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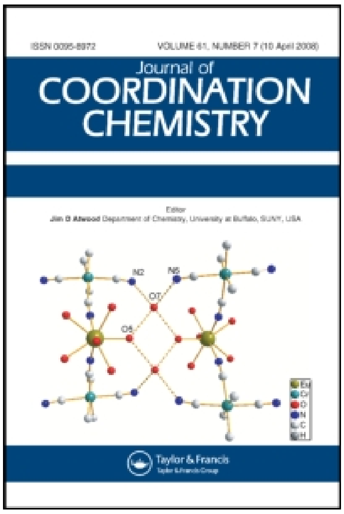

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Synthesis, structure determination, and magnetic properties of pentakis[*bis*(hexafluoroacetylacetonato)1,2,4-triazinecopper(II)]

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Reaction of *bis*(hexafluoroacetylacetonato)copper(II) hydrate with 1,2,4-triazine (tz) in dichloromethane yields pentakis[*bis*(hexafluoroacetylacetonato)triazinecopper(II)] $[Cu(hfac)_2(tz)]_5$ (hfac = hexafluoroacetylacetonate) (**1**). The complex crystallizes in the triclinic space group *P*-1, with cell parameters $a = 11.4124(5)$, $b = 13.3405(5)$, $c = 16.1794(7)$ Å, $\alpha = 93.360(2)^\circ$, $\beta = 108.700(2)^\circ$, $\gamma = 100.293(2)^\circ$ at 120(1) K. In the complex, the copper(II) ions show three types of coordination polyhedra: square planar, square pyramidal, and octahedral (4 + 2). The tz ligand also shows different coordination modes (bridging and monodentate). In addition, disorder is observed in the triazine molecule, either through non-crystallographic two-fold rotation about the longitudinal *N*,*N*-axis, or with respect to a crystallographic center of symmetry. The crystal structure of **1** consists of alternating trimers and dimers. The weak coordination of the tz molecules results in negligible magnetic exchange through the ring.

Keywords: Disorder; 1,2,4-Triazine; Crystal structure; Hexafluoroacetylacetone; Cu(II); Magnetic exchange

1. Introduction

Because of the growing need for solid-state architectures with potential applications as functional materials in fields such as catalysis [1], conductivity [2], zeolitic behavior [3], and magnetism [4], the area of crystal engineering has become one of intense research activity. The syntheses, crystal structures and magnetic study of low-dimensional inorganic solids have received considerable attention from both chemists and physicists over the past few decades, especially as potential materials for testing theories of superconductivity [5]. The magnetic behavior of these materials is highly affected by basic structural parameters such as bond lengths and angles, disorder, lattice packing, *etc*. Magnetic interactions in such samples are highly correlated with the crystal structure and accordingly, different models for magnetic exchange can be designed and tested, including models for dimers, chains, ladders, and layers.

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We are interested in studying the magnetic properties of low-dimensional coordination polymers resulting from the use of different *N*-heterocyclic ligands. Pyrazine and its derivatives are excellent ligands and have been widely used as bridging units in the self-assembly of low-dimensional coordination polymers which show antiferromagnetic properties. Well-known examples include linear chains such as $Cu(pz)(NO_3)_2$ [6] and 2D square layers such as $[Cu(pz)_2](ClO_4)_2$, $[Cu(pz)_2](BF_4)_2$ and $[Cu(pz)_2(NO_3)](PF_6)$ [7, 8]. All of these compounds show Heisenberg-like antiferromagnetic interactions through the bridging pyrazine ligand. The superexchange interactions vary from 11 K (for $Cu(pz)(NO_3)_2$) [6] to 17.5 K (for $[Cu(pz)_2](ClO_4)_2$) [7, 8]. As an extension of this work, we have investigated the use of 1,2,4-triazine (tz) in place of pyrazine, in an attempt to synthesize corresponding linear chain or square layer structures and study their magnetic properties. A new complex, pentakis[*bis*(hfac)(tz)copper(II)] (hfac = hexafluoroacetylacetonate), has been obtained from the reaction of *bis*(hfac)copper(II) hydrate with tz in dichloromethane. Its structure and magnetic properties are reported. To our knowledge, this is the first coordination complex reported with tz as a ligand.

