# A unique methoxo- and fluoro-bridged triangular trinuclear Cu(II) species linked in a lattice *via* mononuclear Cu(II) units. Synthesis, X-ray structure and magnetism of [Cu$_4$(2-aminopyrimidine)$_6$(μ$_3$-OCH$_3$)$_2$(μ-F)$_3$(F)$_2$](BF$_4$)†

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The synthesis, characterisation, crystal structure and magnetic properties of the new and unique trinuclear polymeric Cu(II) compound **1**, [Cu$_4$(ampym)$_6$(μ$_3$-OCH$_3$)$_2$(μ-F)$_3$(F)$_2$](BF$_4$) (in which ampym = 2-aminopyrimidine), is reported. The lattice structure is fascinating and consists of trinuclear Cu(II) units that are connected *via* an ampym molecule to a fourth Cu(II) anion, resulting in a polymeric structure. The trinuclear unit consists of three Cu(II) atoms with two μ$_3$-bridging methoxo groups and 3 bridging fluorides, which is unprecedented. Magnetic measurements on **1** have been carried out from 5 to 300 K. Due to its unique structural nature, no exact model could be obtained and various simplified fitting models were considered. The best result was obtained when considering the coupling through bridging aminopyridine to be dominant, giving a Cu–Cu interaction constant (*J*) of −190(40) cm$^{-1}$.

## Introduction

In 3-D coordination chemistry and crystal engineering the H-bonding system often plays a very important role in the self-assembly of polymeric molecular structures.[1] In this respect the molecule 2-aminopyrimidine (abbreviated as ampym), with two H-bond donor atoms and two H-bond acceptor atoms, is particularly attractive as a very simple self-complementary prototype for chain formation with other organic molecules.[2] Metal compounds with ampym as the only organic ligand, or present as a complementary organic ligand, have been increasingly used.[3–6] Quite a few Cu(II) X-ray structures with ampym acting as a complementary organic ligand, together with a variety of other organic ligands, have recently become available in the literature; in these cases ampym is found to act as a monodentate co-ligand[3] or as a bridging didentate ligand.[4] X-Ray structures of Cu(I) compounds with ampym as the only coordinating organic ligand are relatively rare and so far only one X-ray structure of a Cu(I) compound is known with the ampym ligand.[5]

Different Cu(II) compounds, depending on the nature of the anion and the synthetic method, were investigated by X-ray crystallography. With halides as anions mononuclear and polymeric compounds have been obtained in which ampym acts as a monodentate or a didentate ligand.[6] With other anions like sulfate,[7a,b] triflate,[7c] nitrate[7d] and dicyanamide[7e] mononuclear or polynuclear Cu(II) compounds are obtained, all with ampym acting as a monodenate ligand. X-Ray structures of a dinuclear Cu(II) methoxo-bridged compound[8a] and of a hydroxo-bridged Cu(II) compound[8b] were also recently obtained, again with ampym acting as a monodentate ligand.

It should also be mentioned that the ampym ligand has been shown to be a useful starting material for template synthesis with Cu(II) triflate[9a,b] and Co(II)[9c] forming completely new organic compounds.

In this study we present the structure of a unique polynuclear Cu(II) compound synthesized from Cu(II) tetrafluoroborate and ampym in methanol. The trinuclear chromophore has a quite unique di-methoxo, tris-fluoro bridging system, which is linked *via* four mononuclear Cu(II) ions to generate a polymeric structure. Spectroscopic and magnetic measurements are also presented in this study and a magnetic exchange model is proposed.

## Experimental

### Synthesis of the title compound

Copper(II) tetrafluoroborate (0.3 g, 1.26 mmol) and 0.4 g (2.56 mmol) of ampym (obtained from Acros Organics, Belgium and used without further purification) were each dissolved in 10 ml of hot (but not boiling) methanol. The Cu salt was gradually and carefully added to the ligand solution in such a way that no precipitate was formed. The mixture was filtered and left standing in the open air at room temperature. After a few weeks green crystals appeared. The crystals were filtered and washed with methanol. Anal. found (calcd) for Cu$_4$BC$_{26}$F$_9$H$_{36}$N$_{18}$O$_2$: 29.5 (29.2) %C; 3.3 (3.4) %H; 23.9 (23.6) %N; 15.1 (16.0) %F; 23.3 (23.8) %Cu.

### Physical measurements

C, H, N, F and Cu determinations were performed by the Microanalytical Laboratory of University College, Dublin, Ireland.

