Dalton
Transactions

Cite this: *Dalton Trans.*, 2011, **40**, 847

www.rsc.org/dalton

PAPER

Unexpected multiple bond cleavage and rearrangement of organosulfide ligands in the presence of Cu(II) assisted by solvothermal and solvothermal-microwave conditions†

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Received 6th August 2010, Accepted 18th October 2010
DOI: 10.1039/c0dt00973c

An unprecedented *in situ* multiple bond cleavage of S–S, S–C(sp^2) and C–N in the pyrimidinedisulfide (pym$_2$S$_2$) ligand is observed by the reaction of $CuCl_2 \cdot 2H_2O$ with this ligand under solvothermal and solvothermal-microwave conditions. In this process the formation of the compound [Cu^{II}(μ-Cl)(Cl)L]$_2$, where L represents the new ligand (L = 2-(pyrimidin-2-ylamino)-1,3-thiazole-4-carbaldehyde), is observed. This ligand has been further isolated and X-ray characterized. The similar reaction carried out under solvothermal-microwave conditions gives, in addition to the latter compound, the complex {9·[Cu(pym$_2$S$_3$)(μ-Cl)(Cl)]$_2$·[Cu(pym$_2$S$_2$)(μ-Cl)(Cl)]$_2$}. Coordination of a pyrimidinetrisulfide ligand (pym$_2$S$_3$) is reported for the first time. This work represents an illustrative example of the novel synthetic perspectives attainable *via* solvothermal-microwave procedures.

Introduction

The design and synthesis of novel coordination architectures with *in situ* generated ligands (especially those that are inaccessible by direct preparation) is a topic of great interest in coordination and organic chemistry for both discovering new organic reactions and understanding their mechanism.[1]

A large number of structures of coordination compounds reported to date have been prepared under hydro- or solvothermal conditions by *in situ* metal/ligand reactions in the presence of transition-metal ions. In few cases unexpected chemical, structural and/or compositional changes in the organic ligands occur during the reaction process.[2] Microwave and solvothermal-microwave-assisted synthesis might dramatically reduce the reaction time and this simple and energy-efficient process has become a rapidly developing synthetic method. Although microwave is fairly common for organic syntheses,[3] examples of coordination compounds prepared by this procedure are still very scarce.[4]

On the other hand, organosulfides exhibit versatile binding modes in their coordination to metal ions.[5] In addition, they show a rich redox chemistry[6] based on both oxidative formation and reductive cleavage of the disulfide bonds, which has been explored as an attractive route towards functional ligands and novel materials. In some cases metal–sulfur containing compounds are useful as structural models of biological systems.[7] Although the *in situ* cleavage of S–S or both S–S and S–C(sp^2) bonds in dithiodipyridine ligands have been recently observed under solvothermal conditions in the presence of Co^{2+} or Cu^{2+} ions,[6d,8] the cleavage of S–S, S–C(sp^2) and N–C(sp^2) bonds has not been reported.

In this paper, we deal with the study of the reaction between $CuCl_2$ and bis(2-pyrimidyl)disulfide (pym$_2$S$_2$) under solvothermal and solvothermal-microwave-assisted conditions. The adjustment of the hydrothermal and solvothermal-microwave synthetic conditions leads to an unprecedented *in situ* multiple bond cleavage of S–S, S–C(sp^2) and C–N in the pyrimidinedisulfide (pym$_2$S$_2$) ligand leading to [Cu^{II}(μ-Cl)(Cl)L]$_2$ dimer formation, where L represents a novel 2-(pyrimidin-2-ylamino)-1,3-thiazole-4-carbaldehyde ligand. The complex {9·[Cu(pym$_2$S$_3$)(μ-Cl)(Cl)]$_2$·[Cu(pym$_2$S$_2$)(μ-Cl)(Cl)]$_2$} has also been isolated when the process was carried out under specific solvothermal-microwave conditions. This work describes an example of the potential use of novel synthetic perspectives attainable *via* solvothermal-microwave procedures.

Experimental

Materials

All chemicals were of reagent grade and were used as commercially obtained. The bis(2-pyrimidyl)disulfide ligand was prepared according to the published procedure.[9] FTIR spectra (KBr pellets) were recorded on a Perkin-Elmer 1650 spectrophotometer. Elemental analyses were performed on a Perkin-Elmer 240 B

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† CCDC reference numbers 781619–781621. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt00973c

microanalyzer. ESI-MS spectra were recorded on a mass spectrometer with a QTOF analyzer mode QSTAR pulsar (Applied Biosystems). The microwave oven used for synthesis was an Ethos Synth Lab Station, Milestone Inc. equipped with a PRO-16 rotor (Milestone Inc.). The multimode microwave has a twin magnetron (2 × 800 W, 2.45 GHz) with a maximum delivered power of 1000 W. During the experiments, time, temperature and power were controlled with the "easyWAVE" software package. An advanced fiber-optic temperature sensor (ATC-FO, Milestone Inc.) allowed direct monitoring of the internal temperature; the fibre-optic probe was inserted into a thermowell of the reference vessel. This thermowell warrants optimal thermal exchange with the reaction mixture, yet isolates the probe from physical contact with the media inside the vessel.

