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Structural studies of copper(II) complexes derived from di-2-pyridyl-ketone, $(py)_2CO$

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ABSTRACT

Reaction of $ArSN{=}C(py)_2$ [Ar = 2,4-dinitrophenyl, $(O_2N)_2C_6H_3$] with $CuCl_2{\cdot}2H_2O$ in DMF yielded the tetranuclear complex $[Me_2NH_2][Cu_4Cl_6\{py_2CO_2\}\{py_2C(OH)O\}]$ (**1**) through metal-catalysed hydrolysis of both DMF and the thiazyl chain. Notably direct reaction of dipyridylketone (py_2CO) with $CuCl_2{\cdot}2H_2O$ in DMF yielded the mononuclear pseudo-octahedral complex $[CuCl_2(py_2C(OH)_2)(DMF)]{\cdot}DMF$ (**2**) in which the 1,1-gem diol, $py_2C(OH)_2$ acts as a tripodal ligand. Heating of **2** in DMF/MeOH promoted aggregation and formation of the polymer $[Cu_2Cl_3\{py_2(OMe)O\}]_\infty$ (**3**). The structures of **1**–**3** were determined by X-ray diffraction.

1. Introduction

The conducting and superconducting properties [1] of poly(sulfur-nitride) $(SN)_x$ promoted the development of many C/S/N heterocycles in the mid-1970s as researchers attempted to include C-functionalised groups into the polymer backbone to facilitate fine-tuning of the electronic properties [2]. These heterocycles themselves have spawned research into the development of neutral radical conductors [3], organic magnets [4] and hetero-spin systems involving thiazyl radicals coordinated to transition metal ions [5]. Some years ago we proposed the use of small fragments of $(SN)_x$ as alternatives to conjugated polyenes with applications as molecular wires [6]. Whilst a number of thiazyl chain oligomers, RS_xN_yR, are known (Fig. 1), these typically exhibit simple aryl or alkyl capping groups unsuitable for metal-binding [7–10]. Nevertheless some thiazyl chains have been shown to bind directly *via* chain hetero-atoms to certain metals [11], or *via* phosphine-capping groups [12]. Recently we reported [13] a potential prototype chelate ligand, $ArS{-}N{=}C(py)_2$ (**L**, Ar = 2,4-$(O_2N)_2C_6H_3$) which offers several potential modes for metal-binding (Fig. 2). Here we report that the imine functionality within **L** is, like other imines, susceptible to hydrolysis [14] and attempted coordination of **L** to $CuCl_2{\cdot}2H_2O$ affords the Cu^{II} complexes, $[Me_2NH_2][Cu_4Cl_6\{py_2C(OH)O\}\{py_2CO_2\}]$ (**1**). Attempts to prepare **1** directly from $CuCl_2{\cdot}2H_2O$ and py_2CO afforded $[CuCl_2\{py_2C(OH)_2\}DMF]\ {\cdot}DMF$ (**2**) and $[Cu_2Cl_3\{py_2C(OMe)O\}]_\infty$ (**3**) (Fig. 3). All three complexes bear ligands derived from dipyridylketone, $py_2C{=}O$. However the tetranuclear complex **1** isolated from reaction of **L** with $CuCl_2{\cdot}2H_2O$ differs substantially from the mononuclear complex **2** isolated from the reaction of dipyridylketone with $CuCl_2{\cdot}2H_2O$ under similar conditions.

2. Experimental

2.1. Chemicals and handling

The reagents $Li[N(SiMe_3)_2]$, Me_3SiCl, py_2CO, $CuCl_2{\cdot}2H_2O$ and 2,4-$(O_2N)_2C_6H_3SCl$ were used as received (Aldrich). The synthesis of ligand **L** was undertaken using standard Schlenk line techniques and anhydrous solvents under an atmosphere of dry nitrogen according to the literature method [13]. Whilst **L** appeared air stable for periods in excess of several weeks and could be crystallised from DMF on the open bench, it was stored and manipulated in a glove box (Saffron Scientific). Subsequent coordination chemistry did not exclude oxygen or water and solvents (DMF and MeOH) were used as received.

2.2. Characterisation methods

NMR spectra were recorded on a Bruker Avance DRX500 Dual Cryoprobe or Bruker Avance DPX400 QNP probe. Microanalytical data were determined by combustion using an Exeter CE-440 elemental analyser and mass spectroscopic data collected on a Kratos MS890-EI instrument. Single crystal X-ray diffraction experiments were performed using a Nonius Kappa CCD diffractometer with monochromatic Mo-Kα radiation equipped with an Oxford cryostream which maintained a temperature of 180(2) K. Raw data

