Chemistry, University of Bath, Claverton Down, Bath, UK BA2 7AY*

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Three novel heterotrinuclear complexes, $[Cu_2Zn(NH_3)Cl_3(Me_2Ea)_3]$ **1**, $[Cu_2Zn(NH_3)Br_3(Me_2Ea)_3]$ **2** and $[Cu_2Zn(NCS)_3(Me_2Ea)_3]\cdot CH_3CN$ **3** (Ea = NCH_2CH_2O), have been prepared using zerovalent copper, zinc oxide, an ammonium salt and 2-dimethylaminoethanol (HMe_2Ea) in air. Crystallographic investigations reveal that they contain trinuclear symmetric (**3**) and asymmetric (**1** and **2**) cores, that consist of a portion of a distorted cube in which alternate corners are metal and non-metal atoms and one corner metal site is vacant. The chemical difference between the three compounds produces changes in the coordination environment of the metal atoms and their overall crystal structures. Cryomagnetic measurements reveal that the overall antiferromagnetic coupling in the symmetric complex **3** is stronger compared to the other two complexes, despite their slightly shorter copper–copper separations.

Polynuclear complexes, particularly mixed-metal systems, have received considerable attention from a wide variety of scientific disciplines, including chemistry, biology and physics. This is because of the unusual electronic[1] and magnetic[2] properties that are known to be associated with polynuclear (as opposed to mononuclear) complexes, as well as their occurrence in metalloprotein active sites where the catalytic function depends on cooperation between two or more metal centres.[3] Copper ions, which are the active sites in various metalloproteins, play an essential role in biological processes such as electron transfer, oxidation and dioxygen transport. Numerous dinuclear sites have been found to be asymmetric in character, and a comparison of the physico-chemical properties of the asymmetric complexes with those of their symmetric equivalents may elucidate features found in polynuclear biologically active molecules.[4]

We have previously shown that various metal complexes can be obtained easily through 'one-pot' reaction of a metal powder or metal oxide with a complex-forming agent in a non-aqueous solution.[5] Use of this approach for the synthesis of mixed-metal compounds has resulted in a number of novel Cu/Pb aminoalkoxo complexes being obtained from zerovalent copper and lead salts.[6] Exploring other synthetic possibilities in the preparation of mixed-metal compounds, we used metallic copper, zinc oxide and an ammonium salt as starting materials. We were interested to see what sort of structures are formed under the interaction of metallic copper with d-block metal ions, zinc in particular, in order to develop complexes capable of serving as models for metalloenzymes with oxidase or oxygenase activity. We now report the synthesis, structure and characterization of trinuclear complexes with symmetric and asymmetric Cu_2Zn cores that have rather short Cu···Cu contacts (less than 3.5 Å), distorted square-pyramidal coordination geometries at the copper atoms and contain Cu_2OX (X = Cl, Br, S_{NCS}) fragments. The zinc atom in these systems apparently plays an important role by helping to maintain the structural integrity of the compounds. The two copper ions in the core are antiferromagnetically coupled and therefore EPR silent. The compounds may be expected to model functions of such metalloenzymes as catechol oxidase or superoxide-dismutase as oxidation catalysts.

Experimental

Syntheses

All chemicals were of reagent grade and used as received, all experiments were carried out in air. Elemental analyses for metals were performed by atomic absorption spectroscopy by the Department of Chemistry, National Taras Shevchenko University of Kyiv and for C, H and N by the Department of Chemistry, Cambridge University microanalytical service.

$[Cu_2Zn(NH_3)Cl_3(Me_2Ea)_3]$ (Ea = NCH_2CH_2O) 1. Copper powder (0.64g, 10 mmol), ZnO (0.40g, 5 mmol), NH_4Cl (1.63g, 30 mmol) CH_3OH (20 cm^3) and 2-dimethylaminoethanol (HMe_2Ea) (4 cm^3) were heated to

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60 °C and magnetically stirred until total dissolution of Cu^0 and ZnO was observed (2.5 h). The resulting blue solution was filtered and allowed to stand at room temperature. Dark blue microcrystals of **1** were formed after one day. They were collected by suction filtration and dried *in vacuo*. Mass collected 0.57 g, yield 40%. Anal.(%) found: C, 24.8; H, 5.7; N, 9.6; Cu, 21.9, Zn, 11.4; Cl, 18.4; calc. for $C_{12}H_{33}Cu_2ZnN_4O_3Cl_3$: C, 24.84; H, 5.73; N, 9.66; Cu, 21.90; Zn, 11.27; Cl, 18.33. IR (KBr, cm^{-1}): 3600–3400br, 3300m (NH), 3235w (NH), 3165w (NH), 2990w, 2960w, 2940w, 2910–2850br, 1630w, 1465m, 1275w, 1250m, 1180w, 1090s, 1070sh, 1020m, 950m, 910w, 890w, 790m, 720br, 635m, 530w, 490w, 470w.