Magnetic measurement was performed on a Quantum Design SQUID susceptometer covering the temperature range 5.0–300 K at a magnetic field of 1000 G.

Preparations

Solvothermal synthesis of $[Cu^{II}(\mu\text{-}Cl)(Cl)L]_2$ (1). A mixture of $CuCl_2{\cdot}2H_2O$ (0.088 g, 0.52 mmol) and pym_2S_2 (0.115 g, 0.52 mmol) in 26 mL of CH_2Cl_2–CH_3CN (1 : 1), was fully stirred at room temperature for 30 min, sealed in a 30 mL Teflon-lined autoclave and heated at 90 °C for 20 h. Then, the autoclave was slowly cooled (2.5 °C h^{-1}) to ambient temperature.

Green crystals of **1** were obtained from solution, after the filtrate was allowed to stand in a refrigerator (0 °C) for 2 weeks, washed with Et_2O and dried in air (0.090 g, 51% yield, based on Cu) together with crystals of elemental sulfur (crystal data for S_8: orthorhombic, space group *Fddd*, $a = 10.464(4)$ Å, $b = 12.851(5)$ Å, $c = 24.51(1)$ Å, $V = 3296(2)$ Å^3).

Anal. Calc. for **1** $C_{16}H_{12}Cl_4Cu_2N_8O_2S_2$: C, 28.20%, H, 1.78%, N, 16.45%, S, 9.41%. Found: C, 27.58%, H, 1.99%, N, 16.61%, S, 9.36%. IR selected data (KBr, cm^{-1}): 1661 (vs), 1653 (vs), 1603 (vs), 1561 (vs), 1529 (vs), 1496 (s), 1442 (vs), 1408 (vs), 1225 (s), 1165 (s), 891 (w), 786 (m), 627 (m), 527 (m).

When a solution of **1** in CH_3CN was treated with the Chelex resin for 2 h, the 2-(pyrimidin-2-ylamino)-1,3-thiazole-4-carbaldehyde ligand, compound **3**, was isolated and characterized. ^1H NMR (300 MHz. DMSO-d_6): δ 12.52 (s, 1H, NH), 9.98 (s, 1H, aldehyde), 8.75 (d, J = 4.5 Hz, 2H, pyrimidin), 8.37 (s, 1H, thiazole), 7.17 (t, J = 4.5 Hz, 1H, pyrimidin). IR selected data (KBr, cm^{-1}): 1642 (vs), 1601 (vs), 1579 (vs), 1550 (vs), 1517 (vs), 1452 (vs), 1442 (vs), 1399 (vs), 1229 (s), 1167 (vs), 816 (s), 697 (s), 660 (m), 627 (s).

Solvothermal microwave synthesis of $\{9{\cdot}[Cu(pym_2S_3)(\mu\text{-}Cl)(Cl)]_2{\cdot}[Cu(pym_2S_2)(\mu\text{-}Cl)(Cl)]_2\}$ (2). $CuCl_2{\cdot}2H_2O$ (0.054 g, 0.32 mmol) and pym_2S_2 (0.071 g, 0.32 mmol) in 16 mL of CH_2Cl_2–CH_3CN (1 : 1) were placed in a 70 mL Teflon leaned vessel, sealed and sited into a microwave oven equipped with a rotor. The multimode microwave has a twin magnetron (2 × 800 W, 2.45 GHz) with a maximum delivered power of 1000 W. The temperature was increased from room temperature to 90 °C in 20 min (microwave power was set at 350 W) and kept for 1 h. Then, the vessel was slowly cooled down to room temperature in 9 h. Green crystals of **1** were obtained from the filtrate after it was allowed to stand in a refrigerator (0 °C) for 2 weeks, together with deep green crystals of **2**, which were manually separated, then washed with EtO_2 and dried in air (**1**: 0.044 g 40% yield, based on Cu; **2**: 0.005 8% yield, based on Cu).