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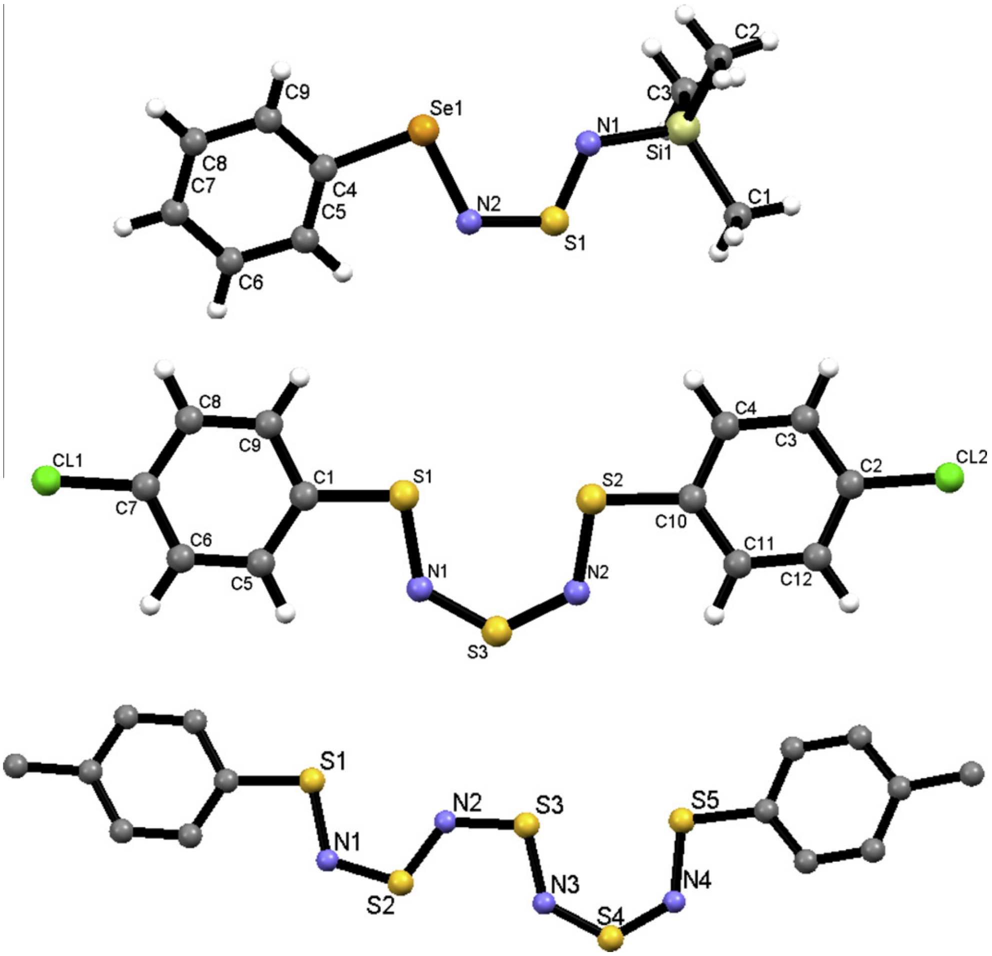

Fig. 1. Crystal structure of selected thiazyl chains; (top) $PhSeNSNSiMe_3$; (centre) (p-$ClC_6H_4)_2S_3N_2$ and bottom; (p-$MeC_6H_4)_2S_5N_4$.

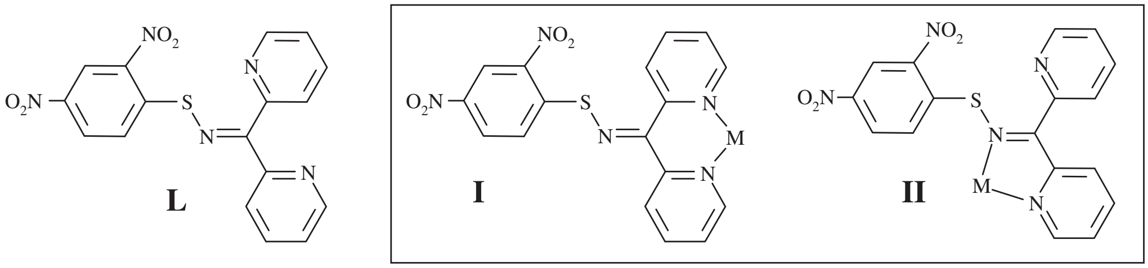

Fig. 2. Structure of ligand **L** (left) and two potential N,N′-coordination modes, **I** and **II** for **L** (right).

were collected [15] and processed using the HKL package and unit cell parameters refined against all data [16]. Structures were solved and refined using the SHELXTL package [17] and were visualised using Mercury [18]. Crystallographic data for complexes **1**–**3** are presented in Table 1. X-band EPR spectra were recorded on a Bruker ER200D EPR spectrometer at room temperature. Simulations of solid state EPR spectra were undertaken using PIP [19] with an in-house windows interface, PIP4WIN (J.M. Rawson, University of Cambridge, 2008).