$[Cu_2Zn(NH_3)Br_3(Me_2Ea)_3]$ 2. This complex was obtained in a similar manner to **1** except for the use of NH_4Br instead of NH_4Cl. Mass collected 1.20 g, yield 67%. Anal.(%) found: C, 20.2; H, 4.6; N, 7.8; Cu, 18.2; Zn, 9.2; Br, 33.2; calc. for $C_{12}H_{33}Cu_2ZnN_4O_3Br_3$: C, 20.20; H, 4.66; N, 7.85; Cu, 17.81; Zn, 9.16; Br, 33.59. IR (KBr, cm^{-1}): 3600–3400br, 3290s (NH), 3240w (NH), 3220m (NH), 3160m (NH), 3010sh, 2990w, 2960w, 2940m, 2910m, 2880m, 2850m, 2830sh, 1620w, 1465m, 1270w 1250m, 1180w, 1090s, 1070s, 1015m, 950m, 910m, 890w, 790m, 720w, 710m, 640m, 605m, 530m, 490m, 470m.

$[Cu_2Zn(NCS)_3(Me_2Ea)_3] \cdot CH_3CN$ 3. This complex was obtained in a similar manner to **1** except for the use of NH_4NCS instead of NH_4Cl in CH_3CN (20 cm^3). Mass collected 1.13g, yield 67%. Anal.(%) found: C, 30.4; H, 4.9; N, 14.5; Cu, 19.1; Zn, 9.7; NCS, 26.4; calc. for $C_{17}H_{33}Cu_2ZnS_3N_7O_3$: C, 30.38; H, 4.95; N, 14.59; Cu, 18.91; Zn, 9.73; NCS, 26.02. IR (KBr, cm^{-1}): 3600–3400br, 3000w, 2970w, 2920sh, 2900m, 2870sh, 2850m, 2810w, 2100sh (CN), 2070s (CN), 1465m, 1280w, 1250w, 1180w, 1080sh, 1070m, 1020m, 950m, 910w, 890w, 830w (CS), 810w (CS), 650m, 600m, 530w, 470w, 435w.

Recrystallisation from CH_3CN gave single crystals suitable for X-ray diffraction studies. The compounds are soluble in CH_3CN and dmf and sparingly soluble in water. All the complexes are indefinitely stable in air.

Physical measurements

Infrared spectra were recorded as KBr disks and in CH_3CN solutions on a UR-10 spectrophotometer in the 4000–400 cm^{-1} region using conventional techniques. UV/VIS spectra were recorded on Perkin Elmer 330 (diffuse-reflectance technique) and Perkin Elmer Lambda 12 (CH_3CN solutions) spectrometers. X-band CH_3CN solution EPR spectra were measured at 293 and 77 K using a Bruker ER 200 D spectrometer, solid EPR spectra were measured at 293 K using a JEOL RE2x spectrometer. Magnetic susceptibility was measured in the temperature range 5–280 K with a fully automated Manics DSM-8 susceptometer equipped with a TBT continuous-flow cryostat and a Drusch EAF 16 NC electromagnet, operating at *ca.* 1.4 T. Data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from the Pascal constants.

Crystallography

Details of the data collection and processing, structure analysis and refinement are summarized in Table 1. Diffraction experiments were performed on Rigaku AFC6S (**1**), Enraf Nonius CAD-4 (**2**) and Rigaku AFC7R (using an Oxford Cryostream low temperature attachment) (**3**) diffractometers all equipped with graphite monochromated Mo-Kα radiation ($\lambda = 0.710\,73$ Å). Data sets were corrected for Lorentz and polarization effects and for the effects of absorption. The structures were solved by direct methods using the teXsan[7a] (**1**), SHELXS 86[7b] (**2**) and SIR 92[7c] (**3**) computer programs, and refined by full-matrix least-squares methods on F^2 using teXsan[7a] (**1**), SHELXL 93[7d] (**2**) and SHELXL 97[7e] (**3**). In general, all non-hydrogen atoms refined anisotropically, hydrogen atoms were fixed in idealised positions and allowed to ride on the atom to which they were attached. Atom C(2) in **3** is disordered over two sites, C(2) and C(2′), related by the crystallographic mirror plane, with an occupancy of 0.5.