Anal. Calc. for **2** $C_{16}H_{12}Cl_4Cu_2N_8S_{5.8}$: C, 24.92%, H, 1.57%, N, 14.53%, S, 24.12%. Found: C, 25.01%, H, 1.60%, N, 14.47%, S, 24.09%. IR selected data (KBr, cm^{-1}): 3063 (w), 1571 (s), 1552 (s), 1384 (vs), 1170 (m), 820 (m), 761 (m), 745 (m), 639 (m).

X-Ray data collection and structure determination†

Crystal data were collected on a Bruker SMART 6 K CCD diffractometer (Mo-Kα radiation for compounds **1** and **2**, and Cu-Kα radiation for compound **3**). Data reduction and cell refinement were carried out using the DENZO and SCALEPACK[10] programs. The structure was solved by standard Patterson methods[11] and refined by full-matrix least-squares methods based on F^2 using the SHELXTL-PLUS,[12] SHELXL-97[13] and WinGX[14] programs. The refinement of the structural model of **2** indicates the existence of a random mixture of bis(2-pyrimidyl)disulfide and bis(2-pyrimidyl)trisulfide. Two substantial maxima in the difference Fourier map were found at a distance of *ca.* 2.0 Å between them and *ca.* 1.8 Å from atoms C1 and C6. The constrained refinement of the disulfide and trisulfide ligands indicated that only 10% of bis(2-pyrimidyl)disulfide is present in the compound. The sum of the occupancy parameters of the two terminal ligands was constrained to be 1.0. The bond distances within the aromatic rings of compound **2** were restrained to be similar in bis(2-pyrimidyl)disulfide and bis(2-pyrimidyl)trisulfide ligands.

All non-hydrogen atoms were refined anisotropically in compounds **1** and **3**. The mentioned disorder in compound **2** did not allow the anisotropic refinement of the carbon and nitrogen atoms. All hydrogen atoms were included in geometrically calculated positions and refined isotropically according to the riding model. Crystal data, data collection and refinement parameters for compounds **1–3** are summarized in Table 1.

Results and discussion

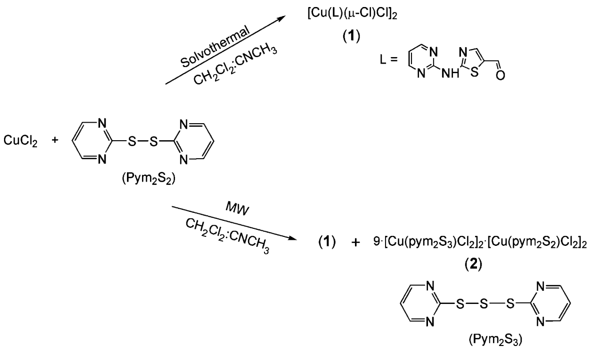
The treatment of $CuCl_2{\cdot}2H_2O$ with pyrimidinedisulfide (pym_2S_2) in CH_2Cl_2–CH_3CN under solvothermal conditions (90 °C, 20 h) leads to the formation of a green crystalline solid characterized as $[Cu^{II}(\mu\text{-}Cl)(Cl)L]_2$ (L = 2-(pyrimidin-2-ylamino)-1,3-thiazole-4-carbaldehyde) (**1**). The same reaction carried out under solvothermal-microwave conditions (90 °C, 1 h) gives compound **1** together with $\{9[Cu(pym_2S_3)(\mu\text{-}Cl)(Cl)]_2{\cdot}[Cu(pym_2S_2)(\mu\text{-}Cl)(Cl)]_2\}$ (**2**) (Scheme 1). Similar results are obtained when the reaction proceeds under milder (60 °C, 1 h) or stronger (90 °C, 3–20 h) solvothermal-microwave-assisted conditions. All these processes produce pale-yellow orthorhombic crystals of elemental sulfur S_8 as a by-product and formation of SO_4^{2-} anions was inferred from the solutions analysis.

The crystal structure of compound **1** consists of centrosymmetric double chloro-bridged copper(II) dimeric entities. The *in situ* formed 2-(pyrimidin-2-ylamino)-1,3-thiazole-4-carbaldehyde molecule is coordinated to the metal centre through its N1 and N2 atoms to establish a six-membered chelating ring. The value of the bite angle is 86.67(7)°. Two bridging and one terminal chlorido anions are also coordinated to the metal centre and complete its $CuCl_3N_2$ coordination environment. The bridging chlorido

