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Preparation of a range of copper complexes of diphenylsulfimide: X-ray crystal structures of $[Cu(Ph_2SNH)_4]Cl_2$ and $[Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(Ph_2SNH)_4]$

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Abstract

Reaction of Ph_2SNH **1** with $CuCl_2$ (molar ratio 2:1) in acetonitrile gives *trans*-$[CuCl_2(Ph_2SNH)_2]$ **2a** which may be isolated as blue crystals (square planar form) by crystallisation from hot MeCN or as green needles (pseudo-tetrahedral form) by slow evaporation of a CH_2Cl_2/petroleum ether solution. In contrast, $[CuBr_2(Ph_2SNH)_2]$ **2b**, most efficiently prepared by reaction of $[Cu(Ph_2SNH)_4]Br_2$ with $CuBr_2$, appears to only exist in a dark green, pseudo-tetrahedral form. When 1.5 equivalents of **1** are reacted with CuX_2 in air, $[Cu_4(\mu_4\text{-}O)(\mu\text{-}X)_6(Ph_2SNH)_4]$ (X=Cl **3a** or Br **3b**) forms as orange crystals. X-ray crystallography reveals **3a** to have the expected tetrahedral arrangement of Cu atoms within an oxo-centered Cu_4Cl_6O core. Four equivalents of **1** react with CuX_2 to give purple $[Cu(Ph_2SNH)_4]X_2$ (X=Cl **4a** or Br **4b**); the X-ray crystal structure of **4a** reveals a square planar structure exhibiting strong hydrogen bonding interactions between the ligands and the counterions. Even in the presence of excess **1**, no more than four of the ligands may be added to a copper centre.

Keywords: Complexes; Copper; Sulfimides; Isomerism; Hydrogen bonding

1. Introduction

As part of our continuing interest in the coordination chemistry of sulfur–nitrogen species [1] we have recently reported on the reactivity of SS′-diphenylsulfimide, Ph_2SNH **1**, towards a number of metal centres. For example, we showed that homoleptic $[Co(Ph_2SNH)_6]Cl_2$ readily forms from **1** and $CoCl_2$ and exhibits strong, concerted, directed hydrogen bonding between both sets of triple N–H units on either side of the coordination octahedron and the chloride counterions [2]. We have also shown that simple complexes of Pt and Pd are isolable [3], though in the former case reactions can be complicated by an unexpected activation of nitrile leaving groups towards sulfimide addition [4]. Another intriguing aspect of the coordination chemistry of **1** came with the observation that *trans*-$[CuCl_2(Ph_2SNH)_2]$, the product of the reaction of **1** with $CuCl_2$, proved to be unusual in its ability to crystallise in either square-planar or pseudo-tetrahedral geometries [5]. Such isomerism appears to be unique for a neutral Cu(II) species, again indicating that the ligand properties of **1** are not as simple as one might imagine. Here we present the results of further investigations into the reactivity of **1** towards Cu(II) centres.

2. Experimental

Except where otherwise stated all reactions were performed under an atmosphere of dry nitrogen using dried, degassed solvents (MeCN and CH_2Cl_2 from calcium hydride, 60/80 petroleum ether from sodium). Copper halides were dried by heating in vacuo and then stored and handled under nitrogen; as noted below, **1** was prepared by a modification of the literature method [6] (the latter, and indeed other published methods, proving to be unreliable in our hands). % Yields, IR and micro-analytical data for **2**–**4** are given in Table 1.