CCDC reference numbers 159629–159631. See http://www.rsc.org/suppdata/nj/b1/b101883n/ for crystallographic data in CIF or other electronic format.

Results and discussion

Syntheses and spectroscopic characterization

The reaction of copper powder with ZnO, 2-dimethylaminoethanol and an ammonium salt in a non-aqueous solvent, in air, using a molar ratio of Cu : ZnO : HMe_2Ea : NH_4X = 2 : 1 : 3 : 3 (X = Cl, Br, SCN) gave blue microcrystals of the trinuclear complexes **1**, **2** and **3**, respectively, according to eqn. (1) for **1** and **2**, and eqn. (2) for **3**. In each reaction, dioxygen is being reduced.

$$2\,Cu(0) + ZnO + 3\,NH_4X + 3\,HMe_2Ea + O_2 \xrightarrow{CH_3OH} [Cu_2Zn(NH_3)X_3(Me_2Ea)_3] + 2\,NH_3 + 3\,H_2O\ (X = Cl, Br) \quad (1)$$

$$2\,Cu(0) + ZnO + 3\,NH_4SCN + 3\,HMe_2Ea + O_2 \xrightarrow{CH_3CN} [Cu_2Zn(NH_3)(SCN)_3(Me_2Ea)_3] + 3\,NH_3 + 3\,H_2O \quad (2)$$

The structural features of the three complexes were determined by IR spectroscopy and from single-crystal X-ray diffraction studies. The IR spectra of complexes **1**, **2** and **3** in the

Table 1 Crystal data and structure refinement for **1**–**3**

	1	2	3
Formula	$C_{12}H_{33}Cl_3Cu_2N_4O_3Zn$	$C_{12}H_{33}Br_3Cu_2N_4O_3Zn$	$C_{17}H_{33}Cu_2N_7O_2S_3Zn$
Formula weight	580.25	718.60	672.13
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$P2_1/c$	$Cmc2(1)$
a/Å	15.004(4)	15.214(3)	14.288(3)
b/Å	10.412(4)	10.478(2)	19.827(4)
c/Å	16.228(2)	16.526(3)	10079(2)
β/°	112.69(1)	113.69(3)	90.00
V/Å^3	2338(1)	2412.4(8)	2855.2(10)
Z	4	4	4
T/K	296	293	180
μ/mm^{-1}	3.22	7.719	2.559
Meas./Indep. reflect.	4122/4560	3773/3928	2703
Data used [$I > 2\sigma(I)$]	2378	3762	1798
R	0.032	0.0679	0.0635
Rw	0.031	0.1665	0.1096

range 4000–400 cm^{-1} are quite similar and show all the characteristic ligand peaks. In the region 3300–3165 cm^{-1}, several distinctive bands due to N–H stretching are observed in the spectra of **1** and **2**. The bands do not shift when the compounds are dissolved in CH_3CN. Taking into account the formation conditions of **1** and **2** and the results of elemental analyses, the complexes were formulated as [$Cu_2Zn(NH_3)X_3(Me_2Ea)_3$], where X = Cl and Br, respectively. In CH_3CN solution and as a KBr disk, the very strong *ν*(CN) vibration (poorly resolved in the solid state, but clearly split in solution at 2100 and 2070 cm^{-1} with an approximate intensity ratio of 1 : 2) and the weak *ν*(CS) absorptions (830, 810 cm^{-1}) of the thiocyanate group can be identified easily for **3**.[8] The *δ*(NCS) mode is obscured by other vibrations. The frequencies of the observed bands imply coordination of the NCS^- group through nitrogen,[8] in accord with the crystal structure of **3** (*vide infra*). The splitting of the *ν*(CN) mode is attributed to bonding of the thiocyanate group to different metals and the resulting lower symmetry.