Table 1 Single-crystal data and structure refinement details

	1	**2**	**3**
Formula	$C_{16}H_{12}Cl_4Cu_2N_8O_2S_2$	$C_{16}H_{12}Cl_4Cu_2N_8S_{5.8}$	$C_8H_6N_4OS$
Mr	681.34	771.11	206.23
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P21/c$	$P21/c$	$P21/c$
a/Å	9.8830(5)	11.9670(6)	5.4675(4)
b/Å	9.6562(5)	6.8657(4)	21.7393(16)
c/Å	12.5052(7)	16.9169(8)	8.3532(5)
β/°	112.968(3)	110.541(3)	120.377(4)
V/Å^3	1098.79(10)	1301.55(12)	856.56(10)
Z	2	2	4
D_{calc}/Mg m^{-3}	2.059	1.984	1.599
Crystal size/mm	0.15 × 0.10 × 0.05	0.21 × 0.10 × 0.09	0.10 × 0.08 × 0.05
Color	Blue	Blue	Colourless
F(000)	676	765.5	424
μ/mm^{-1}	2.648	2.553	3.124
R_{int}	0.0375	0.0589	0.0325
Reflns. collected	26 132	20 691	10 249
Reflns. independent	2845	3681	1612
Reflns.unique [$I > 2\sigma(I)$]	2406	3144	1554
Parameters	154	171	127
GOF/S^a	1.071	1.170	1.116
R_1/wR_2[$I \geq 2\sigma(I)$]^b	0.0248/0.0600	0.0475/0.1147	0.0313/0.0840
R_1/wR_2[all data]^b	0.0349/0.0651	0.0576/0.1189	0.0323/0.0852

^{a} $S = [\sum w(|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$. ^{b} $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$; $wR_2 = \sum w(F_o^2 - F_c^2)^2/\sum w|F_o|^2]^{1/2}$.



Scheme 1 Schematic synthetic procedures.

anions are coordinated to the two copper atoms in an asymmetric fashion with significantly different bond lengths: 2.2751(6) and 2.5754(6) Å, caused by the active Jahn–Teller distortion of the copper(II) ion. A drawing of the dimer structure showing the labelling scheme is given in Fig. 1. Selected bond lengths and angles are reported in Table 2.

Table 2 Selected bond distances (Å) and angles (°) for compound **1**

Cu1–N1	1.977(2)	N1–Cu1–N2	86.67(7)
Cu1–N2	2.079(2)	N1–Cu1–Cl1	91.61(5)
Cu1–Cl1	2.5754(6)	N1–Cu1–Cl2	89.02(5)
Cu1–Cl2	2.3163(6)	N1–Cu1–Cl1^i	178.43(5)
Cu1–Cl1^i	2.2751(6)	N2–Cu1–Cl1	104.22(5)
		N2–Cu1–Cl2	150.90(5)
		N2–Cu1–Cl1^i	93.32(5)
		Cl1–Cu1–Cl2	104.66(2)
		Cl1–Cu1–Cl1^i	89.92(2)
		Cl1^i–Cu1–Cl2	90.23(2)
		Cu1–Cl1–Cu1^i	90.08(2)

Symmetry code: (i) $-x + 1, -y, -z$.

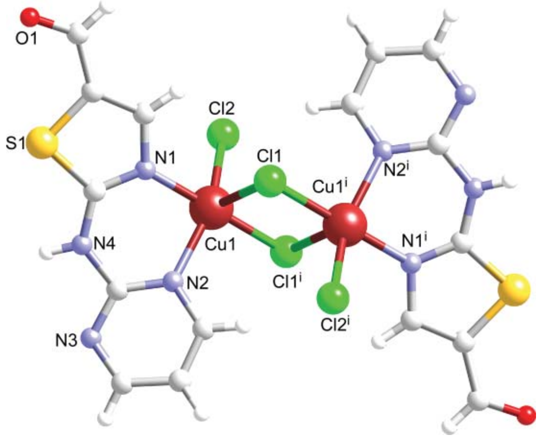


Fig. 1 View of dimeric entity in compound **1**, showing the atom labelling scheme.

The penta-coordination of Cu(II) is very common and usually presents either a square-pyramidal or a trigonal-bipyramidal geometry (or any of the distorted intermediate geometries). The geometry of the $CuCl_3N_2$ chromophore can be quantitatively characterised using the parameter τ, as defined by Addison *et al.*[15] The calculated value of τ = 0.46 (relative to one for a regular trigonal bipyramid and zero for a square pyramid) indicate that the coordination geometry around the metal centre, although intermediate between the two ideal polyhedrons, is closer to an elongated tetragonal pyramid with chlorido anions placed alternatively on equatorial and apical positions. As a result, the geometry of the complex consists of two square pyramids sharing one base-to-apex edge, with parallel basal planes.[16] The copper atom is displaced from the mean equatorial plane towards the corresponding axial chlorido bridging atoms by 0.287 Å.