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Table 1
Analytical and selected data for complexes **2**–**4**

		Yield (%)	IR spectra, cm^{-1} [ν(N–H), ν(S–N)]	Analysis (calculated) (%)		
				C	H	N
$CuCl_2(Ph_2SNH)_2$ **2a**	Blue	76	3292, 913	53.6 (53.7)	3.8 (4.1)	5.1 (5.2)
	Green	73[a]	3202, 918	53.5 (53.7)	4.2 (4.1)	5.2 (5.2)
$CuBr_2(Ph_2SNH)_2$ **2b**		70	3286, 888	45.7 (46.1)	3.7 (3.5)	4.8 (4.4)
$[Cu_4OCl_6(Ph_2SNH)_4]$ **3a**		50	3283[b], 947	44.3 (44.8)	3.5 (3.4)	5.1 (4.4)
$[Cu_4OBr_6(Ph_2SNH)_4]$ **3b**		61	3286[b], 943	36.5 (37.1)	2.9 (2.9)	3.6 (3.6)
$[Cu(Ph_2SNH)_4]Cl_2$ **4a**		89	3081, 940	61.2 (61.4)	4.8 (4.7)	5.7 (6.0)
$[Cu(Ph_2SNH)_4]Br_2$ **4b**		87	3126, 936	55.9 (56.1)	4.3 (4.3)	5.4 (5.5)

[a] Upon crystallisation from the blue form.
[b] Additional N–H stretch at 3319 cm^{-1}.

3. Preparations

3.1. *Ph_2SNH* ***1***

A modification of the route of Vlasova et al. was used [6]; thus Ph_2SNSO_2Ph (7 g, 0.02 mol) was added in a number of portions to well stirred, degassed 95% H_2SO_4 (25 ml) under a blanket of N_2. The resulting mixture was then heated at 80°C for 15 min before being cooled and cautiously poured onto ice (200 ml). After warming, the resulting mixture was taken to pH 11 by addition of 5 M NaOH; the response of the mixture to this appears to be very variable – on some occasions solid **1** precipitated and was then filtered and recrystallised from Et_2O, on other occasions only a pale orange oil was apparent. In the latter case, the entire mixture was extracted into warm Et_2O (typically 2×50 ml), the solvent reduced in volume and the resulting colourless crystalline mass filtered. In either, case typical yield: 1.8 g, 45%; mp 69–70°C (lit. 69°C).

3.2. *$[CuCl_2(Ph_2SNH)_2]$* ***2a*** *blue (square planar) form*

A solution of **1** (75 mg, 0.38 mmol) in acetonitrile (20 ml) was slowly added to a solution of $CuCl_2$ (25 mg, 0.19 mmol) in the same solvent (20 ml) giving a green solution which started to precipitate a blue solid after some 15 min of stirring. At this point the solution was heated until all the solid had dissolved, then lagged and slowly cooled, first to ambient temperatures then overnight in a freezer, yielding well formed blue crystals of the product.

The same material can also be prepared by the reaction of $[Cu(Ph_2SNH)_4]Cl_2$ **4a** (see below) with $CuCl_2$; thus addition of solid $CuCl_2$ (15 mg, 0.11 mmol) to a stirred suspension of **4a** (0.1 g, 0.11 mmol) in MeCN (20 ml) resulted in rapid formation of a green solution which in turn yielded a blue precipitate after 15 min stirring. Crystallisation as before yielded blue crystals of the product. Yield: 87 mg.

3.3. *$[CuCl_2(Ph_2SNH)_2]$* ***2a*** *green (pseudo-tetrahedral) form*

A sample of crystalline blue isomer (75 mg) isolated as above was dissolved in CH_2Cl_2 (15 ml) and 60/80 petroleum ether (15 ml) added. The resulting green mixture was treated with just enough CH_2Cl_2 to redissolve the precipitate that had formed and was then allowed to slowly evaporate in an open round bottom flask overnight, during which time fine well formed green needles were produced together with a small crop of the heavier, more three-dimensional crystals of the blue form. The former were decanted from the latter, filtered and dried in vacuo. Yield: 55 mg. In order to confirm the polymorphism of the system some of the latter green material (12 mg) was redissolved in hot MeCN (2 ml) and the solution cooled over a number of days in a freezer. This resulted in the crystallisation of well formed blocks of the blue isomer (11 mg).