The diffuse reflectance spectra of all the complexes have a similar pattern and exhibit three maxima at *ca.* 318, 350–360 and 650–690 nm. The latter corresponds to a d–d transition in a square-pyramidal environment around Cu(II), which is in agreement with the crystal structures of **1**–**3**. The two bands at high energy are clearly assigned to ligand-to-metal charge transfer bands. The charge transfer region of the solution (CH_3CN, dmf) spectra (300–400 nm) is characterized by the occurrence of intense bands with clear shoulders at about 370 and 390 nm for **1** and **2**, respectively. A broad visible band of low intensity around 630–660 (CH_3CN) and 680–700 nm (dmf) is associated with Cu(II) d–d transitions.

Crystal structures of complexes 1–3

The overall structural configurations of **1** and **2** are similar. The important differences show up as relatively small changes in bond lengths and angles (Table 2). The molecular diagram and numbering scheme of **1** is shown in Fig. 1, which illustrates the general geometry of the two compounds.

The trinuclear skeletons of **1** and **2**, which have no crystallographically imposed symmetry, consist of a portion of a distorted cube in which alternate corners are non-metal (three

Table 2 Selected bond distances (Å) and angles (°) for **1**–**3**[a]

	1, X = Cl	**2**, X = Br	**3**
Cu(1)–O(1)	1.975(4)	1.982(7)	1.971(5)
Cu(1)–O(2)	1.923(4)	1.902(7)	1.910(6)
Cu(1)–N(2)	2.052(5)	2.053(9)	2.023(9)
Cu(1)–N(4)	1.995(4)	1.981(8)	1.904(8), Cu(1)–N(10)
Cu(1)–X(1)	2.636(2)	2.758(2)	2.781(3), Cu(1)–S(2^{i})
Cu(3)–X(3)	2.274(2)	2.412(2)	
Cu(3)–O(1)	1.965(4)	1.956(7)	
Cu(3)–O(3)	1.950(4)	1.930(7)	
Cu(3)–N(3)	2.044(5)	2.042(9)	
Cu(3)–X(1)	2.688(2)	2.801(2)	
Zn(2)–X(2)	2.283(2)	2.417(2)	2.00(1), Zn(2)–N(20)
Zn(2)–O(2)	1.952(4)	1.939(8)	1.921(7)
Zn(2)–O(3)	1.948(4)	1.943(7)	
Zn(2)–N(1)	2.116(5)	2.090(10)	2.09(1)
Zn(2)–O(1)	2.459(4)	2.434(7)	2.387(9)
O(2)–Cu(1)–O(1)	84.1(2)	83.6(3)	84.3(3)
O(1)–Cu(1)–N(2)	164.0(2)	163.9(3)	169.1(4)
O(1)–Cu(1)–N(4)	91.4(2)	91.2(3)	94.7(4), N(10)–Cu(1)–O(1)
O(2)–Cu(1)–N(2)	84.1(2)	84.0(3)	85.3(3)
O(2)–Cu(1)–N(4)	171.2(2)	169.9(4)	165.0(4), N(10)–Cu(1)–(2)
N(4)–Cu(1)–N(2)	98.8(2)	99.4(4)	94.6(4), N(10)–Cu(1)–N(2)
O(2)–Cu(1)–X(1)	98.1(1)	98.6(3)	100.3(2), O(2)–Cu(1)–S(2^{i})
O(1)–Cu(1)–X(1)	86.1(1)	86.4(2)	
N(4)–Cu(1)–X(1)	89.2(1)	89.6(3)	94.3(3), N(10)–Cu(1)–S(2^{i})
N(2)–Cu(1)–X(1)	106.2(2)	105.7(3)	102.8(3), N(2)–Cu(1)–S(2^{i})
O(1)–Cu(3)–X(3)	94.5(1)	94.1(2)	
O(3)–Cu(3)–X(3)	156.0(1)	156.1(2)	
N(3)–Cu(3)–X(3)	97.7(2)	97.7(3)	
O(3)–Cu(3)–O(1)	83.5(2)	83.4(3)	
O(1)–Cu(3)–N(3)	167.0(2)	167.3(3)	
O(3)–Cu(3)–N(3)	83.5(2)	83.8(3)	
O(3)–Cu(3)–X(1)	97.7(1)	97.5(2)	
O(1)–Cu(3)–X(1)	84.9(1)	85.7(2)	
N(3)–Cu(3)–X(1)	96.0(2)	95.7(3)	
X(3)–Cu(3)–X(1)	105.94(7)	106.01(7)	
O(2)–Zn(2)–X(2)	107.4(1)	108.5(2)	106.0(3) O(2)–Zn(2)–N(20)
O(3)–Zn(2)–X(2)	106.3(1)	105.1(2)	106.0(3) O(2^{ii})–Zn(2)–N(20)
N(1)–Zn(2)–X(2)	106.8(2)	107.1(3)	103.0(5) N(1)–Zn(2)–N(20)
O(2)–Zn(2)–O(3)	124.3(2)	125.5(3)	114.8(4) O(2)–Zn(2)–O(2^{ii})
O(2)–Zn(2)–N(1)	103.3(2)	101.9(4)	112.9(2)
O(3)–Zn(2)–N(1)	107.7(2)	107.7(4)	112.9(2) O(2^{ii})–Zn(2)–N(1)
O(3)–Zn(2)–O(1)	71.5(1)	71.4(3)	73.5(2) O(2^{ii})–Zn(2)–O(1)
O(2)–Zn(2)–O(1)	71.6(1)	71.6(3)	73.5(2)
N(1)–Zn(2)–O(1)	77.6(2)	77.7(3)	78.0(4)
X(2)–Zn(2)–O(1)	175.5(1)	174.9(2)	179.0(5) N(20)–Zn(2)–O(1)
Cu(1)···Cu(3)	3.279(1)	3.311(2)	3.406(3) Cu(1)···Cu(1^{ii})
Cu(1)···Zn(2)	3.180(1)	3.161(2)	3.144(2)
Cu(3)···Zn(2)	3.195(1)	3.175(2)	