2. Experimental

Starting materials and solvents were purchased from commercial sources and used as received without further purification. The tz was purchased from SynphaBase. IR spectra were recorded on a Perkin Elmer Paragon 500 spectrometer in the spectral range of 4000–450 cm^{-1} with the samples in the form of KBr pellets.

2.1. *Preparation of* $Cu(hfac)_2 \cdot xH_2O$

$Cu(hfac)_2 \cdot xH_2O$ was prepared according to the literature method [9] and used without further purification. m.p.: 120–124°C (134–136°C for the dihydrate, 95–98°C for anhydrous material) [9]. IR: 3683(m), 3563(w), 1645(s), 1612(m), 1563(m), 1536(m), 1467(s), 1255(vs), 1217(s,br), 1148.2(vs), 1108(s), 807(s), 747(m), 680(s), 597(m), 529(w).

2.2. *Preparation of* $[Cu(hfac)_2(tz)]_5$ *(1)*

A solution of tz (0.045 g, 0.56 mmol) in 5.0 ml CH_2Cl_2 was added dropwise to a stirred solution of $Cu(hfac)_2 \cdot xH_2O$ [0.274 g, 0.56 mmol (assuming $x = 1$)] in 12.0 ml CH_2Cl_2. The resulting dark green solution was stirred for another 0.5 h, followed by filtration. Green, rod-shaped crystals were obtained after evaporation of most of the solvent at room temperature over 1 day and the yield was 0.140 g (45.6%). The complex is not stable at room temperature for extended periods of time and attempts to obtain combustion analysis data were unsuccessful. IR (KBr pellet, cm^{-1}): 1648(s), 1562(m), 1534(m), 1471(s), 1429(w), 1370(w), 1256(vs), 1228(s), 1149(vs), 954(w), 867(w), 805(m), 711(w), 680(m), 595(w).

2.3. *X-ray data collection and refinement for (1)*

All operations were performed on a Bruker–Nonius Kappa Apex2 diffractometer using graphite-monochromated Mo-Kα radiation. All diffractometer manipulations, including data collection, integration, scaling and absorption corrections, were carried out using the Bruker Apex2 software [10]. Preliminary cell constants were obtained from three sets of 12 frames. Data collection was carried out at 120 K using a frame time of 10 s and a detector distance of 60 mm. The optimized strategy used for data collection consisted of five phi and two omega scan sets, with 0.5° steps in phi or omega; completeness was 98.5%. A total of 2873 frames were collected. Final cell constants were obtained from the *xyz* centroids of 9903 reflections after integration.

From the systematic absences, the observed metric constants and intensity statistics, space group $P\bar{1}$ was chosen initially; subsequent solution and refinement confirmed the correctness of this choice. The structure was solved via direct methods using SHELXS [11] and refined via least-squares using SHELXL [11]. Hydrogen atoms were placed in calculated positions and refined as a riding model with fixed isotropic values. Some fluorines of the CF_3 groups have large thermal displacements, suggesting disorder in their positions. Attempts at modeling these with disordered positions improved the refinement, but still resulted in some large thermal displacement values. Final refinement was made excluding disorder in the fluorine atoms. The triazine rings are also disordered with respect to the positions of nitrogen atoms and C–H atoms in the rings. For all three rings, the occupancies of the disordered atoms were allowed to refine and in all cases gave 50(2)%. The occupancies were fixed at 50% in the final refinement and the disordered nitrogen and carbon atoms were constrained to reside in the same position with identical thermal parameters. The final least-squares refinement converged to $R_1 = 0.0417$ ($I > 2\sigma(I)$, 10565 data) and $wR_2 = 0.1038$ (F^2, 13030 data, 745 parameters). Details of the data collection parameters and the crystallographic information for **1** are provided in table 1. Selected bond lengths and angles are given in table 2. The structure has been deposited with the CCDC (656111). A Bruker D8 powder X-ray diffractometer was used to verify that powder samples used for magnetic measurements were the same phase as the single crystal.