3.4. *$[CuBr_2(Ph_2SNH)_2]$* ***2b***

A suspension of $[Cu(Ph_2SNH)_4]Br_2$ **4b** (0.1 g, 0.097 mmol), prepared as detailed below, in MeCN (10 ml) was treated with $CuBr_2$ (22 mg, 0.099 mmol) added with vigorous stirring. The solid immediately started to dissolve and the mixture turned green; after stirring for 20 min the mixture was heated until all the precipitate had redissolved, lagged to promote slow cooling to ambient temperature and then further cooled in a freezer overnight. This yielded a large crop of well-formed dark green crystals. Yield: 85 mg.

3.5. *$[Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(Ph_2SNH)_4]$* ***3a***

A solution of **1** (90 mg, 0.45 mmol) in undried MeCN (10 ml) in air was added to a solution of $CuCl_2$ (40 mg, 0.3 mmol) in the same volume of the same solvent and the mixture stirred then the reaction vessel sealed and allowed to stand. After 1 day a mass of brown/orange crystals was apparent; after 4 days the solution was decanted from this solid which was then washed with a small amount of cold MeCN and dried in vacuo. Yield: 48 mg.

3.6. *$[Cu_4(\mu_4\text{-}O)(\mu\text{-}Br)_6(Ph_2SNH)_4]$* ***3b***

A solution of **1** (90 mg, 0.45 mmol) in undried MeCN

(10 ml) in air was added to a solution of $CuBr_2$ (66 mg, 0.3 mmol) in the same volume of the same solvent and the mixture stirred. The dark mixture began to produce a precipitate within 2–3 min; after a few hours the latter was filtered from the solution, washed with a small amount of cold MeCN and dried in vacuo. Yield: 70 mg.

3.7. [Cu(Ph$_2$SNH)$_4$]Cl$_2$ ***4a***

A solution of **1** (120 mg, 0.6 mmol) in MeCN (10 ml) was treated with solid $CuCl_2$ (20 mg, 0.15 mmol). After vigorous stirring for 20 min the mixture consisted of a pale purple solid and a pale green solution. At this point further **1** (10 mg) was added which resulted in an intensification of the purple colour and a concomitant reduction in the colour of the solution. The mixture was then heated until all the solid had dissolved, lagged to promote slow cooling and placed in the refrigerator. Overnight a crop of well-formed purple crystals was obtained; these were filtered and dried in vacuo. Yield: 124 mg.

3.8. [Cu(Ph$_2$SNH)$_4$]Br$_2$ ***4b***

A solution of **1** (120 mg, 0.6 mmol) in MeCN (10 ml) was treated with solid $CuBr_2$ (33 mg, 0.15 mmol). After vigorous stirring for 30 min the mixture consisted of a very pale purple solid and a quite intense green solution. At this point further **1** (12 mg, 0.06 mmol) was added which resulted in an increase in the amount of precipitate and a reduction in the colour of the solution; addition of further **1** (10 mg, 0.05 mmol) completed the precipitation of the intensely purple product and left only a pale green colour to the solution. The mixture was then heated until all the solid had dissolved, lagged to promote slow cooling and placed in the refrigerator. Overnight a crop of well-formed purple crystals was obtained; these were filtered and dried in vacuo. Yield: 132 mg.

3.9. Crystallography

3.9.1. Crystal data for ***3a***

$C_{52}H_{50}Cl_6Cu_4N_6OS_4$ $M=1370.08$; monoclinic, space group $I2/a$; $a=24.238(1)$, $b=28.949(1)$, $c=17.640(1)$ Å; $\beta=94.78(1)°$; $U=12334.0(2)$ Å^3, $Z=8$, calculated density 1.476 g cm^{-3}. Orange needle, dimensions $0.01\times0.03\times0.2$ mm, μ (Mo Kα)$=1.796$ mm^{-1}, $\lambda=0.71073$ Å, $F(000)=5552$.

