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Preparation and crystal structures of two forms of *trans*-[$CuCl_2\{N(H)SPh_2\}_2$]; an unusual example of square planar/pseudo-tetrahedral isomerism in a neutral copper(II) complex

Paul F. Kelly,* Alexandra M. Z. Slawin and Kevin W. Waring

Department of Chemistry, Loughborough University, Loughborough, Leics., UK LE11 3TU

At ambient temperatures, in acetonitrile, *S*,*S*-diphenylsulfimide reacted with $CuCl_2$ (molar ratio 2:1) to give *trans*-[$CuCl_2\{N(H)SPh_2\}_2$]; depending upon the crystallisation technique this can be isolated as either blue (perfect square-planar geometry) or green (pseudo-tetrahedral) crystals which do not interconvert in the solid state.

The ability of some complexes of the late transition metals, in particular copper and nickel, to exhibit variable isomerism between square planar and tetrahedral (or pseudo-tetrahedral) geometries is well known.[1] For example, many salts of $[CuCl_4]^{2-}$ exhibit thermochromic effects due to such structural changes while a number of nickel(II) complexes (typically those involving phosphine ligands) can exist in the two respective forms (or even, in some cases, exhibit both geometries within the same unit cell). What appears to be a much rarer scenario, however, is isomerism such as this occurring for *neutral* copper(II) species. Indeed, we have yet to confirm the occurrence of any such example in the literature. We have, however, isolated an example of just such a complex during investigations into the co-ordination chemistry of *S*,*S*-diphenylsulfimide, $N(H)SPh_2$ **I**.

Our interest in the co-ordination chemistry of compound **I** stems from our general investigations into the interaction of sulfur–nitrogen chain species with transition-metal centres. During such work we have tended to concentrate upon long-chain species such as ($Me_3SiNSNSNSNSiMe_3$), which can act as a source of a range of S–N ligands *via* reaction with simple platinum-group complexes.[2] While the latter is amongst the longest S–N chain species that may be isolated as a discrete molecule, **I** is clearly a good example of the shortest such chain. Interest in its chemistry is dominated by its use in organic chemistry as, for example, a source of aziridines.[3] In contrast, its co-ordination chemistry is very much underdeveloped, with a recently reported uranium species being the only metal complex so far noted.[4] We have been able to show that in fact **I** readily co-ordinates to a wide range of late-transition-metal units, including $CuCl_2$.†

When a solution of compound **I** (75 mg, 0.38 mmol) in acetonitrile (20 cm^3) is slowly added to a solution of $CuCl_2$ (25 mg, 0.19 mmol) in the same solvent (20 cm^3), the expected complex [$CuCl_2\{N(H)SPh_2\}_2$] **1** forms. If the solution is reasonably concentrated the latter spontaneously precipitates at ambient temperatures; if this precipitate is redissolved by heating, a small amount of diethyl ether added and the solution lagged to promote slow cooling, a good yield of **1** may be obtained as well formed blue crystals (henceforward designated **1a**) which analyse as a straightforward 2:1 complex (Found: C, 53.6; H, 3.8; N 5.1. Calc. for $C_{24}H_{22}CuCl_2N_2S_2$: C, 53.7; H, 4.1; N, 5.2%).

X-Ray crystallography reveals these to have a *trans* arrangement of the ligands with the sulfimides bound, as expected, by their nitrogen atoms (Fig. 1).‡ The overall geometry about the copper is square planar, with no discernable axial intermolecular interactions up to 6 Å from the copper. Such interactions are probably precluded by the fact that the two sets of phenyl rings are arranged roughly perpendicular to the $CuCl_2N_2$ plane, providing a steric barrier to any axial close approaches.

If a variation upon the above crystallisation procedure is performed whereby the **1a** that initially precipitates in acetonitrile is filtered off and the remaining solution treated with diethyl ether and cooled in a freezer, a combination of blue crystals of **1a** and green crystalline material **1b** is generated. Our initial assumption was that the latter would prove to be the *cis* analogue of **1a**; in fact X-ray crystallography reveals it to again be a *trans* arrangement but now with a pseudo-tetrahedral geometry about the copper (Fig. 2). The level of distortion from