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† Electronic supplementary information (ESI) available: fitting of the magnetic coupling according to Scheme 2(a). See http://www.rsc.org/suppdata/nj/b3/b304979e/

Ligand-field spectra were obtained on a Perkin–Elmer Lambda900 spectrophotometer using the diffuse reflectance technique, with MgO as a reference. X-Band powder EPR spectra were obtained on a Jeol RE2x electron spin resonance spectrometer using DPPH ($g = 2.0036$) as a standard. FTIR spectra were recorded on a Perkin–Elmer Paragon 1000 FTIR spectrophotometer, equipped with a Golden Gate ATR device, using the reflectance technique (4000–300 $cm^{-1}$, resol. 4 $cm^{-1}$).

Magnetic susceptibility measurements (5–280 K) were carried out using a Quantum Design MPMS-5 5T SQUID magnetometer (measurements carried out at 1000 Gauss). Data were corrected for magnetisation of the sample holder and for diamagnetic contributions, which were estimated from the Pascal constants.

### Crystallographic data collection and refinement of the structure

A crystal of $0.20 \times 0.15 \times 0.95$ $mm^3$ was selected and mounted on a glass fiber using the oil drop method; data were collected on a Rigaku AFC-7S diffractometer (graphite-monochromated MoKα radiation, $\omega - 2\theta$ scans). The intensity data were corrected for Lorentz and polarisation effects, for absorption (psi-scan absorption correction) and extinction. The structures were solved by direct methods. The programs TEXSAN,[10a] SHELXS-97[10b] and SHELXL-97[10c] were used for data reduction, structure solution and structure refinement, respectively. Refinement of $F^2$ was done against all reflections. The weighted $R$ factor, $wR$, and goodness of fit $S$ are based on $F^2$. Conventional $R$ factors are based on $F$, with $F$ set to zero for negative $F^2$. All non-H atoms were refined anisotropically. All H atoms were introduced in calculated positions and refined with fixed geometries with respect to their carrier atoms. Two of the three crystallographically independent Cu atoms were found to be in special positions (mirror plane related). The disordered tetrafluoroborate anion was refined in two positions as rigid groups with occupational factor 0.5.

**Crystal data.** $C_{26}H_{36}BCu_4F_9N_{18}O_2$, $M = 1068.70$, monoclinic, space group $C2/c$ (No.15), $a = 11.899(6)$, $b = 21.435(8)$, $c = 16.727(7)$ Å, $\beta = 108.64(4)°$, $U = 4043(3)$ Å$^3$, $T = 193(2)$ K, $Z = 4$, $\mu$(MoKα) = 2.170 $cm^{-1}$, 7453 reflections measured, 3661 unique ($R_{int} = 0.1486$), which were used in all calculations. The final $R = 0.076$, with $wR(F^2)$ of 0.144 (all data).‡

### Results and discussion

Ampym reacts in methanol with Cu(BF$_4$)$_2$ to give the trinuclear, polymeric compound [Cu$_4$(ampym)$_6$($\mu_3$-OCH$_3$)$_2$($\mu$-F)$_3$-(F)$_2$](BF$_4$) (**1**). The F$^-$ ions are clearly formed from BF$_4^-$ decomposition, a phenomenon known for some time and usually prominent with H-bond donor ligands.[11] In the infrared spectrum of **1** the N–H vibration of the amino group of the ligand is observed at 3277 $cm^{-1}$, suggesting H-bond donor properties, and a strong $\nu_{C=N}$ ring vibration is observed[7c,12] at 1573 $cm^{-1}$. The characteristic vibrations of the tetrafluoroborate anion are observed[12c] at 1035, 795, 526 and 325 $cm^{-1}$. The ligand-field spectrum measured as a solid with the diffuse reflectance technique shows a broad band at $14.5 \times 10^3$ $cm^{-1}$ and a very broad band centred around $7.0 \times 10^3$ $cm^{-1}$, which are normal ligand-field transitions for (distorted) octahedrally compressed or elongated surrounded Cu(II).[12d]

The numbering scheme for this structure, in which Cu1 and F2 lie on a 2-fold axis and Cu3 on a centre of symmetry, is depicted in Fig. 1 with relevant bond length and bond angle
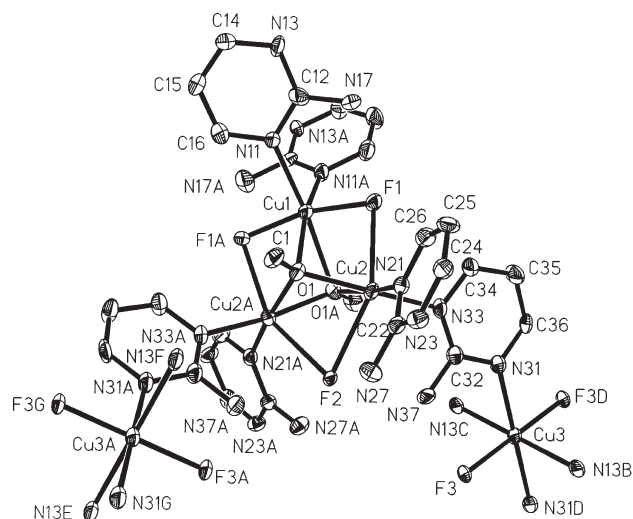
† CCDC reference number 209271. See http://www.rsc.org/suppdata/nj/b3/b304979e/ for crystallographic data in .cif or other electronic format.