2.4. *Magnetic data collection*

Magnetic susceptibility data for **1** were collected on a Quantum Design MPMS-XL SQUID magnetometer. The green crystals were powdered and packed into a small gelatin capsule. Powder X-ray diffraction was used to ensure that the material was the same phase as the single crystal structure. The magnetization of the sample was measured as a function of magnetic field from 0 to 50 kOe at 1.8 K; no hysteresis was observed. The moment is linear with applied field to at least 10 kOe at low temperature. The magnetic moment of the sample was then measured from 1.8 to 325 K in a fixed applied field of 1 kOe. The susceptibility data were processed and corrected for diamagnetism of the sample holder, temperature-independent paramagnetism of the Cu(II) ion ($\chi = 60 \times 10^{-6}$ emu mol^{-1}) and for the diamagnetism ($\chi_{\text{dia}} = -186.13 \times 10^{-6}$ emu mol^{-1}) of the constituent atoms using Pascal's constants.

Table 1. Crystal data and structure refinement for **1**.

Experimental formula	$C_{13}H_5F_{12}N_3O_4Cu$
Formula weight	558.74
Cell formula units (Z)	5
Temperature (K)	120(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell parameters (Å, °)	
a	11.4124(5)
b	13.3405(5)
c	16.1794(7)
α	93.360(2)
β	108.700(2)
γ	100.293(2)
Volume (Å^3)	2277.86(16)
Density (Calcd Mg m^{-3})	2.037
Absorption coefficient (mm^{-1})	1.348
F(000)	1365
Crystal size (mm^3)	0.14 × 0.21 × 0.55
θ range for data collection (°)	1.34-30.18
Limiting indices	
	$-16 \leq h \leq 16$
	$-18 \leq k \leq 18$
	$-22 \leq l \leq 22$
Reflections collected	39,223
Independent reflections	13,030
Refinement method	Full-matrix least-squares on F^2
Absorption correction	Multi-scan
Data/restraints/parameters	13030/0/794
Goodness of fit on F^2	1.032
Final R^* indices ($I > 2\sigma(I)$)	$R_1 = 0.0417$, $wR_2 = 0.1038$
Final R^* indices (all data)	$R_1 = 0.0545$, $wR_2 = 0.1114$
Largest diff. peak and hole (e Å^{-3})	1.30 (near F18) and −0.89 (near F14)

3. Results and discussion

The $[Cu(hfac)_2(tz)]_5$ complex (**1**) was prepared by treating the strong Lewis acid, $Cu(hfac)_2$, with triazine in CH_2Cl_2 in a 1 : 1 ratio. Green, rod-like crystals were isolated after slow evaporation overnight and characterized as an air-stable material. The infrared spectrum of the complex displays three strong bands in the range of 1148–1256 cm^{-1}, characteristic of the stretching vibrations of CF_3 groups. The tz shows very weak absorptions at 1429, 1370, 954, 867 and 711 cm^{-1}, similar to those observed for 1,2,4,5-tetrazine (tetz) in the related complex $Cu(hfac)_2$(tetz) [12].

Complex **1** crystallizes in the triclinic space group P-1 as trimeric and dimeric units. Thermal ellipsoid plots of the molecular units of the complex are shown in figures 1 (trimer) and 2 (dimer). Selected bond lengths and angles are listed in table 2. In each unit cell, there are five Cu(II) ions. For each Cu(II), four coordination sites are occupied by four oxygen atoms of the hfac ligands. Bond lengths and angles within the *bis*(hfac)copper(II) moieties are normal and are comparable to the similar reported compounds [12, 13].

Similar to the reported tetrazine complex [12], there are three coordination modes for Cu(II) ions as shown in figure 3. Cu1 is nearly square planar with the four coordination