3.9.2. Crystal data for ***4a***

$C_{48}H_{44}Cl_2CuN_4S_4$ $M=939.59$; monoclinic, space group $P2_1/n$; $a=14.960(2)$, $b=10.372(1)$, $c=15.185(2)$ Å; $\beta=105.663(8)°$; $U=2268.7(4)$ Å^3, $Z=2$ (molecule located about a crystallographic centre of symmetry), calculated density 1.375 g cm^{-3}. Purple prism of dimensions $0.2\times0.20\times0.20$ mm, μ (Cu Kα)$=3.78$ mm^{-1}, $\lambda=1.54178$ Å, $F(000)=974$.

3.9.3. Data collection and processing

In the case of **3a** data were collected (using a Bruker SMART diffractometer with graphite monochromated Mo Kα radiation) using small slices: 26828 data collected, 8892 data used ($R_{int}=0.0571$). Data were corrected for Lorentz and polarisation effects and an empirical absorption correction was applied resulting in transmission factors ranging from 0.698 to 1.00.

In the case of **4a** data were collected (using a Rigaku AFC7S diffractometer with graphite monochromated Cu Kα radiation) by the ω–2θ scan technique to a maximum 2θ value of 120.2°. Of 3757 measured reflections, 3604 were unique. Data were corrected for Lorentz and polarisation effects and an empirical absorption correction was applied resulting in transmission factors ranging from 0.45 to 1.00

3.9.4. Structure analysis and refinement

The structures were solved by direct methods and refined by full-matrix least-squares against F^2 (**3a**) or F (**4a**).

In the case of **3a** two acetonitrile molecules disordered into four locations were found; the full and half weight solvents were refined anisotropically whereas the two quarter weight occupancies were refined isotropically. The N–H protons were located from a ΔF map and refined isotropically subject to a distance constraint. Refinement against F^2 lead to $R_1=0.0512$, $wR_2=0.1182$ with $I>2\sigma(I)$. The maximum/minimum residual electron densities in the final ΔF map were 0.715 and -0.318 e Å^{-3}; calculations were performed using SHELXTL [7].

For **4a** non-hydrogen atoms were refined anisotropically; hydrogen atoms were included but not refined. Refinement against F lead to $R=0.062$ $[R=\Sigma(|F_o|-|F_c|)/\Sigma|F_o|]$, $Rw=0.057$. The maximum/minimum residual electron densities in the final ΔF map were 0.86 and -0.6 e Å^{-3}; calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation [8].

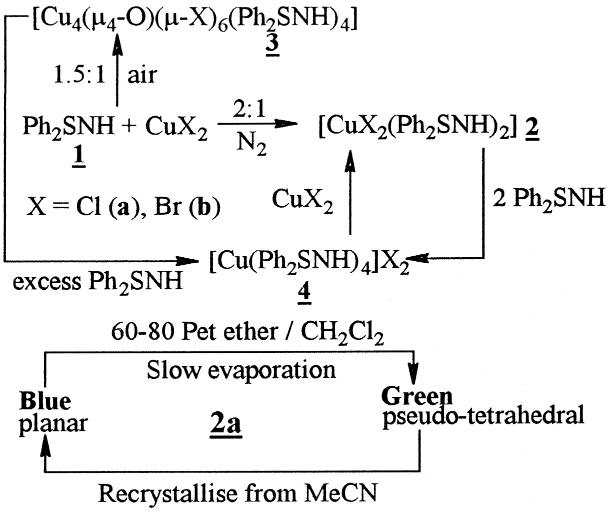
4. Results and discussion

4.1. Preparation of [CuX$_2$(Ph$_2$SNH)$_2$]

In a recent communication we noted that reaction of Ph_2SNH with $CuCl_2$ in MeCN in the ratio 2:1 resulted in the formation of *trans*-[CuCl$_2$(Ph$_2$SNH)$_2$]. Intriguingly we found that the latter could be crystallised in two forms: blue (which proved to have square-planar geometry) and green (pseudo-tetrahedral) [5]. Such isomerism is well-known for ionic Cu(II) species but is much rarer for neutral complexes – indeed we have yet to confirm the existence of any other example. To build upon these initial results, and in order to gain a more complete picture of the reactivity of **1** towards copper centres, we have now developed methods to specifically isolate reasonable quantities of either isomer (in our preliminary work we noted that appearance of the green form seemed to be unpredictable and in very low yield) and have investigated the effect that changing the nature of the halogen has on the system; in addition we have determined the ability of copper to coordinate more than two units of **1** and have isolated the first examples of oxo cluster complexes of this ligand.