**Fig. 1** ORTEP 50% probability plot of the cation of the title compound. Hydrogen atoms and the non-coordinating tetrafluoroborate anion are omitted for clarity. Atoms with an "A" are generated by inversion symmetry: $-x, y, -z + \frac{1}{2}$.

information given in Table 1. A simplified picture of this quite complicated structure is given in Scheme 1. The structure can be best described as methoxy- and fluoro-bridged trinuclear Cu(II) units (composed by Cu1–Cu2–Cu2A), which form a three-dimensional polymeric lattice structure *via* bridging ampym ligands connected to four mononuclear Cu species (Cu3) (see Fig. 2). The trinuclear unit (Cu1–Cu2–Cu2A) contains two bridging methoxo anions and three bridging fluoro anions. The two methoxo anions are bridging to all three copper atoms with two short distances [O1–Cu2 (Cu2A) 1.978(6) Å] and one long distance [O1–Cu1 2.253(7) Å]. All three crystallographically independent Cu(II) atoms have a different distortion of the octahedral geometry. Cu1 is surrounded by two oxygen atoms of a bridging methoxo group [Cu1–O1 2.253(7) Å], two bridging fluoro atoms [Cu1–F1 1.893(5) Å] and two nitrogen atoms of bridging ampym ligands [Cu1–N11 2.181(9) Å], giving a compressed octahedral geometry. The three linear angles of the octahedron are almost equal at about 166° [F1–Cu1–F1A 165.1(3)°, N11A–Cu1–O1 166.4(3)°].

Cu2 is surrounded by two oxygen atoms of a bridging methoxo group [Cu2–O1 1.978(6), Cu2–O1A 1.969(7) Å], two nitrogen atoms, one of a bridging ampym ligand [Cu2–N33 1.998(8) Å] and one of a monodentate ampym ligand [Cu2–N21 2.023(9) Å] and, forming the axial ligands, two bridging fluoro atoms [Cu2–F1 2.320(5), Cu2–F2 2.428(6) Å]. These Cu–F distances are relatively long, which is not uncommon for such systems.[11] The occurrence of $\mu_3$-Cu–O$_{methoxo}$ distances with two short [Cu–O = 1.978(6) Å] and one long [Cu–O = 2.253(7) Å] distance has been reported earlier in the literature.[13] The two angles of the basal plane of the distorted octahedron are 168.9(3)° (O1–Cu2–N33) and 169.8(3)° (O1A–Cu2–N21), while the axial trans angle is 154.0(2)° (F1–Cu2–F2). The third Cu atom of the trinuclear triangle (Cu2A) is symmetry related to Cu(2).

The fourth Cu atom (Cu3) is completely different from the other Cu atoms, also by its symmetry, as it is located at a centre of symmetry. It is surrounded by four nitrogen atoms of bridging ampym ligands [Cu–N distances of 2.269(9) and 2.332(9) Å] and two trans non-bridging fluoro atoms with a distance of 1.860(5) Å, resulting in a compressed octahedral geometry. The ampym ligands are all connected to the three other copper atoms (Cu1, Cu2), thus forming a three-dimensional polymeric compound.