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

Cu1–O42	1.9413(15)	N14–Cu2–N21	173.88(7)
Cu1–O44	1.9368(15)	N21–Cu2–O52	84.67(7)
Cu2–O52	1.9806(16)	N11–N12/C12–C13	119.9(2)
Cu2–O54	2.0187(16)	C16/N16–N11–N12/C12	117.8(2)
Cu2–O62	2.0149(16)	N12/C12–C13–N14	123.8(2)
Cu2–O64	1.9793(16)	C13–N14–C15	115.1(2)
Cu2–N21	2.282(2)	N14–C15– N16/C16	122.5(2)
Cu2–N14	2.310(2)	C15–N16/C16–N11	120.9(2)
N11–N12/C12	1.332(3)	N22/C22–N21–C26/N26	119.1(3)
C12/N12–C13	1.356(4)	N21–N22/C22–C23	118.7(2)
N14–C13	1.338(3)	N22/C22–C23–N24	124.5(3)
N14–C15	1.325(3)	C23–N24–C25	113.9(3)
C15–C16/N16	1.370(4)	N24–C25–N26/C26	124.2(2)
N16/C16–N11	1.331(3)	C25–C26/N26–N21	119.6(2)
N21–N22/C22	1.318(3)	N31–Cu3–O72	95.00(7)
N22/C22–C23	1.366(5)	N31–Cu3–O74	97.89(7)
C23–N24	1.328(4)	N31–Cu3–O82	94.49(7)
N24–C25	1.328(4)	N31–Cu3–O84	94.83(7)
C25–C26/N26	1.346(4)	N32/C32–N31–C36	117.3(2)
N21–C26/N26	1.336(3)	N31–C32/N32–C36	118.95(19)
Cu3–O72	1.9503(16)	C32–C36–N31	123.7(2)
Cu3–O74	1.9496(16)		
Cu3–O82	1.9508(16)		
Cu3–O84	1.9312(15)		
Cu3–N31	2.286(2)		
N31–C32/N32	1.327(3)		
C32–C36	1.364(3)		
N31–C36	1.337(3)		

Note: [a]Sites containing disordered atoms are labeled with both atoms (i.e. N12/C12).

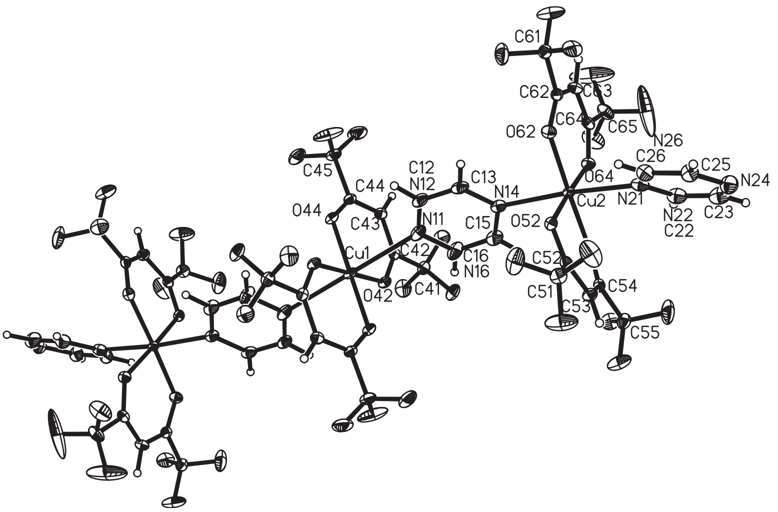


Figure 1. The trimeric unit for Cu(hfac)$_2$(tz) (**1**) showing 30% probability thermal ellipsoids. Only the asymmetric unit is labeled; fluorine and hydrogens have not been labeled for clarity. Cu1 lies on an inversion center. For disordered atoms in the triazine rings, both labels are shown (i.e. C22, N22).

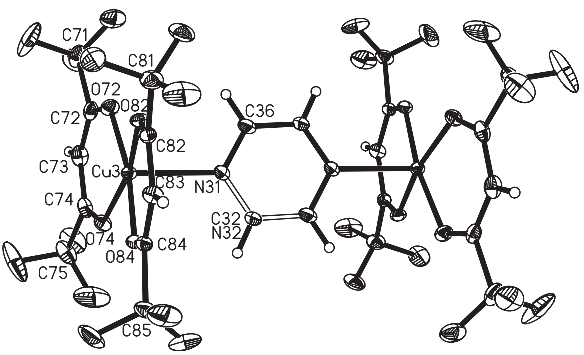


Figure 2. The dimeric unit for Cu(hfac)$_2$(tz) (**1**) showing 30% probability thermal ellipsoids. Only the asymmetric unit is labeled; fluorine and hydrogens have not been labeled for clarity. The center of the triazine ring lies on an inversion center. For disordered atoms in the triazine ring, both labels are shown (C32, N32).