Simple recrystallisation of crude **2a** from hot MeCN results in the formation of the blue isomer, which may be isolated as very well-formed, three-dimensional blue crystals if the solution is cooled slowly. Conversely, if the original material is dissolved in CH_2Cl_2, 60/80 petroleum ether added and the mixture allowed to slowly evaporate then the faster loss of CH_2Cl_2 results in crystallisation of **2a** from the mixture as very fine, long needles of the green form. In the latter case a small amount of the blue material sometimes forms, but the difference in size and density of the two types of crystal makes it easy to decant the needles of the green isomer off from their blue counterparts. Although this method does not lend itself to scaling up too far, we have found that it can certainly be used on amounts in the order of 100 mg or so, allowing isolation of reasonable amounts of this isomer for the first time.

If samples of the green isomer of **2a** thus formed are redissolved in a small volume of hot MeCN and the solutions cooled in a freezer, the material crystallises out in the blue form, thus confirming that a true polymorphism is present. This begs the question as to the nature of the driving force behind this unique isomerism, and some insight into this problem may be gained by the results obtained from the analogous reaction with $CuBr_2$. The copper bromide reaction proceeds in much the same manner as the chloride, giving a green mixture, although in this case the oxo cluster **3b** (see below) tends to form as substantial impurity. The latter can be avoided by first forming pure $[Cu(Ph_2SNH)_4]Br_2$ **4b** as detailed below and then treating this with one equivalent of $CuBr_2$ as in Scheme 1. The $[CuBr_2(Ph_2SNH)_2]$ thus formed may be isolated as dark green crystals from MeCN. The results of an X-ray study on these crystals is not formally presented here as the data[1] resulted in a poor solution due to disorder at one of the sulfurs; however, the results are good enough to confirm that the geometry at the metal centre is pseudo-tetrahedral (with, for example a N–Cu–N angle of 149.9°), a conclusion that also fits in with the colour of the material. Crucially, we have found no evidence for the formation of any other isomer (i.e. square-planar) of this material – crystallisation from hot MeCN, from petroleum ether/CH_2Cl_2 or by slow diffusion of Et_2O into CH_2Cl_2 only results in the formation of the green material. Thus it seems that the act of changing from the chloride to bromide ligands mitigates against the formation of a square-planar isomer. What, if anything, this tells us about the driving forces behind the isomerism in **2a** is not necessarily clear, though it possibly indicates that intramolecular interaction (or, in solution before crystallisation, intermolecular interaction) between the N–H units and the halide ligands could play a part. If this were the case then changing the electronegativity of the halide would clearly be expected to have a significant effect. In proposing this model, however, we should clearly add the caveat that we have no definitive proof of its veracity; one observation which would add weight to the suggestion would come with the structure of analogues of **2** in which the N–H groups had been replaced with N–R, where R was alkyl or aryl. In such cases there would be minimal interaction between the R group and the chloride. Unfortunately, attempts to prepare analogous complexes of, for example, Ph_2SN^nBu have so far only resulted in dark red/brown coloured products from which we have yet to isolate crystalline material. Work in this area is, however, still ongoing.



Scheme 1. The formation of **2**, **3** and **4** and the two isomers of **2a**.

4.2. Formation of oxo clusters

As we have seen, formation of **2a** can be achieved by reaction of 2 equivalents of **1** with $CuCl_2$ in dry MeCN under a nitrogen atmosphere; if 1.5 equivalents of **1** are employed instead, and the reaction performed in air using undried MeCN, a different product may be isolated. In this case the solution gradually deposits an orange crystalline

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[1] Monoclinic, $a = 21.637(1)$, $b = 12.468(1)$, $c = 18.364(1)$ Å, $\beta = 100.29(1)°$. The structure exhibits disorder in one of the ligands resulting in two occupancies for the associated sulfur atom of 70:30%. However, the associated phenyl groups could not be resolved into separate occupancies and were refined in one full weight position. This model worked fairly well and gave unambiguous results for the geometry at the Cu as no significant disorder is noted for either nitrogen.