**Table 1** Selected bond lengths (Å) and angles (°) for the title compound[a]

| | | | |
|---|---|---|---|
| Cu(2)–O(1)A | 1.969(7) | Cu(1)–F(1) | 1.893(5) |
| Cu(2)–O(1) | 1.978(6) | Cu(1)–N(11) | 2.181(9) |
| Cu(2)–N(33) | 1.998(8) | Cu(1)–O(1) | 2.253(7) |
| Cu(2)–N(21) | 2.023(9) | Cu(3)–F(3) | 1.860(5) |
| Cu(2)–F(1) | 2.320(5) | Cu(3)–N(13)D | 2.269(9) |
| Cu(2)–F(2) | 2.428(6) | Cu(3)–N(31) | 2.332(9) |
| Cu(1)–Cu(2) | 2.911(2) | Cu(1)–Cu(2)A | 2.911(2) |
| Cu(2)–Cu(2)A | 2.898(3) | | |
| F(1)A–Cu(1)–F(1) | 165.1(3) | O(1)A–Cu(2)–F(1) | 80.0(2) |
| F(1)–Cu(1)–N(11)A | 94.3(3) | O(1)–Cu(2)–F(1) | 80.4(2) |
| F(1)–Cu(1)–N(11) | 96.2(3) | N(33)–Cu(2)–F(1) | 95.8(3) |
| N(11)A–Cu(1)–N(11) | 91.0(5) | N(21)–Cu(2)–F(1) | 97.1(3) |
| F(1)A–Cu(1)–O(1) | 83.4(2) | F(1)–Cu(2)–F(2) | 154.0(2) |
| N(11)A–Cu(1)–O(1) | 166.4(3) | F(3)B–Cu(3)–F(3) | 180.0 |
| N(11)–Cu(1)–O(1) | 102.6(3) | F(3)B–Cu(3)–N(13)C | 91.7(3) |
| O(1)–Cu(1)–O(1)A | 63.8(3) | F(3)–Cu(3)–N(13)C | 88.3(3) |
| O(1)A–Cu(2)–O(1) | 74.3(3) | N(13)C–Cu(3)–N(13)D | 180.0 |
| O(1)A–Cu(2)–N(33) | 94.8(3) | F(3)B–Cu(3)–N(31) | 87.7(2) |
| O(1)–Cu(2)–N(33) | 168.9(3) | F(3)–Cu(3)–N(31) | 92.3(2) |
| O(1)A–Cu(2)–N(21) | 169.8(3) | N(13)C–Cu(3)–N(31) | 85.7(3) |
| O(1)–Cu(2)–N(21) | 95.6(3) | N(13)D–Cu(3)–N(31) | 94.3(3) |
| N(33)–Cu(2)–N(21) | 95.2(3) | | |

| Hydrogen bonds | D–H | H⋯A | D⋯A | D–H⋯A |
|---|---|---|---|---|
| N17–H17A⋯F1 | 0.880 | 1.841 | 2.697 | 158.6 |
| N17–H17B⋯F3 | 0.880 | 1.827 | 2.659 | 156.9 |
| $[-x-\frac{1}{2}, y+2, -z+2]$ | | | | |
| N27–H27A⋯F2 | 0.880 | 1.802 | 2.680 | 176.2 |
| N37–H37A⋯F2 | 0.880 | 1.830 | 2.700 | 169.3 |
| N37–H37B⋯F3 | 0.880 | 1.865 | 2.698 | 157.2 |
| N27–H27B⋯N23 | 0.880 | 2.131 | 3.010 | 176.2 |
| $[-x-\frac{1}{2}, -y-2, -z]$ | | | | |

[a] Symmetry transformations used to generate equivalent atoms: A: $[-x, y, -z+1/2]$; B: $[-x-1/2, -y-1/2, -z+1]$; C: $[x, -y, z+1/2]$; D: $[-x-1/2, y-1/2, -z+1/2]$.

All other distances and angles of the ampym ligand itself are consistent with literature values.[14a,b] The compressed geometry for a *trans*-difluorocuprate appears to be rare and only two other cases were found[14c,d] in the Cambridge database. The

crystal lattice is stabilised by strong hydrogen bonds between the amine nitrogen of ampym and the fluoride ions with distances that vary from 2.66 to 2.70 Å and between the amine nitrogen and a nitrogen of the pyrimidine ring with a distance of 3.010 Å. Further details of the hydrogen bonds are included in Table 1. The $BF_4$ counter ion is non-coordinating and located in the lattice on a disordered position, with no short H-bond contacts.



**Scheme 1** Simplified scheme of the structure (L = ampym ligand, while an arrow denotes a link to the polymeric structure).
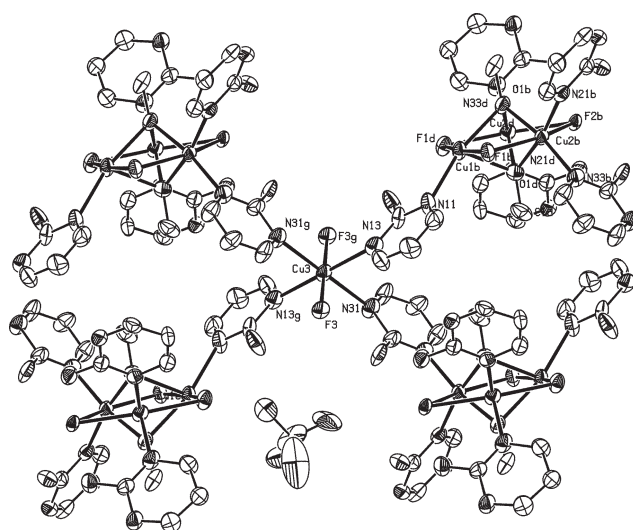


**Fig. 2** View of the polymeric structure of compound **1** with Cu3 in the centre.

The EPR spectra at room temperature of the title compound shows an absorption at $g_\perp = 2.13$ with an unresolved $g_\parallel$ of 2.32. The fact that more than one Cu site is present in the lattice apparently results in an exchange-narrowed signal and no indications for the compressed Cu geometry are seen.