Table 3 Selected bond distances (Å) and angles (°) for compound **2**

Cu1–Cl1	2.2760(9)	Cu1–Cl2	2.2705(10)
pym$_2$S$_3$		***pym$_2$S$_2$***	
Cu1–N1	2.050(4)	Cu1–N1A	2.115(12)
Cu1–N3	2.062(4)	Cu1–N3A	2.119(14)
Cu1–S2	2.6616(11)	Cu1–S2A	2.689(10)
		Cu1–Cl1^{i}	2.7545(10)
Cl1–Cu1–Cl2	94.97(4)	Cl1–Cu1–Cl1^{i}	85.65(3)
		Cl12–Cu1–Cl1^{i}	93.44(3)
pym$_2$S$_3$		***pym$_2$S$_2$***	
N1–Cu1–N3	88.8(2)	N1A–Cu1–N3A	88.1(8)
N1–Cu1–S2	84.58(13)	N1A–Cu1–S2A	82.4(6)
N1–Cu1–Cl1	177.17(17)	N1A–Cu1–Cl1	173.6(7)
N1–Cu1–Cl2	86.87(16)	N1A–Cu1–Cl2	89.6(7)
N1–Cu1–Cl1^{i}	96.40(13)	N1A–Cu1–Cl1^{i}	98.6(6)
N3–Cu1–S2	85.12(10)	N3A–Cu1–S2A	63.6(6)
N3–Cu1–Cl1	89.12(11)	N3A–Cu1–Cl1	87.0(5)
N3–Cu1–Cl2	171.07(10)	N3A–Cu1–Cl2	175.0(4)
N3–Cu1–Cl1^{i}	94.78(10)	N3A–Cu1–Cl1^{i}	91.3(5)
S2–Cu1–Cl1	93.37(3)	S2A–Cu1–Cl1	90.73(19)
S2–Cu1–Cl2	86.71(4)	S2A–Cu1–Cl2	111.7(2)
S2–Cu1–Cl1^{i}	179.01(3)	S2A–Cu1–Cl1^{i}	154.8(2)

Symmetry code: (i) $-x$, $-y$, $-z$. pym$_2$S$_3$ = bis(2-pyrimidyl)trisulfide; pym$_2$S$_2$ = bis(2-pyrimidyl)disulfide.

Within the Cu(μ-Cl)$_2$Cu core, the Cu–Cu distance of 3.4387(5) Å is close to the average value for chlorido bridged copper(II) dimers (3.476 Å) in CSD.[17] The Cu$_2$Cl$_2$ core corresponds to an almost ideal square as reflected from the Cl–Cu–Cl and Cu–Cl–Cu bond angles of 89.92 and 90.08°, respectively. Moreover, the small Cu–Cl–Cu angle plays an important role in determining the magnetic coupling within the dimer.

The dimeric entities assemble together by means of N–H···Cl hydrogen bonds to give rise to 1D supramolecular chains which are further connected through weak C–H···N/O hydrogen bonds to provide the overall 3D cohesiveness to the crystal structure. No evidence of Cl···Cl contacts has been observed.

The crystal structure of compound **2** is closely related to that of compound **1**. It consists of centrosymmetric double chlorido-bridged copper(II) dimeric entities by using the *in situ* generated pym$_2$S$_3$ ligand as both terminal and blocking ligand. The similar coordination capability of the disulfide and trisulfide analogous allows the randomly partial substitution of the pym$_2$S$_3$ ligand for the initial pym$_2$S$_2$ molecule, with 90 and 10% occupation rates, respectively (Fig. 2). Selected bond lengths and angles are reported in Table 3.

The CuCl$_3$N$_2$S chromophore of copper(II) ion exhibits the typical tetragonally elongated octahedron, with two *trans* axial bonds distances [Cu–Cl1^{i}: 2.7545(10) and Cu–S2/S2A: 2.6616(11)/2.689(10) Å] substantially longer than the equatorial ones (*ca.* 2.27 Å for chlorido atoms and 2.05–2.12 Å for the nitrogen atoms, respectively). The pym$_2$S$_3$ ligand is *fac*-coordinated to the metal centre through three donor positions: N1, S2 and N3. Although this coordination mode generates two equivalent and robust five membered chelate rings for pym$_2$S$_3$, in the case of pym$_2$S$_2$ a strained four membered chelate ring is present. This could be the reason for Cu–N bond distances established with the pym$_2$S$_2$ ligand (*ca.* 2.12 Å) being longer than with pym$_2$S$_3$ (*ca.* 2.06 Å). The bridging chlorido anions are coordinated asymmetrically with significantly different bond lengths: 2.2760(9) and 2.7545(10) Å. Within the Cu(μ-Cl)$_2$Cu core, the Cu–Cu distance is 3.7040(9) Å, and the Cl–Cu–Cl and Cu–Cl–Cu bond angles are 85.65(3)° and 94.35(3)°, respectively.