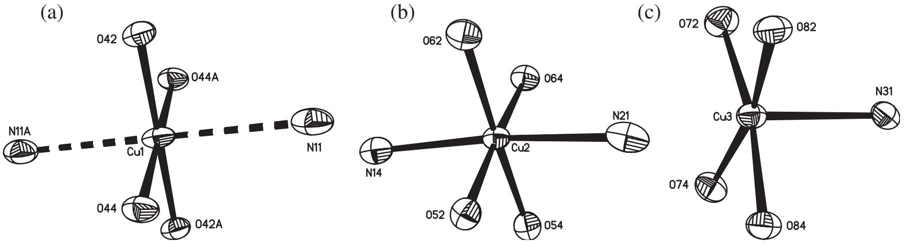
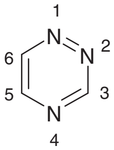


Figure 3. The copper coordination polyhedra in **1**. (a) four coordinate Cu1 with a weak interaction between Cu1 and the nitrogen atoms in the axial direction (denoted by dashed lines); (b) six coordinate Cu2 and (c) five coordinate Cu3.

sites occupied by oxygen atoms from hfac ligands; the metal ion sits on an inversion center. The bond lengths Cu1–O42 and Cu1–O44 are 1.9413(15) and 1.9368(15) Å, respectively, and the angle O42–Cu1–O44 is 92.74(7)°. In the axial direction, the Cu1 ... N11 distance is 2.598(3) Å. Although too long to be considered a conventional bond, the distance is significantly shorter than the sum of the van der Waals radii, suggesting that some interaction exists. This interaction is stronger than the corresponding interaction in the tetrazine complex as measured by the significantly shorter Cu ... N distance [2.817(3) Å for the tetz complex [12], 2.598(3) Å for **1**]. Therefore, the Cu1 coordination polyhedron can be taken as nearly square planar, with weak interactions in the axial direction as shown in figures 1 and 3(a).

As shown in figures 1 and 3(b), the coordination sites of Cu2 are occupied by four oxygen atoms from two hfac ligands and two nitrogens from two triazine rings (one via the proximal N-atom and one via the distal N-atom), forming a tetragonally distorted octahedron. The bond lengths Cu2–O52, Cu2–O54, Cu2–O62 and Cu2–O64 are normal, varying from 1.9793(16) to 2.0187(16) Å, and form the equatorial plane of the octahedron. Along the axial direction, the Cu2–N14 and Cu2–N21 bond lengths [2.310(2) and 2.282(2) Å, respectively] are much longer than typical Cu–N bonds, indicating a Jahn–Teller distortion.



Scheme 1. Numbering sequence for 1,2,4-triazine (tz).

The Cu3 coordination polyhedron is a square pyramid as shown in figures 2 and 3(c). The four equatorial coordination sites are again occupied by four oxygens from two hfac ligands, forming the base of the pyramid with bond lengths varying from 1.9312(15) to 1.9508(16) Å. The triazine ligand is coordinated to the copper center via one of its nitrogens and sits at the apex of the pyramid with a Cu3–N31 bond distance of 2.286(2) Å. As determined by the continuous symmetry measure (CSM) approach [14, 15], the polyhedron is close to a perfect square pyramid, giving $S_{C4v} = 0.206$ [$S_{D3h} = 5.407$ for trigonal bipyramidal]. The triazine ring pushes the two hfac ligands of each Cu3 away from the inversion center, forming an inverted umbrella-like structure in the dimers.

In addition to the variable coordination geometries exhibited by the Cu(II) ions, the triazine ligand itself provides an interesting study in coordination. The tz is a dissymmetric ring in which the nitrogens have different coordination ability because of the unsymmetrical electron distribution within the ring. The ring is labeled as shown in scheme 1. The triazine rings in the complex are labeled as N11 . . ., N21 . . ., and N31 . . . in figures 1 and 2. All three unique triazine rings show disorder in the crystal.