The temperature dependence of the molar magnetic moment and of the inverse molar susceptibility per Cu(II) ion of **1** are presented in Fig. 3. Considering only the high-temperature range ($T > 200$ K), the linear behaviour of the inverse susceptibility yields a Weiss constant of $-112$ K, which indicates the presence of rather strong antiferromagnetic coupling between Cu ions. The low temperature region is complex, probably arising from various magnetic components. The magnetic moment decreases smoothly from 1.75 $\mu_B$ at 300 K, which is consistent with non-coupled Cu(II) ions (spin-only value is 1.73), to 1.5 $\mu_B$ at *ca.* 40 K, whereby it begins to drop more markedly, down to 0.78 $\mu_B$ at 6 K. Below this temperature another change of behaviour occurs with a stabilisation at approximately 0.65 $\mu_B$.

Several possible magnetic pathways arising from the complex 3-D structure of **1** have to be considered to explain the observed behaviour. First, $\mu_3$-methoxide and $\mu$-fluoride bridges form triangular Cu$_3$ units, whose organisation has no known equivalent in the literature. Comparable double $\mu_3$-methoxide bridges in trinuclear compounds have been reported,[13] but no magnetic characterisation was performed. Considering the asymmetric character of both the methoxo and fluoro bridges between Cu1 and Cu2 (Cu1 is 0.5 Å closer to F and Cu2 is 0.3 Å closer to O1) only weak antiferromagnetic coupling would be expected. The other pathway occurs though the Cu–ampym–Cu–ampym–Cu connections between the triangular units. Pyrimidine was shown to be a ferromagnetic coupler between first-row transition metals (V, Co, Cu) through a spin-polarisation mechanism[15] when its coordination occurs in an axial-axial or axial-equatorial fashion.[16] When an equatorial-equatorial coordination was observed, which is the case in compound **1**, only an overall antiferromagnetic coupling (up to $J = 60$ cm$^{-1}$) was detected,[16b,d] which arises from an overlap of the Cu(II) magnetic d$_{x^2-y^2}$ orbitals and a molecular pyrimidine orbital contributed by two nitrogen lone pairs. Obviously, due to the structural complexity of **1**, no exact analytical solution can be obtained, but since no 3-D order is observed at low temperature, a simplified molecular view may be successful in obtaining a global picture of the magnetic scheme.

In view of the structure of **1**, two mathematical options were considered. The first one [See Scheme 2(a)] considers a mononuclear Cu(II) atom, which is surrounded by four mutually
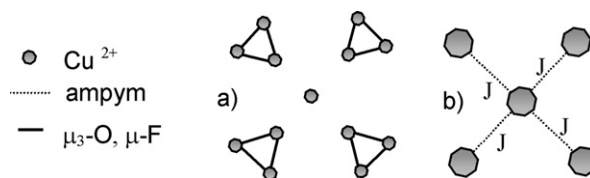


**Scheme 2** (a) Schematic representation of one of the proposed magnetic coupling schemes (drawn co-planar for clarity), and (b) simplified exchange-coupling unit adopted in this case (see text).

isolated trinuclear (Cu1–Cu2–Cu2A) units, neglecting the interaction between the trinuclear units and the mononuclear Cu atom through ampym bridges. This option does not give satisfactory results (see the Electronic supplementary information) as apparently the coupling through the pyrimidine is, if not dominant, important. So a second possibility [shown in Scheme 2(b)] was formulated, which considered the interaction through the ampym bridges to be dominant, yielding a pseudo-pentamer, and treating the interpentamer interaction through the trinuclear units in the mean-field approximation. The Hamiltonian describing the exchange coupling of the corresponding pentanuclear unit [Scheme 2(b)], $H = -JS_1 \sum_{i=2}^{5} S_i$, yields the following expression for the susceptibility:[15]

$$\chi = \frac{N_A g^2 \beta^2}{4k_B T - zJ' \times F(T,J)} \times F(T,J) + \text{TIP} \quad \text{with}$$

$$F(T,J)$$
$$= \frac{\exp(3x) + \exp(-5x) + 10\exp(7x) + 10\exp(-9x) + 35\exp(11x)}{\exp(3x) + \exp(-5x) + 2\exp(7x) + 2\exp(-9x) + 3\exp(11x)}$$