[a] Symmetry transformations used to generate equivalent atoms (indicated by superscript): i: $-x + 1, -y - 1, z - 1/2$; ii: $-x + 1, y, z$.

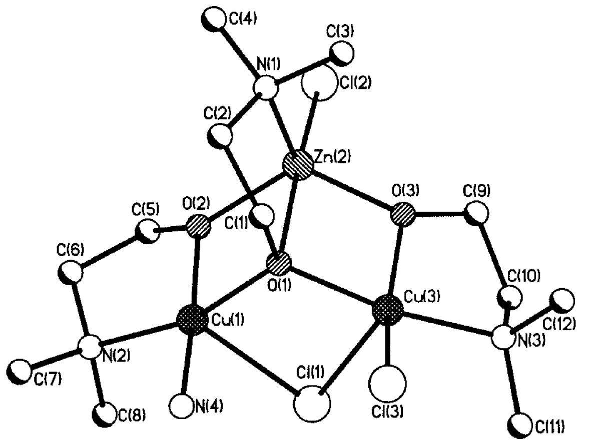

Fig. 1 Molecular structure of **1**, showing the atom numbering scheme (H atoms omitted for clarity).

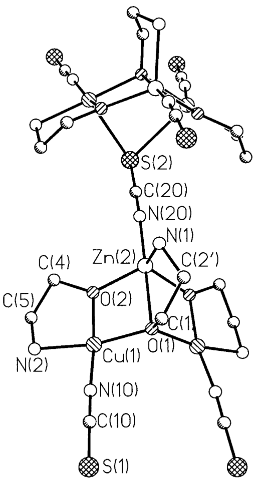

Fig. 2 Molecular structure of **3** with atom numbering scheme, showing the intermolecular Cu–S_{NCS} interactions in the polymeric chain (H atoms omitted for clarity).

oxygens and one chlorine) and metal atoms, and one corner metal site is vacant. The coordination geometry around the terminal, crystallographically independent copper atoms is distorted square pyramidal, $Cu(1)N_2O_2X$ and $Cu(3)NO_2X_2$, X = Cl (**1**), Br (**2**). The trigonality indices, τ, are very small (0.12 and 0.10, respectively; a τ value of zero corresponds to a regular square pyramid), and in agreement[9] with this geometry. The equatorial coordination around Cu(1) involves an ammonia molecule and donor atoms of the Me_2Ea groups with four approximately equal short distances (Table 2). The halogen atom X(3) and donor atoms of Me_2Ea groups form the corresponding basal plane at Cu(3). The equatorial Cu–O/N distances lie in the range 1.902(7)–2.053(9) Å, commonly observed for this kind of compound.[10] The two copper square pyramids are tilted toward each other as a result of the bridging function of the axial halogen atom, X(1). The axial copper–X(1) bonds are somewhat longer compared with the corresponding in-plane distances (Table 2), consistent with the Jahn–Teller effect in the d^9 electronic configuration.