2.3. Synthesis

2.3.1. Synthesis of 2,4-$(O_2N)_2C_6H_3SN{=}C(py)_2$, L

This compound was prepared according to the literature method [13] but full experimental details are provided here; a solution of dipyridylketone (0.500 g, 2.71 mmol) in Et_2O (15 mL) was added to a solution of Li[N$(SiMe_3)_2$] (0.450 g, 2.69 mmol) in Et_2O (15 mL) and the resultant orange solution stirred for 16 h at room temperature. Me_3SiCl (0.360 mL, 2.85 mmol) was added and the solution stirred for a further 3 h at room temperature. The solution was filtered, dried *in vacuo* and redissolved in CH_2Cl_2 (20 mL). A solution of 2,4-$(O_2N)_2C_6H_3SCl$ (0.680 g, 2.90 mmol) in CH_2Cl_2 (10 mL) was added to give a yellow precipitate of 2,4-$(O_2N)_2C_6H_3SN{=}C(py)_2$ (**L**) which was stirred for a further 18 h to ensure complete reaction prior to filtration and drying *in vacuo*. Yield 0.56 g, 1.47 mmol, 54%. Crystals suitable for X-ray diffraction were obtained by slow evaporation of a DMF solution at 40 °C and the structure reported previously [13]. ^1H NMR (400 MHz, d^7-DMF): $\delta = 9.10$ (d, 8.8 Hz, 1H), 9.03 (d, 2.4 Hz, 1H), 8.97 (dt, 5.2 Hz, 1.2 Hz, 1H), 8.73 (dd, 9.2 Hz, 2.4 Hz, 1H), 8.6 (m, 1H), 8.40 (dt, 8.0 Hz, 1.2 Hz, 1H), 8.08 (m,

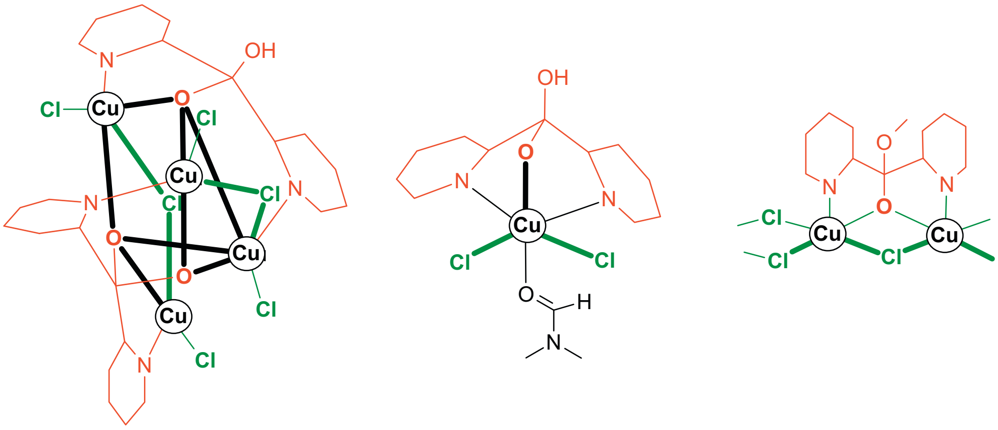

Fig. 3. Structures of copper complexes **1**–**3**.

2H), 7.77 (dt, 8.0 Hz, 1.2 Hz, 1H), 7.58–7.66 (m, 2H); +EI-MS m/z 382.06 (M^+); IR (ν_{max}/cm^{-1}): 1502w ($\nu_{NO2(asym)}$), 1334w ($\nu_{NO2(sym)}$), 1592w ($\nu_{C{=}N}$).

2.3.2. Synthesis of $[Me_2NH_2][Cu_4Cl_6\{py_2C(OH)O\}\{py_2CO_2\}]$ (**1**)

A slightly more than twofold equivalent of **L** (200 mg, 0.60 mmol) was added to a solution of $CuCl_2{\cdot}2H_2O$ (35 mg, 0.26 mmol) in DMF (8 mL). The resultant green solution was stirred at room temperature for 18 h then allowed to stand for 48 h during which time a few blue/green crystals of **1** formed which were suitable for X-ray diffraction but which appeared to decompose over *ca.* 7–14 days. The paucity of crystalline sample precluded other analytical data.

2.3.3. Synthesis of $[CuCl_2\{py_2C(OH)_2\}(DMF)]\cdot DMF$ (**2**)

Dipyridylketone (0.180 g, 0.98 mmol) was added to a solution of $CuCl_2{\cdot}2H_2O$ (0.269 g, 2.01 mmol) in DMF (8 mL). The resultant green solution was stirred at room temperature for 18 h then allowed to stand. After 3 days, large green crystals of **2** had formed (0.110 g, 0.23 mmol, 23%) which proved suitable for X-ray diffraction. *Anal.* Calc. for $C_{17}H_{24}CuCl_2N_4O_4$: C, 42.29; H, 5.01; N, 11.60. Found: C, 42.16; H, 4.93; N, 11.48%; IR (ν_{max}/cm^{-1}) 3354br,m (ν_{OH}), 1648s (ν_{CO}).

2.3.4. Synthesis of $[Cu_2Cl_3\{py_2C(OMe)O\}]_\infty$ (3)

Dipyridylketone (18 mg, 0.10 mmol) was added to a solution of $CuCl_2{\cdot}2H_2O$ (27 mg, 0.20 mmol) in DMF (1 mL) containing two drops of MeOH. The resultant green solution was stirred at room temperature for 2 h and then heated to 40 °C. Slow solvent evaporation at 40 °C resulted in dark green crystals of **3** (37 mg, 0.08 mmol, 80%) suitable for X-ray diffraction. *Anal.* Calc. for $C_{12}H_{11}Cu_2Cl_3N_2O_2$: C, 32.12; H, 2.57; N, 6.24. Found: C, 32.67; H, 2.78; N, 6.51%; IR (ν_{max}/cm^{-1}) 3354br,m (ν_{OH}), 1648s (ν_{CO}).

3. Results and discussion

We have previously reported [13] the synthesis of the thiazyl chain **L** which exhibits the potential to act as an N,N′-chelate ligand

Table 1
Crystal data and structure refinement details for complexes **1**–**3**.