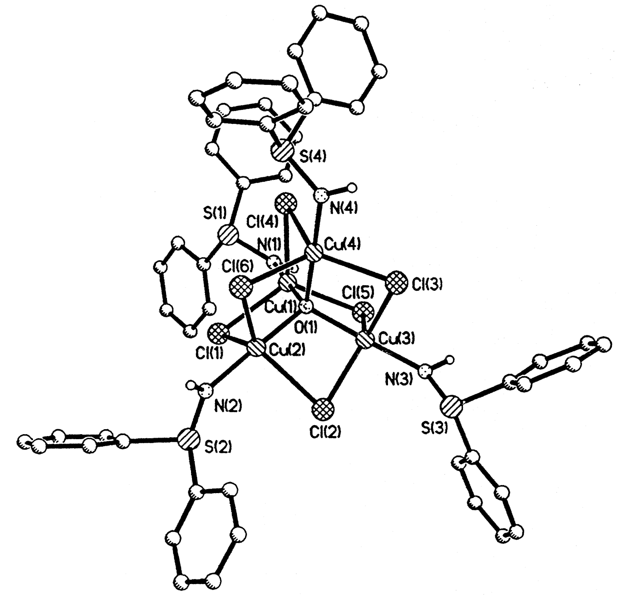

Fig. 1. The molecular structure of $[Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(Ph_2SNH)_4]$, **3a.**

material which X-ray crystallography reveals as the cluster compound $[Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(Ph_2SNH)_4]$ **3a** (Fig. 1). This is an example of a well known class of oxo cluster species of the general type $[Cu_4OCl_6L_4]$, which have been reported with a range of ligands L including pyridine, triphenylphosphine etc. [9]. Such products commonly form when copper halide reactions are performed using the hydrated material or when products are refluxed in air. Studies have shown that the oxygen in the product comes from water in the system; in the case of **3a** results go some way to confirming this though the mechanism is not straightforward. If the reaction is performed in scrupulously dried and degassed MeCN no **3a** forms; if dried oxygen is bubbled through, or thoroughly degassed water added to such a solution then a minimal yield of **3a** is obtained (≈7 and 3%, respectively). Interestingly, if *both* degassed water and dried O_2 are added to the original anaerobic solution then a larger yield is obtained (23%); the highest yield of all, 50%, is obtained when the reaction is performed in the presence of water and oxygen from the start. The latter result is not surprising and, by analogy with other systems investigated, probably suggests that initial solutions of $CuCl_2$ in MeCN are in equilibrium with $[Cu_4OCl_6(MeCN)_4]$ making the formation of **3a** a simple substitution reaction. Quite why the presence of both O_2 and water would be required for the formation of **3a** from the anhydrous starting system is not obvious. The structure of **3a** consists of a Cu_4OCl_6 core in which the copper atoms are tetrahedrally displaced about the centre oxygen at an average Cu–O bond length of 1.90 Å, a distance which is typical for such clusters (Table 2). While the average S–N bond distance (1.583 Å) within the sulfimide ligands is similar to that of other complexes of **1**, the average angle at the nitrogen (121.9°) is significantly smaller than in any complex of **1** we have yet prepared (including **4a**, Table 3). The latter observation may well indicate that there is a weaker H . . . Cl interaction between the N–H hydrogens and the bridging chlorides in **3a** than is found in either the terminal chloride complexes such as **2a** or the ionic chlorides such as **4a**.