where $\chi = -J/(8k_B T)$ and $g$, $N_A$, $k_B$ and $\beta$ have their usual meanings. The term $zJ'$ introduces interpentamer interactions (with $z$ nearest neighbours) to account for the 3-D character of the real magnetic coupling scheme. TIP was fixed at $1.4 \times 10^{-4}$ cm$^3$ mol$^{-1}$ per Cu(II) ion to limit the free parameters and a least-squares fit with free $g$, $J$ and $zJ'$ parameters was performed. The best result, which is represented in Fig. 3 as the drawn line, was obtained for $g = 2.27(5)$, $J = -190(40)$ cm$^{-1}$ and $zJ' = -10(1)$ cm$^{-1}$. The agreement is correct, although the real magnetic scheme has a 3-D character that cannot be reproduced by the model used. Nevertheless, the global picture obtained is reasonable: two antiferromagnetic interactions are present, one through the pyrimidine rings and one inside the trinuclear units, that is through the methoxy and fluoro bridges. As expected the antiferromagnetic coupling through the latter bridges is very weak. An MSDA analysis[16e,f] appeared not to be relevant, as the vibrational effects and/or Jahn–Teller effects are deeply buried under the side effects, the 3 Cu ions are different and the ligands themselves are quite bulky. On the other hand, the unsaturated $\pi$-system of the pyrimidine rings could offer a much stronger antiferromagnetic pathway. The orientation of the Cu–pyrimidine coordination proves to be relevant for the sign of the interaction: the equatorial-equatorial mode in **1** allows a strong overlap of the magnetic d$_{x^2-y^2}$ Cu(II) orbitals.

## Conclusions

It can be concluded that, by using the ligand 2-aminopyrimidine and Cu(BF$_4$)$_2$, a unique polymeric Cu(II) structure built up from trinuclear units and mononuclear units is obtained. The ligand is apparently basic enough to dehydronate the methanol, a phenomenon observed before in other dinuclear alkoxo compounds.[17] The ligand-induced degradation of the tetrafluoroborate anion to form F anions in the presence of certain N-donor ligands has also been observed before in the literature.[11,14d,18] However, this is the first time that these
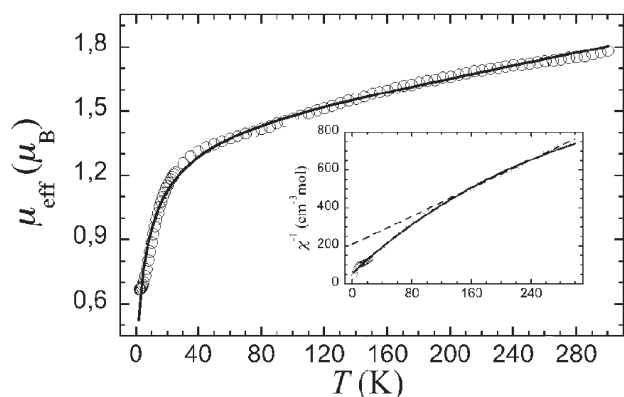


**Fig. 3** Temperature dependence of the effective magnetic moment and the inverse susceptibility per Cu(II) ion of the title compound. The dashed line in the inset shows the Curie–Weiss behaviour for a Weiss constant of $-112$ K. The full lines represent the best theoretical fit (see text).

two bridging anions are found in the same trinuclear unit. Due to the above mentioned complications, no accurate fitting of the magnetic behaviour could be performed, although an overall antiferromagnetic interaction, mainly occurring through ampym bridges, has been demonstrated to be a very good approximation.

## Acknowledgements

## References

1  (*a*) D. C. Sherrington and K. A. Taskinen, *Chem. Soc. Rev.*, 2001, **30**, 83; (*b*) S. H. M. Söntjens, J. T. Meijer, H. Kooijman, A. L. Spek, M. H. P. van Genderen, R. P. Sijbesma and E. W. Meijer, *Org. Letters*, 2001, **3**, 3887; (*c*) R. P. Sijbesma, F. H. Beijer, L. Brunsveld, B. J. B. Folmer, J. H. K. K. Hirschberg, R. F. M. Lange, J. K. L. Lowe and E. W. Meijer, *Science*, 1997, **278**, 1601.

2  (*a*) D. E. Lynch, T. Latif, G. Smith, K. A. Byriel and C. H. L. Kennard, *J. Chem. Crystallogr.*, 1997, **27**, 567; (*b*) D. E. Lynch, T. Latif, G. Smith, K. A. Byriel, C. H. L. Kennard and S. Parsons, *Aust. J. Chem.*, 1998, **51**, 403; (*c*) V. Bertolasi, P. Gilli, V. Ferretti and G. Gilli, *Acta Crystallogr., Sect. B.*, 2001, **57**, 591; (*d*) S. Goswami, R. Mukherjee, K. Ghosh, I. A. Razak, S. S. S. Raj and H.-K. Fun, *Acta Crystallogr., Sect. C*, 2001, **56**, 477; (*e*) J. A. R. Navarro, E. Freisinger and B. Lippart, *Inorg. Chem.*, 2000, **39**, 1059; (*f*) K. Kobayashi, T. Shirasaka, K. Yamaguchi, S. Sakamoto, E. Horn and N. Furukawa, *Chem. Commun.*, 2000, 41; (*g*) N. Shan, A. D. Bond and W. Jones, *Tetrahedron Lett.*, 2002, **43**, 3101.