Compound	**1**	**2**	**3**
Formula	$C_{24}H_{25}Cl_6Cu_4N_5O_4$	$C_{17}H_{24}Cl_2CuN_4O_4$	$C_{12}H_{11}Cl_3Cu_2N_2O_2$
FW	914.35	482.84	448.58
CCDC deposit number	890382	890383	890384
Crystal system	orthorhombic	triclinic	triclinic
Space group	$P2_12_12_1$	$P\bar{1}$	$P\bar{1}$
a (Å)	8.4796(3)	7.9062(2)	7.7405(2)
b (Å)	19.0914(6)	9.2306(2)	8.8843(2)
c (Å)	19.5491(7)	14.8078(4)	11.9126(3)
α (°)	90	94.2784(8)	78.2995(11)
β (°)	90	97.1989(2)	76.1188 (11)
γ (°)	90	91.9660(8)	66.9589(10)
V (Å^3)	3164.75(19)	1068.11(5)	726.39(3)
Z	4	2	2
T (K)	180(2)	180(2)	180(2)
D_{calc} (g cm^{-3})	1.919	1.501	2.051
λ (Å)	0.71073	0.71073	0.71073
μ (mm^{-1})	3.199	1.302	3.481
Crystal size (mm)	0.12 × 0.06 × 0.06	0.46 × 0.32 × 0.12	0.32 × 0.16 × 0.10
θ range (°)	3.37–21.97	1.39–27.45	2.91–27.49
Reflections collected	26011	11465	10423
Unique reflections	3811	4840	3313
R_{int}	0.2029	0.0527	0.0580
Parameters	223	261	191
GOF (F^2)	1.126	1.058	1.044
R_1 [$I > 2\sigma(I)$]	0.072	0.0408	0.0347
wR_2 (all data)	0.155	0.1074	0.0917
Flack parameter	0.07(5)	–	–
Peak/hole (e Å^{-3})	+0.57/–0.68	+0.49/–0.82	+0.50/–1.04

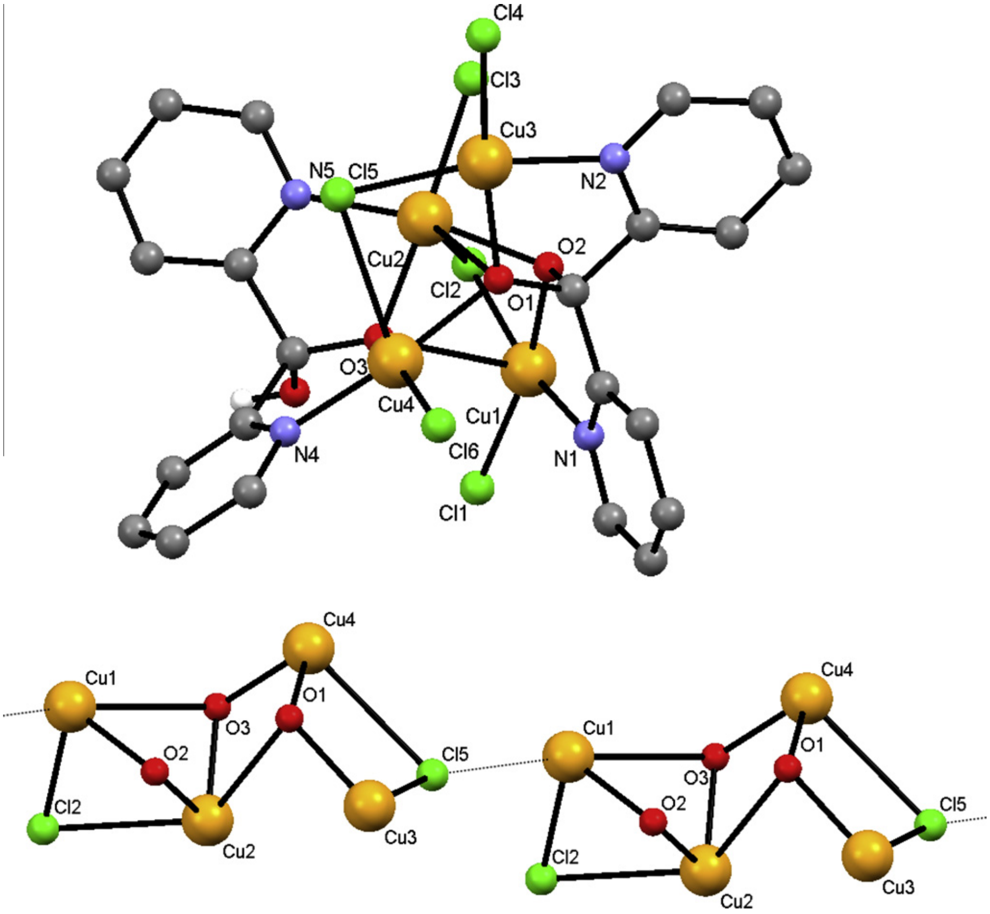

Fig. 4. (Top) Crystal structure of **1** (the $Me_2NH_2^+$ cation and H atoms of the pyridyl rings are omitted for clarity); (bottom) the core structure of **1** highlighting the tetranuclear nature of **1** and the longer inter-cluster contacts (dotted line) linking these tetranuclear units.

in a variety of modes (Fig. 2). Ligand **L** appears air stable in the solid state and crystals suitable for X-ray diffraction were previously grown from 'wet' DMF on the open bench at 40 °C, suggesting that **L** exhibits some stability towards hydrolysis, yet the coordination chemistry of **L** remained unexplored.