The formation of the analogous bromine complex $[Cu_4(\mu_4\text{-}O)(\mu\text{-}Br)_6(Ph_2SNH)_4]$ **3b**, which we have characterised by IR and microanalysis, is much more facile and indeed is hard to avoid; even traces of water in the system appear to take the reaction mixture through to this product. It is for this reason that we prefer to prepare **2b** from **4b** rather than directly from **1** plus $CuBr_2$, as the latter method invariably generates significant amounts of **3b** contami-

Table 2
Selected bond distances (Å) and angles (°) in complex **3a**

Cu(1)–O(1)	1.904(4)	Cu(1)–Cl(1)	2.444(2)	Cu(1)–Cl(5)	2.476(2)
Cu(1)–Cl(4)	2.413(2)	Cu(1)–N(1)	1.932(5)	N(1)–S(1)	1.586(5)
Cu(2)–O(1)	1.906(4)	Cu(2)–Cl(1)	2.458(2)	Cu(2)–Cl(2)	2.489(2)
Cu(2)–Cl(6)	2.385(2)	Cu(2)–N(2)	1.930(5)	N(2)–S(2)	1.576(5)
Cu(3)–O(1)	1.898(4)	Cu(3)–Cl(2)	2.410(2)	Cu(3)–Cl(3)	2.499(2)
Cu(3)–Cl(5)	2.407(2)	Cu(3)–N(3)	1.929(5)	N(3)–S(3)	1.584(6)
Cu(4)–O(1)	1.909(4)	Cu(4)–Cl(3)	2.372(2)	Cu(4)–Cl(4)	2.517(2)
Cu(4)–Cl(6)	2.430(2)	Cu(4)–N(4)	1.928(5)	N(4)–S(4)	1.586(6)
Cu(1)–O(1)–Cu(2)	110.0(2)	Cu(1)–O(1)–Cu(3)	108.9(2)	Cu(1)–O(1)–Cu(4)	110.5(2)
Cu(1)–N(1)–S(1)	122.3(3)	Cu(2)–O(1)–Cu(3)	110.8(2)	Cu(2)–O(1)–Cu(4)	106.7(2)
Cu(2)–N(2)–S(2)	123.2(3)	Cu(3)–O(1)–Cu(4)	109.9(2)	Cu(3)–N(3)–S(3)	122.1(3)
Cu(4)–N(4)–S(4)	119.8(3)				

Table 3
Selected bond distances (Å) and angles (°) in complex **4a**

Cu–N(1)	1.991(4)	Cu–N(2)	1.977(4)	N(1)–S(1)	1.592(4)
N(2)–S(2)	1.591(4)	N(1)–Cu–N(2)	87.7(2)	Cu–N(1)–S(1)	126.3(3)
Cu–N(2)–S(2)	124.2(3)	N(2)–Cu–N(1A)	92.3(2)		

nant. The similarity in the IR spectra of **3a** and **3b** suggests that structural differences between the two are probably minimal.

4.3. Preparation of [Cu(Ph$_2$SNH)$_4$]X$_2$

Reaction of **3b** with excess **1** results in the breaking up of the cluster structure and formation of the homoleptic [Cu(Ph$_2$SNH)$_4$]$^{2+}$ cation; the latter is is best prepared, however, in a more direct manner by addition of four equivalents of **1** to CuCl$_2$ or CuBr$_2$. In both cases the products can be isolated as purple crystalline material from MeCN. Efficient formation of [Cu(Ph$_2$SNH)$_4$]Cl$_2$ **4a** and, especially, [Cu(Ph$_2$SNH)$_4$]Br$_2$ **4b** can only be achieved by addition of a slight excess of **1** ($\approx$15%) above the precise stoichiometric amount. Thus when exactly four equivalents of **1** are added to CuBr$_2$ the solution retains a quite intense green colour and there is only a pale precipitate; it is only upon addition of the extra **1** that the colour of the solution is discharged and an intensely purple precipitate produced. This presumably indicates that there is appreciable dissociation of the complexes in solution. The crystal structure of **4a** confirms the presence of the four sulfimide ligands in a square-planar arrangement about the copper centre (Fig. 2) with all the ligands bound by their nitrogen donors. The most interesting aspect of the structure arises from the relative orientations of the four ligands. They arrange themselves in such a way that two pairs of *cis* sulfurs extend on to opposite sides of the CuN$_4$ plane. An important consequence arising from the resulting orientation of the N–H groups is that each pair can cooperate in significant interactions with the chloride counterion. One result of this strong interaction (average H–Cl distance 2.20 Å) is that rather than occupying the expected axial positions (and thus making up an overall octahedral coordination environment via long Cl–Cu bonds) as might be expected, the chlorides actually lie substantially nearer the CuL$_4$ coordination plane. The side-on view shown in Fig. 2 highlights this; the Cu–N–Cl angle is 46° indicating just how strong this N–H . . . Cl interaction is. The strength of the latter is, of course, undoubtedly heightened by the fact that there are two such hydrogen bonds acting cooperatively. In addition, it should be noted that there are no significant long range interactions between the Cu axial position and chlorides from other units; indeed the longest such interaction is as far out as 9.3 Å. Four appears to be the maximum number of diphenylsulfimide ligands that copper will accommodate. Thus if either six equivalents of **1** are used in the synthesis from the start, or if solutions of **4** are heated in the presence of excess **1**, **4** is the only isolable product.