3  (*a*) E. J. O'Reilly, G. Smith, C. H. L. Kennard and A. H. White, *Aust. J. Chem.*, 1983, **36**, 183; (*b*) E. J. O'Reilly, G. Smith and C. H. L. Kennard, *Inorg. Chim. Acta.*, 1984, **90**, 63; (*c*) C. H. L. Kennard, S. W. Stewart, E. J. O'Reilly, G. Smith and A. H. White, *Polyhedron*, 1985, **4**, 697; (*d*) T. C. W. Mak, C. H. L. Kennard, G. Smith, E. J. O'Reilly, D. S. Sagatys and J. C. Fulwood, *Polyhedron*, 1987, **6**, 855; (*e*) D. E. Lynch, *Acta Crystallogr.. Sect. C*, 2001, **57**, 158.

4  (*a*) G. Smith, E. J. O'Reilly, C. H. L. Kennard and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1985, 243; (*b*) G. Smith, C. H. L. Kennard and K. A. Byriel, *Polyhedron*, 1991, **10**, 873; (*c*) G. Smith, E. J. O'Reilly, H. L. Carrell, C. J. Carrell and C. H. L. Kennard, *Polyhedron*, 1996, **15**, 1995; (*d*) D. E. Lynch, *Acta Crystallogr., Sect. C*, 2000, **56**, e425; (*e*) A. García-Raso, J. J. Fiol, F. Bádenas, E. Lago and E. Molins, *Polyhedron*, 2001, **20**, 2877; (*f*) A. J. Blake, P. Hubberstey and C. L. Sampson, *Acta Crystallogr., Sect. E*, 2002, **58**, m99.

5  Q.-H. Jin, X.-M. Lu, H.-J. Zhu and X.-P. Ji, *Chin. J. Chem.*, 2000, **18**, 928.

6  (*a*) C. Zanchini and R. D. Willett, *Inorg. Chem.*, 1990, **29**, 3027; T. Manfredini, G. C. Pellacani, A. Bonamartini-Corradi, L. P. Battaglia, G. G. T. Guarini, J. G. Giusti, G. Pon, R. D. Willett and D. X. West, *Inorg. Chem.*, 1990, **29**, 2221; (*c*) R. Corzo-Suárez, S. García-Granda, I. Díaz, V. Fernández-Herrero and J. Luis Martínez, *Acta Crystallogr., Sect. C*, 1997, **53**, 1786; (*d*) G. Pon, R. D. Willett, B. A. Prince, W. T. Robinson and M. M. Turnbull, *Inorg. Chim. Acta.*, 1997, **255**, 325.

7  (*a*) P. O. Lumme, P. Kekarainen, H. Knuuttila, T. Kurkirinne, M. Latvala, L. Rönkönharju and S. Salonen, *Finn. Chem. Lett.*, 1981, 25; (*b*) P. O. Lumme, H. Knuuttila and E. Lindell, *Acta Crystallogr., Sect. C*, 1996, **52**, 51; (*c*) G. A. van Albada, W. J. J. Smeets, A. L. Spek and J. Reedijk, *J. Chem. Crystallogr.*, 2000, **30**, 11; (*d*) G. A. van Albada, I. Mutikainen, U. Turpeinen and J. Reedijk, *Acta Crystallogr., Sect E*, 2002, **58**, m55; (*e*) G. A. van Albada, M. E. Quiroz-Castro, I. Mutikainen, U. Turpeinen and J. Reedijk, *Inorg. Chim. Acta.*, 2000, **298**, 221.

8  (*a*) H.-L. Zhu, C.-X. Ren and X.-M. Chen, *J. Coord. Chem.*, 2002, **55**, 667; (*b*) G. A. van Albada, I. Mutikainen, W. J. J. Smeets, A. L. Spek, U. Turpeinen and J. Reedijk, *Inorg. Chim. Acta.*, 2002, **327**, 134.

9  (*a*) G. A. van Albada, I. Mutikainen, U. Turpeinen and J. Reedijk, *Eur. J. Inorg. Chem.*, 1998, 547; (*b*) G. A. van Albada, P. J. van Koningsbruggen, I. Mutikainen, U. Turpeinen and J. Reedijk, *Eur. J. Inorg. Chem.*, 1999, 2269; (*c*) M. Eiraku Masaki and M. M. Turnbull, *Heterocycles*, 2002, **57**, 47.