In order to probe its potential coordination chemistry, we examined its reaction chemistry with $CuCl_2{\cdot}2H_2O$; when **L** was stirred with $CuCl_2{\cdot}2H_2O$ for 18 h in DMF and then permitted to stand for a further 2–3 days a small number of blue–green crystals of compound **1** formed whose structure was determined by X-ray diffraction to be the tetranuclear complex $[Me_2NH_2][Cu_4Cl_6\{py_2C(OH)O\}\{py_2CO_2\}]$ (**1**) (Fig. 4). The presence of the Lewis acidic copper(II) ion clearly promotes hydrolysis not only of **L** (which otherwise appears stable in DMF) but also some hydrolysis of the solvent itself which acts as a source of the dimethylammonium counter-ion $[Me_2NH_2]^+$.

When attempting to prepare **1** directly from py_2CO and $CuCl_2{\cdot}2H_2O$ in DMF using the crystallographically determined 1:2 ratio under otherwise identical conditions, the mononuclear complex $[CuCl_2\{py_2C(OH)_2\}(DMF)]{\cdot}DMF$ (**2**·DMF) was isolated in moderate yield. The 1,1-gem-diol ligand is generated from hydrolysis of the dipyridylketone, py_2CO. Both hydrolysis [20] and other solvolysis [21] reactions of this ligand have been reported previously leading to a range of polynuclear complexes whose magnetism has been studied extensively. Coordination complexes of the parent dipyridylketone appear more common for the heavier *d*-block elements of the second and third row in which the lower Lewis acidity afforded by the larger size and smaller charge reduces the tendency for solvolysis [22]. In some organometallic complexes, metal coordination appears to activate the ligand to nucleophilic attack at the carbonyl C [23].

An IR spectrum of **2**·DMF revealed a broad OH peak at 3345 cm^{-1} suggesting hydrogen-bonding between a pendant hydroxyl of the $py_2C(OH)_2$ ligand and the DMF solvate which was confirmed by the crystallographic analysis. The room temperature solid state EPR spectrum of **2**·DMF at X-band revealed a broad, near-axial, spectrum with little g-anisotropy ($g_{\parallel} = 2.23$, $g_{\perp} = 2.21$) consistent with significant dipolar line broadening.

The failure of **2** to either aggregate or undergo deprotonation of the $py_2C(OH)_2$ ligand (both processes are required for formation of **1**), prompted us to try and drive aggregation by heating **2** in DMF solution. No clear evidence for reaction was observed upon heating in DMF. However in the presence of trace MeOH, the polymeric complex $[Cu_2Cl_3\{py_2C(OMe)O\}]_\infty$ (**3**) was formed which has previously been characterised by Papadopoulos et al. [24] from the reaction of $CuCl_2{\cdot}2H_2O$ with py_2CO in MeOH. Similar copper-polymers with the $\{py_2(OR)O\}^-$ (R = H, Me, Et) ligands have been reported [25]. The structures of **1**–**3** are described below.

3.1. Crystal structure of 1

Complex **1** crystallises in the acentric orthorhombic space group $P2_12_12_1$ with one molecule in the asymmetric unit. The asymmetric unit of **1** contains four independent copper(II) centres (Fig. 4) with the geometry about each Cu centre summarised in Table 2. Cu(1) is pseudo-six-coordinate, adopting a strongly distorted octahedral geometry (bond angles between 'cis' ligands in the range (69.6–97.1°)) with an axially elongated Cl_3O_2N donor set in which

Table 2
Copper–ligand bond lengths (Å) and angles (°) in complexes **1**–**3**.

Compound 1							
Cu(1)		Cu(2)		Cu(3)		Cu(4)	
Cu(1)–Cl(1)	2.214(5)	Cu(2)–O(2)	1.99(1)	Cu(3)–O(1)	1.94(1)	Cu(4)–Cl(6)	2.217(4)
Cu(1)–Cl(2)	2.290(4)	Cu(2)–Cl(3)	2.237(4)	Cu(3)–Cl(4)	2.238(5)	Cu(4)–O(1)	1.96(1)
Cu(1)–N(1)	2.00(1)	Cu(2)–N(5)	1.97(1)	Cu(3)–N(2)	1.97(1)	Cu(4)–N(4)	1.97(1)
Cu(1)–O(2)	1.97(1)	Cu(2)–O(3)	1.97(1)	Cu(3)–Cl(5)	2.269(5)	Cu(4)–O(3)	1.96(1)
Cu(1)–O(3)	2.75(1)	Cu(2)–O(1)	2.72(1)			Cu(4)–Cl(5)	2.840(4)
Cu(1)–Cl(5)′	3.082(5)	Cu(2)–Cl(2)	2.682(5)				