The zinc atom has three quite short bonds with the nitrogen and oxygen atoms, N(1), O(2) and O(3), of the three Me_2Ea groups and a longer bonding distance to the halogen atom X(2) in a distorted tetrahedral geometry. In addition, Zn(2) is weakly bonded to the oxygen atom O(1) at *ca.* 2.45 Å, which implies that the Zn(2) coordination sphere approximates a trigonal pyramid (the τ value is 0.85). The μ-alkoxo and μ-halogeno bridges between the metal centres result in copper–copper and copper–zinc separations of approximately 3.30 and 3.16–3.20 Å, respectively (Table 2). The trinuclear units show no significant intermolecular contacts in the solid state. In fact, neither the coordinated ammonia nor the halogeno ligands have any strong intra- or intermolecular hydrogen bonds (N···Cl/Br contacts are 3.4–3.7 Å).

Complex **3** has a symmetrical trinuclear core (containing a crystallographic mirror plane) similar to that of **1** and **2** (Fig. 2, Table 2). The copper atom in **3** adopts a square-pyramidal coordination sphere, with a chromophore $\{CuN_2O_2S\}$ in which the axial sulfur atom belongs to a thiocyanate group of the neighbouring molecule. The arrangement of the nearest nitrogen and oxygen atoms around the zinc atom closely resembles a tetrahedron; the fifth Zn(2)–O(1) contact is significantly longer, but still within coordination distance (Table 2), making a trigonal bipyramidal geometry. The chemical difference between **3** and the two compounds described above produces changes in the coordination environment of the metal atoms and the overall crystal packing. The exogenous μ-SCN bridge in **3**, in contrast to the μ-halogeno bridging in **1** and **2**, forces a larger copper–copper separation of 3.406(3) Å in the thiocyanate complex [the copper–zinc distance is 3.144(2) Å].

Additional interesting intermolecular association in the structure of **3** occurs through the Cu–S interactions between the S(2) atom of the SCN group coordinated to Zn(1) and two copper atoms of the adjacent complex molecule. As a consequence, a polymeric chain assembly is evident along the *c*-axis of the crystal (see Fig. 2). The chains are held together through intermolecular interactions. The acetonitrile solvent molecules of crystallization occupy cavities in the crystal lattice.

Magnetic properties

The EPR spectra of **1**–**3** are very weak, in a few cases showing some minor impurities, and are ascribed to dinuclear Cu/Cu units with a large zero-field splitting. The study of this splitting requires high-field EPR and is left for future investigation. The temperature dependence of the molar magnetic susceptibility of **1**, **2** and **3**, measured as solids in the range 5–280 K, is shown in Fig. 3–5 in the form χ_m *vs.* T and $\chi_m T$ *vs.* T. At room temperature, the $\chi_m T$ values of 0.74, 0.63 and 0.61 cm^3

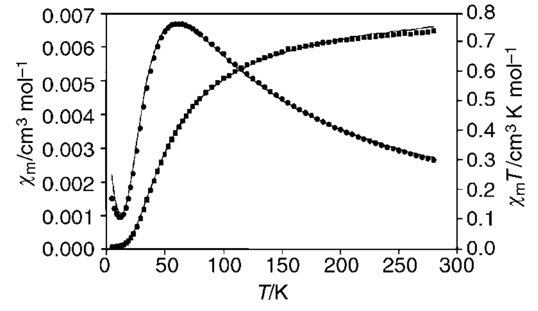

Fig. 3 Plots of χ_m (dots) and $\chi_m T$ (squares) *vs.* T for complex **1**. The solid line was calculated from eqn. (3) with $2J = -68\ cm^{-1}$, $g = 2.05$.