The N11 triazine ring coordinates with Cu2 via N14 as a monodentate ligand. This ring also has a weak interaction with Cu1 through N11 [Cu1 . . . N11 = 2.598(3) Å]. The ring is disordered with respect to the positions of nitrogen and carbon (and the attached hydrogen atom) at positions 12 and 16. Position 12 shows a 50 : 50 occupancy for N12 and C12–H12, while position 16 shows the equivalent disorder for N16 and C16–H16. The N21 triazine ring behaves as a purely monodentate ligand, coordinating to Cu2 through N21. The shortest distance for the other nitrogen atoms in this ring to their next nearest metal ion is greater than 5 Å, too long to be considered as any type of interaction. The ring is disordered in a similar fashion to that of the N11 ring, with the atoms in the 22 and 26 sites sharing positions.

The N31 triazine ring is bidentate bridging coordinating to two symmetry-equivalent copper ions through the two nitrogens at positions 1 and 4 in the ring. In this complex, the N31 triazine ring is located on a crystallographic inversion center and is thus disordered in the structure unit as shown in figure 4. The symmetry of the crystallographic inversion center, compared to the symmetry of the triazine ring, required at least a two-site disorder as shown in figure 4. By comparing corresponding bond lengths and bond angles of similar compounds, such as pyridazine complexes [16], the atoms were assigned as shown in figure 4, with the disordered atoms shown as dotted circles. The triazine rings are nearly planar. The N11 ring shows a mean deviation of 0.0076 Å, while the N21 ring shows a deviation of 0.0043 Å. The rings are canted 34.2(1)° relative to each other and deviate slightly from linearity with respect to the N14–Cu2–N21 bond angle [173.88(7)°]. The N31 ring is planar as required by symmetry.

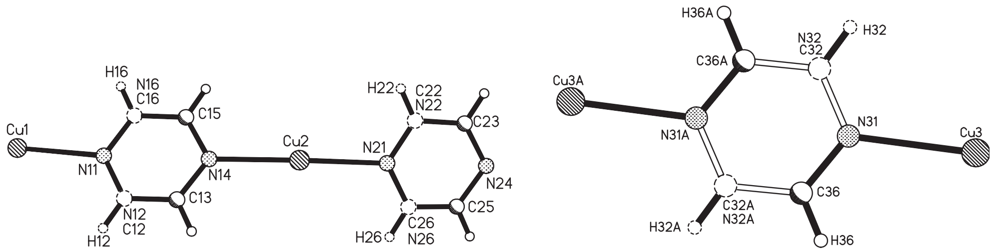


Figure 4. Disorder in the 1,2,4-triazine rings. The N11 and N21 triazine rings show disorder about a two-fold axis connecting the *para*-nitrogen atoms, while the N31 ring is disordered across an inversion center (disordered atoms are shown as dotted circles).

Table 3. Comparison of corresponding coordination bond lengths and weak interactions between copper and nitrogen in complex **1** and its tetrazine analog Cu(hfac)$_2$(tz) [12].

Complex **1** Cu(hfac)$_2$(tz)		Tetrazine analog Cu(hfac)$_2$(tetz)	
Cu1 ··· N11	2.598(3)	Cu3 ··· N14	2.817(3)
Cu2–N21	2.279(3)	Cu2–N22	2.466(3)
Cu3–N31	2.286(2)	Cu1–N11	2.343(3)

There are few reported Cu(II) complexes using substituted tz compounds as ligands [17]. Although all the nitrogen atoms in the triazine ring can potentially serve as donors to form bonds with Cu(II), in virtually all cases these ligands form bonds with Cu(II) using the nitrogen atom at the 2-position of the ring with Cu–N bond distances varying from 1.954 [17e] to 2.120 Å [17b]. In addition, there are a few reports of complexes of substituted tzs where the triazine ring behaves as a bridging ligand via the N1 and N4 atoms [18], or via the N1 and N2 atoms [19], and one where it serves as a monodentate ligand via N4, although in this case it is a requirement of the chelation observed [20]. To our knowledge, complex **1** is the first coordination compound using unsubstituted tz as a ligand. The Cu–N bond distances in **1** are much longer than those seen in complexes using substituted triazine, indicating that tz shows weaker coordination strength. Pyrazine is known to be a weaker base ($pK_a = 0.65$) than pyridine ($pK_a = 5.3$) [21] due to the competing electron-withdrawing character of the two nitrogen atoms in pyrazine ring compared to the single nitrogen atom in pyridine. The tz has three nitrogen atoms dispersing the electron density even further. As a result, triazine is expected to be an even weaker base and poorer electron donor than pyrazine, although better than tetrazine (table 3) [22]. In fact, attempts to prepare related complexes of tz with Cu(acac)$_2$, CuBr$_2$ and CuCl$_2$ were unsuccessful in our laboratory. Similar to its tetrazine analog Cu(hfac)$_2$(tetz) [12], a triazine coordination complex could only be synthesized and isolated with the use of the strong Lewis acid Cu(hfac)$_2$.