10  (*a*) *TEXSAN: Single Crystal Structure Analysis Software, v. 1.6.*, Molecular Structure Corporation, The Woodlands, TX , USA, 1993; (*b*) G. M. Sheldrick, *SHELXS-97, Program for solution of crystal structures*, University of Göttingen, Germany, 1997; (*c*) G. M. Sheldrick, *SHELXL-97, Program for refinement of crystal structures*, University of Göttingen, Germany, 1997.

11  (*a*) F. S. Keij, R. A. G. de Graaff, J. G. Haasnoot, A. J. Oosterling, E. Pedersen and J. Reedijk, *J. Chem. Soc., Chem. Commun.*, 1988, 423; (*b*) F. S. Keij, R. A. G. de Graaff, J. G. Haasnoot, J. Reedijk and E. Pedersen, *Inorg. Chim. Acta.*, 1989, **156**, 65; (*c*) A. J. Oosterling, R. A. G. de Graaff, J. G. Haasnoot, F. S. Keij, J. Reedijk and E. Pedersen, *Inorg. Chim. Acta.*, 1989, **163**, 53; (*d*) J. Reedijk, *Comments Inorg. Chem.*, 1982, **1**, 379.

12  (*a*) P. O. Lumme and H. Knuuttila, *Polyhedron*, 1995, **14**, 1553; (*b*) X. Yao, L. Zheng and X. Xin, *J. Solid. State Chem.*, 1995, **117**, 333; (*c*) K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th edn., John Wiley & Sons, New York, 1986; (*d*) B. J. Hathaway, in *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gill and J. A. McCleverty, Pergamon Press, Oxford, 1987, vol. 5, ch. 53.

13  (*a*) W. H. Watson and W. W. Holley, *Croat. Chem. Acta.*, 1984, **57**, 467; (*b*) W. Bidell, V. Shklover and H. Berke, *Inorg. Chem.*, 1992, **31**, 5561; (*c*) M. Mikuriya, R. Nukada, H. Morishita and M. Handa, *Chem. Lett.*, 1995, 617.

14  (*a*) S. Furberg, J. Grøgaard and B. Smedsrud, *Acta. Chem. Scand. Ser. B*, 1979, **33**, 715; (*b*) J. Scheinbeim and E. Schempp, *Acta Crystallogr., Sect. B.*, 1976, **32**, 607; (*c*) J. Emsley, N. M. Reza, H. M. Dawes and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1986, 313; (*d*) R. W. M. ten Hoedt, J. Reedijk and G. C. Verschoor, *Recl. Trav. Chim. Pays-Bas*, 1981, **100**, 400.

15  O. Kahn, *Molecular Magnetism*, VCH, Weinheim, 1993.

16  (*a*) S. Mitsubori, T. Ishida, T. Nogami and H. Iwamura, *Chem. Lett.*, 1994, 285; (*b*) T. Ishida, K. Nakayama, M. Nakagawa, W. Sato, Y. Ishikawa, M. Yasui, F. Iwasaki and T. Nogami, *Synth. Met.*, 1997, **85**, 1655; (*c*) F. Lloret, G. De Munno, M. Julve, J. Cano, R. Ruiz and A. Caneschi, *Angew. Chem., Int. Ed.*, 1998, **37**, 135; (*d*) T. Ezuhara, K. Endo, K. Matsuda and Y. Aoyama, *New. J. Chem.*, 2000, **24**, 609; (*e*) F. L. Hirshfield, *Acta Crystallogr., Sect. A.*, 1976, **32**, 239; (*f*) L. R. Falvello, *J. Chem. Soc., Dalton Trans.*, 1997, 4463.

17  (*a*) G. A. van Albada, M. T. Lakin, N. Veldman, A. L. Spek and J. Reedijk, *Inorg. Chem.*, 1995, **34**, 4910; (*b*) G. A. van Albada, W. J. J. Smeets, A. L. Spek and J. Reedijk, *Inorg. Chim. Acta.*, 1997, **260**, 151; (*c*) S. Amani Komaei, G. A. van Albada, I. Mutikainen, U. Turpeinen and J. Reedijk, *Eur. J. Inorg. Chem.*, 1998, 1577; (*d*) S. Amani Komaei, G. A. van Albada, I. Mutikainen, U. Turpeinen and J. Reedijk, *Polyhedron*, 1999, **18**, 1991.

18  (*a*) W. C. Velthuizen, J. G. Haasnoot, A. J. Kinneging, F. J. Rietmeijer and J. Reedijk, *J. Chem. Soc., Chem. Commun.*, 1983, 1366; (*b*) F. J. Rietmeijer, R. A. G. de Graaff and J. Reedijk, *Inorg. Chem.*, 1984, **23**, 151; (*c*) E. van der Voort, P. van der Sluis, A. L. Spek and J. L. de Boer, *Acta Crystallogr., Sect. C*, 1987, **43**, 887.