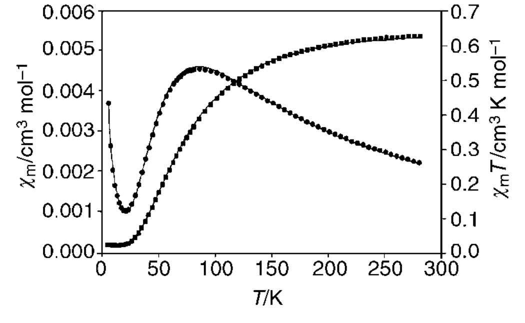

Fig. 4 Plots of χ_m (dots) and $\chi_m T$ (squares) *vs.* T for complex **2**. The solid line was calculated from eqn. (3) with $2J = -96\ cm^{-1}$, $g = 2.11$.

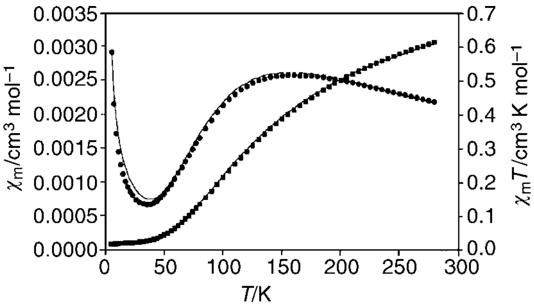

Fig. 5 Plots of χ_m (dots) and $\chi_m T$ (squares) *vs.* T for complex **3**. The solid line was calculated from eqn. (3) with $2J = -179$ cm^{-1}, $g = 2.05$.

K mol^{-1} ($\mu_{eff} = 2.42$, 2.24 and 2.22 μ_B) for **1**, **2** and **3**, respectively, are in agreement with the presence of two weakly coupled $S = 1/2$ centres. On lowering the temperature, the value of $\chi_m T$ decreases, reaching a minimum value of 0.01–0.02 cm^3 K mol^{-1} at 5 K for all the three complexes. This behaviour is typical of an antiferromagnetic exchange interaction between the copper(II) ions in the compounds. As is commonly observed[2a,11] within complexes possessing an antiferromagnetic interaction between metal centres, the presence of a monomeric impurity is evident at low temperatures, through a slight increase in χ_m.

The magnetic data were fitted by the Bleaney–Bowers equation [eqn.(3)] for a dinuclear copper(II) system where the symbols have their usual meanings, $N\alpha$ was fixed to 60×10^{-6} cm^3 mol^{-1}.

$$\chi_m = [N\beta^2 g^2/3k(T-\theta)][1 + 1/3 \exp(-2J/kT)]^{-1}(1-\rho) + (N\beta^2 g^2 \rho/4kT) + N\alpha \qquad (3)$$

The best data fits (solid lines in Fig. 3, 4 and 5) give: $2J = -68$ cm^{-1}, $g = 2.05$, $\rho = 0.01$, $\theta = 0$ with $R = 1.77\%$ (**1**), $2J = -96$ cm^{-1}, $g = 2.11$, $\rho = 0.03$, $\theta = -1$ with $R = 1.20\%$ (**2**) and $2J = -178$ cm^{-1}, $g = 2.05$, $\rho = 0.02$, $\theta = -3$ with $R = 1.28\%$ (**3**); which reveals that the order of antiferromagnetic interactions is **1** < **2** < **3**. Somewhat surprisingly, this trend is in contrast to the increase in Cu···Cu distance from **1** to **3**, but correlates nicely with the Cu–O–Cu angle in the complexes: 112.7(2) < 114.4(3) < 119.5(5)°. The increase in the Cu–O–Cu angle of 2–5° would more than account for the observed increase in coupling based on a correlation of J with the angle for essentially coplanar Cu(II) species with Cu–O–Cu bridges.[12] However, in the present case, it is not possible to analyze in detail the magnetic data simply in terms of an increasing Cu–O–Cu angle, since the principal metal planes are not coplanar and a greater number of exchange pathways are available.