Magnetization data as a function of applied field were collected for **1** from 0 to 50 k Oe at 1.8 K. The magnetization of the sample increased linearly with external applied field up to 10 K Oe. Magnetization data as a function of temperature were then

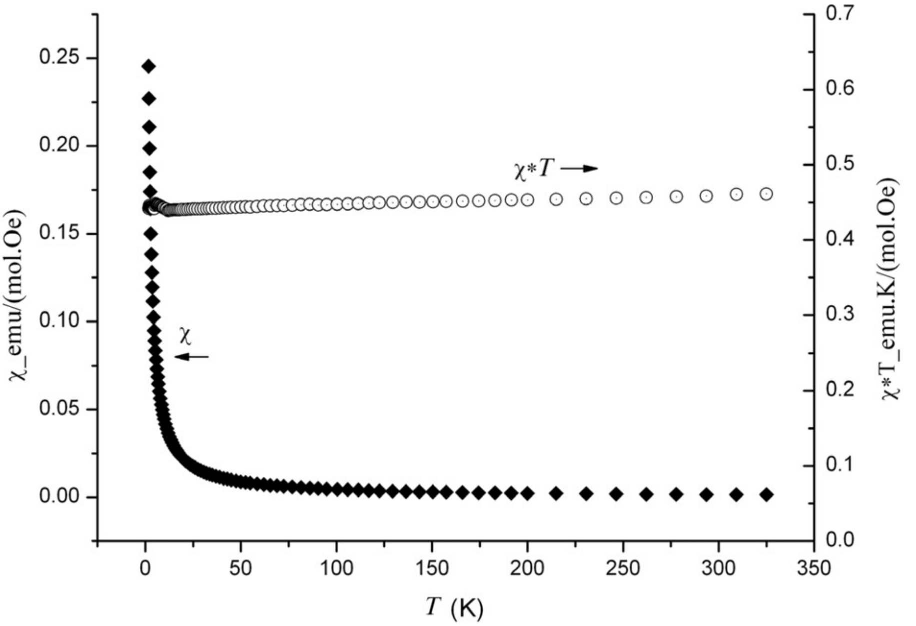


Figure 5. Magnetic susceptibility measurement for **1** (open circle: $\chi * T$ *vs.* T and solid diamond: χ *vs.* T).

collected from 1.8 K to 325 K at a fixed external field of 1000 Oe. Plots of χ *versus* T and χ^*T *versus* T are shown in figure 5.

As we can see from the plot, no maximum is observed in the χ *versus* T curve and the product of χ^*T is virtually a constant over the entire temperature range measured, indicating no significant exchange interactions within the sample. Complex **1** is a simple paramagnetic material; the Cu(II) ions are magnetically isolated one from another. This is not surprising as super-exchange interactions decrease with increasing bond lengths.

4. Conclusion

A new complex of $Cu(hfac)_2(tz)$ (**1**) was synthesized using unsubstituted tz as a ligand. Green crystals were obtained by slow evaporation and the crystal structure was determined. In the structure, the copper(II) shows three types of coordination polyhedra, including square planar, pyramidal and octahedral. Triazine exists both as a monodentate and bidentate ligand in the structure. The packing of **1** consists of alternating trimeric and dimeric units, with disordered tz rings throughout. The long Cu–N coordination bond lengths suggest that tz is a poor ligand, which is supported by the lack of detectable magnetic exchange within the sample. Efforts to enhance the poor donor ability of the triazine ring through the addition of electron-donating ligands are in progress.

Supplementary material

Crystallographic data (atomic coordinates, thermal displacement parameters and a complete list of bond distances and angles) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center with a deposition number 656111. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK or www.ccdc.cam.uk/data_request/cif

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