The supramolecular crystal structure is based on an intricate network of S···S contacts (3.26 Å), weak C–H···Cl hydrogen bonds and parallel face-to-face interactions among the pyrimidine rings: interplanar distance of 3.17 Å and lateral offset of 2.27 Å for pym$_2$S$_3$.

The formation of **1** implies cleavage of the S–S, S–C(sp^2) and N–C(sp^2) bonds in the pym$_2$S$_2$ ligand. Inspection of all the solutions of the solvothermal processes by means of ESI-MS spectrometry show two peaks at *m/z* 223.01 and 159.07, assigned to the monoprotonated cations of the pym$_2$S$_2$ and 2,2′-bipym ligands, respectively, and three peaks at *m/z* 252.96, 284.93 and 317.08 assigned to radical cations [Cu(pym$_2$S)]$^{\bullet+}$, [Cu(pym$_2$S$_2$)]$^{\bullet+}$ and [Cu(pym$_2$S$_3$)]$^{\bullet+}$, respectively. These data, together with the presence of S$_8$ and SO$_4^{2-}$ as by-products, suggest an intricate mechanism. Technical limitations, inherent to the solvothermal process, do not allow performing a step-by-step analysis of the whole process. However, it seems likely that in a first step the homolytic rupture of the S–S and S–C(sp^2) bonds, and subsequent formation of free-radical intermediates: [2-pymS-S]$^{\bullet}$, [2-pymS]$^{\bullet}$ and [2-pym]$^{\bullet}$, could take place, followed by self-recombination of these radicals. Additionally, it is probably that part of the S$^{\bullet}$ radicals self-recombine to give the observed S$_8$. This is the first time that the oxidation of dithiodipyrimidines to SO$_4^{2-}$ has been reported. However, similar desulfurisation processes have already been reported for closely related pyridine-4-thiol[18] and dithiodipyridine[4d] ligands.

The cleavage of the N–C(sp^2) bond of the *in situ* generated pyrimidine-2-thione should take place. The presence of pyrimidine-2-thione to get the formation of **1**, has been shown in the reaction between CuCl$_2$ and pyrimidine-2-thione under

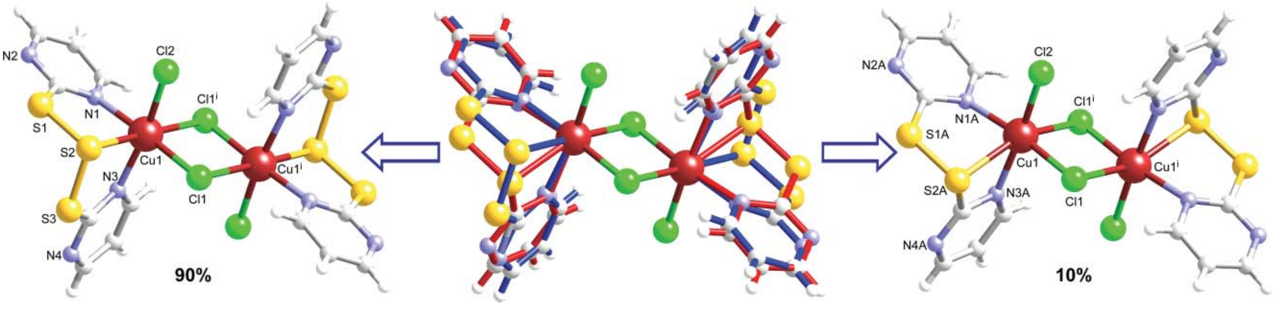


Fig. 2 View of dimeric entity in compound **2** showing the ligand disorder.

similar solvothermal conditions (CH_2Cl_2–CH_3CN, 90 °C, 20 h), where **1** is obtained together with the polymer $[Cu(pymH)Cl]_n$. We have also verified that H_2O appears to be required for formation of compound **3**.[19] Thus, we carried out the same reactions using anhydrous solvents with Schlenk techniques. In that case, compound **1** was not observed, but $[Cu(pymH)Cl]_n$ together with S_8 was obtained. Likewise, the need of Cu^{2+} to produce the cleavage of the N–C(sp^2) bond has been demonstrated, because the analogous reaction carried out between $NiCl_2 \cdot 6H_2O$ and pym_2S_2 (CH_2Cl_2–CH_3CN, 90 °C, 20 h) does not lead to the formation of the analogous compound. Instead, the preliminary X-ray diffraction measurements indicate that crystal structure consists of dimer $[Ni_2Cl_4(pym_2S)(pym_2S_3)]$ complexes.[20]