The magnitude of the exchange parameter reported here for **3** is significantly larger than reported earlier for the compound $[Cu_2Pb(SCN)_3L_3]_2$,[6a] with a closely related trinuclear core. This observation suggests that efficient exchange pathways responsible for the magnetic coupling in **1**–**3** exist; whether or not the diamagnetic zinc(II) ions play a role cannot be deduced. In fact, large-range ferromagnetic coupling between copper(II) centres through the diamagnetic zinc(II) has been observed in $[Cu_2Zn(Hdmg)_2(dmg)_2(H_2O)] \cdot 0.5H_2dmg \cdot H_2O$ (H_2dmg = dymethylglyoxime).[13]

In conclusion, zerovalent copper, zinc oxide and an ammonium salt were employed successfully to synthesize mixed-metal complexes containing 2-dimethylaminoethanol, in air. The trinuclear compounds obtained have symmetric and asymmetric Cu_2ZnO_3X ($X = Cl$, Br, S_{SCN}) cores with structures that can be described as a cube with one missing vertex. The anionic X^- ligands of the complexes **1**–**3** mediate significant changes in the structures and magnetic coupling. Further work on the biocatalytic activities of the compounds is in progress and will be presented in subsequent papers.

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References

1 M. D. Ward, *Chem. Soc. Rev.*, 1995, **24**, 121.

2 (*a*) O. Kahn, *Molecular Magnetism*, VCH, New York, 1993; (*b*) O. Kahn, *Adv. Inorg. Chem.*, 1995, **43**, 179; (*c*) D. Gatteschi, *Adv. Mater.*, 1994, **6**, 635.

3 W. Kaim and B. Schwederski, *Bioinorganic Chemistry: Inorganic Elements in the Chemistry of Life*, Wiley, Chichester, 1995.

4 E. Fenton and H. Okawa, *Chem. Ber. Recueil*, 1997, **130**, 433.

5 See, for example: S. R. Petrusenko, V. N. Kokozay, O. Yu. Vassilyeva and B. W. Skelton, *J. Chem. Soc., Dalton Trans.*, 1997, 1793; K. V. Domasevitch, J. A. Rusanova, O. Yu. Vassilyeva, V. N. Kokozay, P. J. Squattrito, J. Sieler and P. R. Raithby, *J. Chem. Soc., Dalton Trans.*, 1999, 3087; V. V. Skopenko, V. N. Kokozay, O. Yu. Vassilyeva and V. A. Pavlenko, in *Direct Synthesis of Coordination and Organometallic Compounds*, ed. A. D. Garnovskii and B. I. Kharissov, Elsevier Science, 1999, ch. 3, 5.

6 (*a*) L. A. Kovbasyuk, O. Yu. Vassilyeva, V. N. Kokozay, W. Linert, J. Reedijk, B. W. Skelton and A. G. Oliver, *J. Chem. Soc., Dalton Trans.*, 1998, 2735; (*b*) L. A. Kovbasyuk, O. Yu. Vassilyeva, V. N. Kokozay, W. Linert, B. W. Skelton and A. G. Oliver, *New J. Chem.*, 1998, **22**, 931 and references therein.

7 (*a*) teXsan, Version 1.7-1, Molecular Structure Corporation, The Woodlands, TX, 1985, 1992, 1995; (*b*) A. Altomare, M. C. Burla, M. Camalli, C. Giacovazzo, A. Guagliardi and G. Polidori, *J. Appl. Crystallogr.*, 1994, **27**, 435; (*c*) G. M. Sheldrick, SHELXS 86, Program for the Solution of Crystal Structures, University of Göttingen, Germany, 1986; (*d*) G. M. Sheldrick, SHELXL 93, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1993; (*e*) G. M. Sheldrick, SHELXL 97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.

8 *Chemistry of Pseudohalides*, ed. A. Golub, H. Kohler and V. Skopenko, Elsevier, Amsterdam, 1986; M. Kabešová, R. Boca, M. Melník, D. Valigura and M. Dunaj-Jurco, *Coord. Chem. Rev.*, 1995, **140**, 115.

9 A. W. Addison, T. N. Rao, J. Reedijk, J. Vanrijn and G. C. Verschoor, *J. Chem. Soc., Dalton Trans.*, 1984, 1349.

10 A. F. Wells, *Structural Inorganic Chemistry*, 5th edn., Clarendon Press, Oxford, 1986.

11 K. S. Murray, *Adv. Inorg. Chem.*, 1995, **43**, 261.

12 D. Lewis, K. McGregorog, W. Hatfield and D. Hodgson, *Inorg. Chem.*, 1974, **13**, 1013.

13 R. Ruiz, M. Julve, J. Faus, F. Lloret, M. Munoz, Y. Journaux and C. Bois, *Inorg. Chem.*, 1997, **36**, 3434.