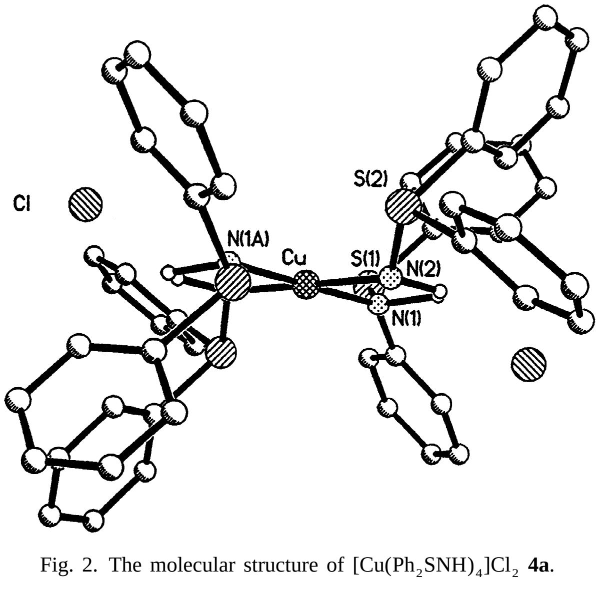

Fig. 2. The molecular structure of [Cu(Ph$_2$SNH)$_4$]Cl$_2$ **4a**.

As Table 1 indicates, the IR spectra of all the complexes prepared in this work show both N–H and S–N stretches which vary significantly from complex to complex (most other bands due to the ligands that are common to all vary only minimally in wavenumber). The S–N stretches occur in the range 888–947 cm^{-1} and so can be quite diagnostic; the precise pattern behind the variations in position is, however, difficult to glean. The most dramatic of contrasts within the spectra come with the N–H stretches. In the case of neutral species, such as **2**, the latter are weak; in contrast the cationic species **4** exhibit strong, broad bands that are comparable in magnitude to any other ligand bands in the spectra. This difference undoubtedly originates from the strong interactions between the N–H groups and the counterions noted in the crystal structure of **4a**.

To conclude it is apparent that **1** shows excellent ligand properties towards copper centres. The isomerism shown by **2a** appears to be unique for a neutral Cu(II) species and the methods outlined here allow isolation of pure samples of each isomer in good yield. The lack of analogous behaviour for **2b** indicates that the isomerism in such systems is significantly dependent upon the halide present. Strong interactions between N–H groups and halide counterions are a prominent feature of **4** (as they are for the related cobalt species [Co(Ph$_2$SNH)$_6$]Cl$_2$) and suggest that, in the presence of an appropriate anion, it may well be possible to generate extended arrays in which metal centres are linked by such interactions. We are currently investigating this possibility.

Supplementary data

Supplementary data are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ on request quoting the deposition numbers CCDC 127562 (**3a**) and CCDC 127563 (**4a**).

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