Finally, the new organic ligand, compound **3**, has been isolated from **1** by treating a CH_3CN solution of this compound with a Chelex resin for 2 h. Structural X-ray diffraction studies were performed on single crystals obtained from slow evaporation of a CH_3CN–MeOH solution. All bond distances and angles are within their usual values.[21] The lack of steric hindrance between the thiazole and pyrimidine rings allows a planar conformation of the molecule (Fig. 3). It is worth noting that the free molecule presents a *syn*-conformation of the thiazole ring with respect to the central amine group, in contrast to what happens in compound **1** where the chelation to the metal centre stabilises the *anti*-conformation of the 2-(pyrimidin-2-ylamino)-1,3-thiazole-4-carbaldehyde molecule.

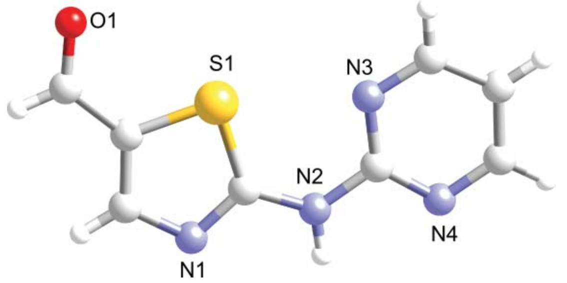


Fig. 3 View of compound **3**.

Although the S–S bond cleavage in organosulfur ligands is easy under solvothermal conditions, the C–S bond cleavage is much less common and it has been only recently reported,[4c,18] and the N–C(sp^2) bond cleavage in this kind of ligand is here reported for the first time. These results open new perspectives towards the development of alternative ways for the synthesis of organic ligands. Under solvothermal-microwave conditions, together with **1**, compound **2** is isolated. Its formation could be explained from self-recombination of the *in situ* generated $pymS^{\bullet}$ and $pymS_2^{\bullet}$ radicals. It is worth noting that compound **2** was not detected under solvothermal conditions. It seems likely that formation of compound **2** requires microwave irradiation. Varying reaction times in the solvothermal microwave conditions give rise to a mixture of **1** and **2**.

Although the mechanism has yet to be investigated in detail, the present result is the first example of a combination of cleavage of both S–S, S–C(sp^2) and C(sp^2)–N bonds in organosulfur ligands.

The thermal variation of the molar magnetic susceptibility *vs.* the temperature ($\chi_M T$) for complex **1** is shown in Fig. 4. At room temperature, the value for $\chi_M T$ is *ca.* 0.85 cm^3 K mol^{-1} which is slightly higher than that expected for two non-interacting Cu(II) $S = 1/2$ ions (0.75 cm^3 K mol^{-1} for $g = 2.0$). When cooling down the sample, the $\chi_M T$ product remains constant down to 150 K and below this temperature it shows a continuous increase reaching a maximum of *ca.* 0.93 cm^3 K mol^{-1} at 11 K. Below 11 K, $\chi_M T$ decreases to reach a value of *ca.* 0.88 cm^3 K mol^{-1} at 5 K. This behaviour indicates that complex **1** presents predominant ferromagnetic interactions, as suggested by the increase in $\chi_M T$ observed at low temperatures. The decrease observed at low temperatures can be attributed to the presence of antiferromagnetic interactions between the $S = 1$ dimers at low temperatures and/or to a zero field splitting (ZFS) of the $S = 1$ ground spin state.

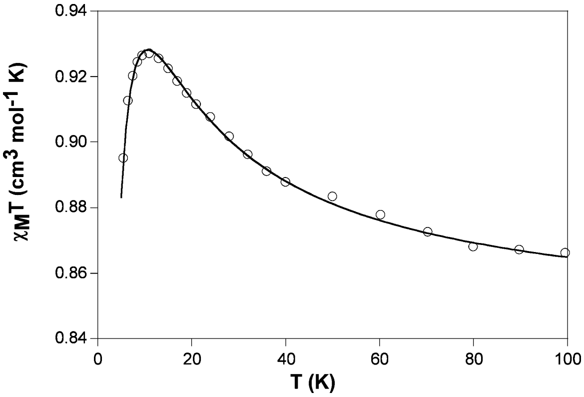


Fig. 4 Thermal dependence plot of χ_M *vs.* T for compound **1**. Solid line corresponds to the best theoretical fit.