Compound 2		Compound 3			
Cu(1)		Cu(1)		Cu(2)	
Cu(1)–Cl(1)	2.2775(7)	Cu(1)–Cl(3)	2.2542(7)	Cu(2)–Cl(1)	2.2424(8)
Cu(1)–Cl(2)	2.2791(7)	Cu(1)–Cl(3)′	2.7132(8)	Cu(2)–Cl(1)′	2.7084(8)
Cu(1)–O(2)	2.678(2)	Cu(1)–N(1)	1.997(3)	Cu(2)–Cl(2)	2.325(1)
Cu(1)–N(1)	2.042(2)	Cu(1)–O(1)	1.943(2)	Cu(2)–O(1)	1.963(2)
Cu(1)–N(2)	2.044(2)	Cu(1)–Cl(2)	2.320(1)	Cu(2)–N(2)	1.983(3)
Cu(1)–O(1S)	2.340(2)				

Compound 1							
Cu(1)		Cu(2)		Cu(3)		Cu(4)	
Cl(1)Cu(1)Cl(2)	96.4(2)	Cl(2)Cu(2)Cl(3)	108.6(2)	Cl(4)Cu(3)Cl(5)	95.8(2)	Cl(5)Cu(4)Cl(6)	98.4(2)
Cl(1)Cu(1)N(1)	96.9(4)	Cl(2)Cu(2)O(1)	127.7(2)	Cl(4)Cu(3)O(1)	170.7(3)	Cl(5)Cu(4)O(1)	72.7(3)
Cl(1)Cu(1)O(2)	166.5(3)	Cl(2)Cu(2)O(2)	74.6(3)	Cl(4)Cu(3)N(2)	95.2(4)	Cl(5)Cu(4)N(4)	105.1(4)
Cl(1)Cu(1)O(3)	97.1(3)	Cl(2)Cu(2)N(5)	99.5(4)	Cl(5)Cu(3)O(1)	87.9(3)	Cl(5)Cu(4)O(3)	100.6(3)
Cl(2)Cu(1)N(1)	166.7(4)	Cl(2)Cu(2)O(3)	93.6(3)	Cl(5)Cu(3)N(2)	168.6(4)	Cl(6)Cu(4)O(1)	93.6(3)
Cl(2)Cu(1)O(2)	84.8(3)	Cl(3)Cu(2)O(1)	92.5(2)	O(1)Cu(3)N(2)	80.8(5)	Cl(6)Cu(4)N(4)	96.2(4)
Cl(2)Cu(1)O(3)	85.2(3)	Cl(3)Cu(2)O(2)	92.5(3)			Cl(6)Cu(4)O(3)	160.6(3)
N(1)Cu(1)O(2)	81.9(5)	Cl(3)Cu(2)N(5)	98.7(4)			O(1)Cu(4)N(4)	170.2(5)
N(1)Cu(1)O(3)	92.0(5)	Cl(3)Cu(2)O(3)	157.2(3)			O(1)Cu(4)O(3)	88.5(4)
O(2)Cu(1)O(3)	69.6(4)	O(1)Cu(2)O(2)	56.8(3)			N(4)Cu(4)O(3)	82.5(5)
		O(1)Cu(2)O(3)	69.3(4)				
		O(2)Cu(2)N(5)	168.6(5)				
		O(2)Cu(2)O(3)	88.8(4)				
		N(5)Cu(2)O(3)	81.8(5)				

Compound 2		Compound 3			
Cu(1)		Cu(1)		Cu(2)	
Cl(2)Cu(1)Cl(1)	93.79(3)	Cl(3)Cu(1)Cl(2)	95.44(3)	Cl(2)Cu(2)Cl(1)	96.45(3)
Cl(2)Cu(1)O(2)	104.13(4)	Cl(3)Cu(1)O(1)	176.07(7)	Cl(2)Cu(2)O(1)	81.83(6)
Cl(2)Cu(1)N(1)	175.74(6)	Cl(3)Cu(1)N(1)	98.62(7)	Cl(2)Cu(2)N(2)	156.01(8)
Cl(2)Cu(1)N(2)	91.54(6)	Cl(3)Cu(1)Cl(3)	85.05(3)	Cl(2)Cu(2)Cl(1)	109.29(3)
Cl(2)Cu(1)O(1s)	93.00(5)	Cl(2)Cu(1)O(1)	82.38(6)	Cl(1)Cu(2)O(1)	81.83(6)
Cl(1)Cu(1)O(2)	102.38(4)	Cl(2)Cu(1)N(1)	151.12(8)	Cl(1)Cu(2)N(2)	96.74(8)
Cl(1)Cu(1)N(1)	89.13(6)	Cl(2)Cu(1)Cl(3)	109.52(3)	Cl(1)Cu(2)Cl(1)	86.87(3)
Cl(1)Cu(1)N(2)	170.83(6)	O(1)Cu(1)N(1)	81.99(9)	O(1)Cu(2)N(2)	82.2(1)
Cl(1)Cu(1)O(1s)	97.44(5)	O(1)Cu(1)Cl(3)	98.76(6)	O(1)Cu(2)Cl(1)	101.36(6)
O(2)Cu(1)N(1)	72.17(7)	N(1)Cu(1)Cl(3)	96.78(7)	N(2)Cu(2)Cl(1)	91.37(8)
O(2)Cu(1)N(2)	69.02(7)				
O(2)Cu(1)O(1s)	152.69(6)				
N(1)Cu(1)N(2)	85.17(8)				
N(1)Cu(1)O(1s)	89.70(8)				
N(2)Cu(1)O(1s)	89.72(8)				

the final Cl atom to complete the coordination sphere arises from another tetra-nuclear unit which is symmetry-related *via* translation parallel to *x* (1 + *x*, *y*, *z*). The 'axial' bond lengths Cu(1)–O(3) and Cu(1)–Cl(5)′ (2.75(1) and 3.082(5) Å) are substantially longer than the equatorial distances (1.97(1)–2.290(4) Å) consistent with a substantial Jahn–Teller elongation. Notably the Cu(1)–Cl(5)′ distance is longer than other axially elongated Cu–Cl bonds observed in **1**–**3** (Table 2) and it is arguable whether the geometry is best described as octahedral or square pyramidal. Cu(2) is also six-coordinate but exhibits a Cl_2O_3N donor set. Two of the donor O atoms to Cu(2) are provided by the same ligand leading to a strained 4-membered ring and a more substantial distortion from octahedral symmetry (bond angles at Cu(2) for 'cis' ligands fall in the range 56.8(3)–124.4(5)°). This Cu-centre is also axially elongated along a ClCuO axis. The 'axial' bond lengths Cu(2)–O(1) and Cu(2)–Cl(2) (2.72(1) and 2.682(5) Å) are substantially longer than the equatorial distances (1.97(1)–2.237(4) Å) consistent with a Jahn–Teller elongation. Unlike Cu(1) and Cu(2), Cu(3) is square planar with a Cl_2NO donor set with 'cis' bond angles in the range 80.7(5)–95.8(2)° (sum 359.6°, compared with 360° for a perfectly planar 4-coordinate geometry). Cu(4) exhibits a square-based pyramidal geometry with a Cl_2NO_2 donor set with one Cl atom in the axial position. Again the axial Cu–Cl bond length (2.840(4) Å) is substantially longer than the equatorial distances (1.96(1)–2.217(4) Å). Cu(4) is approximately square-based pyramidal with a τ value of 0.16 (0 for perfectly square pyramidal and 1 for a trigonal bipyramid [26]) and a $CuClNO_2$ square base. The Cu(4)–O bond lengths at 1.96(1) Å are comparable with the Cu(4)–N 1.97(1) Å and are a little shorter than the Cu(4)–Cl(6) bond length (2.217(4) Å). The axial Cu(4)–Cl(5) bond length is markedly longer at 2.840(4) Å. Notably each Cu^{II} centre is N,O-chelated by a $py_2C(OH)O^-$ or $\{py_2CO_2\}^{2-}$ ligand with a Cl located *trans* to the O donor. A combination of bridg-

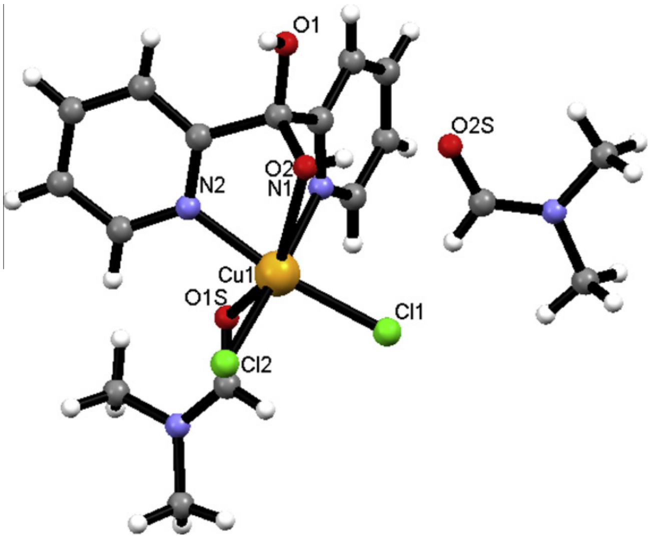

Fig. 5. Asymmetric unit of **2** including hydrogen-bonded DMF solvate molecule.

ing μ$_2$- and μ$_3$-O atoms plus μ$_2$-Cl atoms link the four cupric ions together. With one $py_2CO_2^{2-}$ and one $py_2C(OH)O^-$ ligand along with six Cl^- ions, the net negative charge on the complex is charge balanced by an $Me_2NH_2^+$ counterion (formed by hydrolysis of DMF) which is weakly hydrogen bonded to the μ$_2$-O atom O(2) and Cl(4).

These tetranuclear clusters are additionally linked via longer Cu–Cl···Cu μ$_2$-bridges (Cu(1)...Cl(5) at 3.082(5) Å) generating a one-dimensional polymer structure (Fig. 4, bottom).

3.2. Crystal structure of 2

Complex **2** crystallises in the triclinic space group $P\bar{1}$ with one molecule of **2** and a DMF solvent molecule in the asymmetric unit (Fig. 5). The copper(II) centre occupies a distorted octahedral environment (cis bond angles fall in the region 69.02–102.34°) with a hydroxyl group of the $py_2C(OH)_2$ ligand and the DMF O-atom located in the axially-elongated positions (Table 2).

The tridentate N,N′,O coordination geometry of **2** is similar to a number of other mononuclear copper(II) complexes of the neutral $py_2C(OH)_2$ ligand which have previously been reported in which the $py_2C(OH)_2$ ligand invariably acts as a tridentate N_2O donor [27]. The DMF lattice solvent appears hydrogen-bonded to the complex (O(2)···O(2S) = 2.711(3) Å).