Taking into account the crystal structure of compound **1**, we have fitted the magnetic susceptibility data to a simple ferromagnetic $S = 1/2$ dimer.[22] A Weiss constant (Θ) was introduced into the temperature term to account for both intermolecular effects and zero-field splitting. This model reproduces very satisfactorily the magnetic data of complex **1** in the whole temperature range with the following set of parameters: $g = 2.128(2)$, $J = 9.9(2)$ cm^{-1}, and $\Theta = -1.28(1)$ K (solid line in Fig. 3). As expected (see below), the intradimer magnetic coupling is ferromagnetic and the interdimer one is much weaker and antiferromagnetic.

There have been several attempts to establish magneto–structural correlations in dinuclear dichlorido-bridged Cu(II) complexes, from the pioneering work of Willett and co-workers[23] and Hatfield and co-workers[24] that related the magnetic coupling with the Cu–Cl–Cu angle (α) and with the α/R ratio, respectively (where R is the Cu–Cl bridge distance), to the more recent studies of Rodríguez *et al.*,[25] Mrozinski and co-workers[26] and Julve and co-workers.[27] All these correlations indicate that the exchange coupling constant J depends on the value of the Cu–Cl–Cu bridging angle, α, as well as on the bond length of the axial (longer) Cu–Cl bond, R in SP geometry. In complex **1**, an α/R value of 35.0° $Å^{-1}$ is measured, for which the empirical correlation predicts[23] an antiferromagnetic interaction with a J value of *ca.* -9 cm^{-1}. This value is in contradiction to the experimental one ($J = +9.9$ cm^{-1}).

However, these parameters are not the only factors playing an important role in determining the magnetic coupling. The different types of arrangement of the two copper(II) polyhedral have a great influence on the magnetic behaviour of such complexes. The global arrangement of the two square pyramids gives rise to three types of geometries: (a) square pyramids sharing one base-to-apex edge but with parallel basal planes (Type-I), (b) square pyramids sharing one base-to-apex edge with the two bases nearly perpendicular to one another (Type-II) and (c) square pyramids sharing a basal edge with coplanar basal planes (Type-III). Complex **1** belongs to the Type-I class of compounds and in this case the extent of this magnetic coupling is decided by the small structural deviations from the ideal square Cu_2Cl_2 core. Recently, Mrozinski and co-workers[26] established a theoretical correlation between the magnetic coupling and both parameters (α and R) showing that for small α values and short Cu–Cl distances the magnetic coupling is ferromagnetic. These structural parameters in compound **1** (90.1° and 2.58 Å), that predict a moderately strong ferromagnetic coupling, are very close to those reported for the $[Cu_2Cl_2(Mebta)_6](ClO_4)_2$ (Mebta = 1-methylbenzotriazole) compound, which has a similar J value of 10.4 cm^{-1} (92.9° and 2.55 Å).[26]

Conclusions

In summary, the results shown here are an interesting example of the synthetic potential of the reactions carried out under solvothermal and solvothermal-microwave conditions using organosulfur ligands in the presence of redox active metal ions. An unprecedented *in situ* multiple bond cleavage of S–S, S–C(sp^2) and C–N in the pym_2S_2 ligand is produced by reaction with $CuCl_2$. In fact, the C–N bond cleavage for these types of organosulfur ligands is reported here for the first time. This process has enabled a novel organic compound, 2-(pyrimidin-2-ylamino)-1,3-thiazole-4-carbaldehyde to be isolated. Moreover, the *in situ* formed ligand coordinates to Cu(II) ion leading to the formation of the dimetallic complex $[Cu^{II}(\mu\text{-}Cl)(Cl)L]_2$ (L = 2-(pyrimidin-2-ylamino)-1,3-thiazole-4-carbaldehyde). In addition, the analogous reaction carried out under solvothermal microwave conditions leads to the subsequent Cu(II) dimetallic complex and to the $\{9[Cu(pym_2S_3)(\mu\text{-}Cl)(Cl)]_2\cdot[Cu(pym_2S_2)(\mu\text{-}Cl)(Cl)]_2\}$ compound. Preliminary results, suggest that the analogous reactions carried out with Ni(II), instead of Cu(II), proceed only through the S–S bond breakage and subsequent rearrangement leading to the complex $[Ni_2Cl_4(pym_2S)(pym_2S_3)]$.

Acknowledgements

Financial support by the MEC (projects no. MAT2007-66476-C02-02, MAT2008-05690/MAT, FP6-029192) and Comunidad de Madrid (project S-2009-MAT-1467) is gratefully acknowledged. We thank Prof. T. Torres for helpful discussions.

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