3.3. Crystal structure of 3

Complex **3** also crystallises in the triclinic space group $P\bar{1}$ with two five-coordinate copper(II) ions in the asymmetric unit. There are three crystallographically independent Cl^- ions and a $py_2C(OMe)O^-$ ligand which exhibits an unusual N,N′,μ$_2$-O bridging mode between the two metal ions (Fig. 6), compared to **2** (above). The geometry at both Cu(1) and Cu(2) appear intermediate between square-based pyramidal and trigonal bipyramidal based

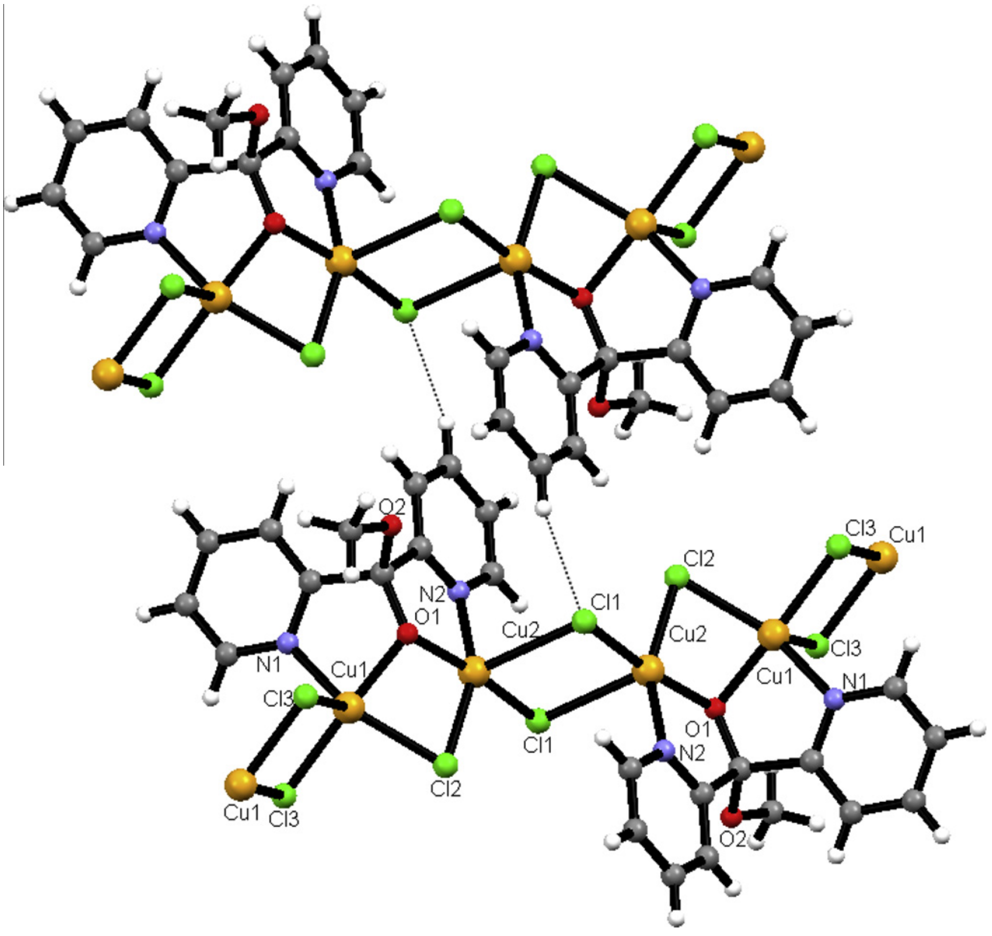

Fig. 6. Part of the polymeric structure of **3**, $[Cu_2Cl_3(py_2C(OMe)O)]_\infty$, illustrating interchain Cl...H contacts.

on Addison's τ values; τ = 0.42 for Cu(1) and 0.26 for Cu(2) (τ = 1.0 for trigonal bipyramidal and 0.0 for square-based pyramidal [26]), suggesting Cu(2) adopts a geometry somewhat closer to square-based pyramidal. In both cases one Cu–Cl bond length is substantially longer than the others, consistent with a Jahn–Teller elongation of the five-coordinate geometry.

The structure of **3** has been reported previously [24] along with several other halo- and pseudo-halogen variants and alkoxy derivatives [25]. The one-dimensional polymeric chains are linked via weak C–H…Cl contacts (C(23)…Cl(1) at 3.440(4) Å, C–H…Cl 131.5(2)°, Fig. 6).

4. Conclusions

Whilst the thiazyl ligand $py_2C{=}NSAr$ appears air and moisture stable both in the solid state and in solution, the presence of a Lewis-acidic metal appears to promote hydrolytic decomposition, leading to isolation of the tetranuclear complex $[Me_2NH_2][Cu_4Cl_6\{py_2C(O)OH\}(py_2CO_2)]$ (**1**). Whilst it is not clear why complex **1** cannot be accessed directly from $CuCl_2{\cdot}2H_2O$, DMF and dipyridylketone, both mononuclear (**2**) and polymeric (**3**) copper complexes can be isolated in this fashion. Further studies with milder Lewis acidic metal complexes are required to probe the potential of **L** as a ligand to metal ions and these are currently underway.

Appendix A. Supplementary data

CCDC 890382–890384 contains the supplementary crystallographic data for **1**–**3**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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