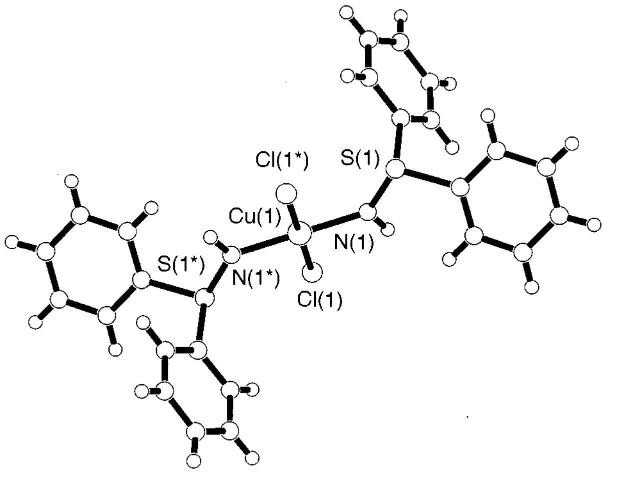

Fig. 1 Crystal structure of complex **1a**. Selected bond distances (Å) and angles (°): Cu–N(1) 1.911(8), Cu–Cl(1) 2.271(3), N(1)–S(1) 1.582(9); N(1)–Cu–Cl(1) 87.0(3), N(1)–Cu–N(1*) 180.0, Cl(1)–Cu–Cl(1*) 180.0, Cu–N(1)–S(1) 129.0(5)

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† For example $[Co\{N(H)SPh_2\}_6]^{2+}$ results from the 6:1 reaction of **I** with $CoCl_2$ while [$Pt\{N(H)SPh_2\}Cl(PMe_2Ph)_2$][$BF_4$] can be isolated from the reaction of **I** with [$PtCl_2(PMe_2Ph)_2$] and [NH_4][BF_4]. Details of such reactions will be published in due course.

‡ Crystal data[5] for complex **1a**. $C_{24}H_{22}Cl_2CuN_2S_2$, $M = 537.02$, monoclinic, Space group $C2/c$ (no. 15), $a = 17.038(2)$, $b = 8.928(5)$, $c = 16.234(2)$ Å, $\beta = 97.537°$, $U = 2448(1)$ Å^3, $T = 20$ °C, $Z = 4$ (the molecule possesses a crystallographic centre of symmetry), μ(Cu-Kα) = 4.99 mm^{-1}, $R = 0.058$ ($R' = 0.050$) for 866 observed reflections [$I > 3\sigma(I)$].

Crystal data[5] for complex **1b**. $C_{24}H_{22}Cl_2CuN_2S_2$, $M = 537.02$, monoclinic, space group $P2_1/a$ (no. 14), $a = 11.443(5)$, $b = 16.114(4)$, $c = 14.267(2)$ Å, $\beta = 109.62(3)°$, $U = 2478(2)$ Å^3, $T = 20$ °C, $Z = 4$, μ(Cu-Kα) = 4.93 mm^{-1}, $R = 0.053$ ($R' = 0.048$) for 1748 observed reflections [$I > 2\sigma(I)$]. CCDC reference number 186/645.

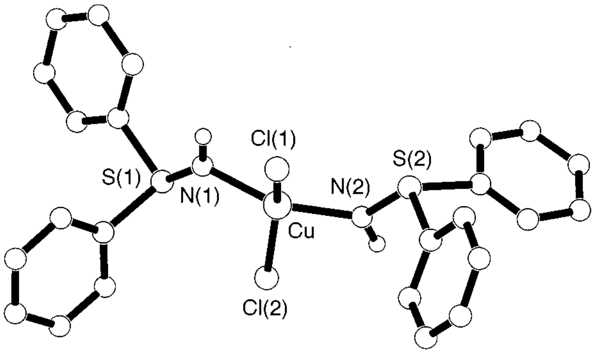

Fig. 2 Crystal structure of complex **1b**. Selected bond distances (Å) and angles (°): Cu–N(1) 1.932(8), Cu–N(2) 1.919(8), Cu–Cl(1) 2.280(2), Cu–Cl(2) 2.284(2), N(1)–S(1) 1.607(7), N(2)–S(2) 1.584(7); N(1)–Cu–N(2) 157.6(3), Cl(1)–Cu–Cl(2) 153.1(1), N(1)–Cu–Cl(1) 90.5(2), N(1)–Cu–Cl(2) 96.2(2), N(2)–Cu–Cl(1) 93.8(2), N(2)–Cu–Cl(2) 89.9(2), Cu–N(1)–S(1) 122.9(4), Cu–N(2)–S(2) 125.4(4)

planar can be quantified by the N(2)–Cu–N(1) and Cl(1)–Cu–Cl(2) angles of 157.6 and 153.1° respectively (the corresponding angles both being *precisely* 180° in **1a**). In other respects, however, there is minimal difference between the two structures; thus the average Cu–N and S–N bond lengths in **1b** (1.926 and 1.596 Å respectively) compare well with those in **1a** (1.911 and 1.582 Å) while the angles at the nitrogens (*i.e.* S–N–Cu) are also similar (125.4° in **1b** compared to 129° in **1a**).

The difference in packing arrangements in the two cases manifests itself in their IR spectra. Thus the ν(N–H) stretch in **1b** is seen at 3202 cm^{-1}, which is some 90 cm^{-1} lower than in **1a**, presumably reflecting the fact that the N–H bond is now free to interact with Cu–Cl bonds of neighbouring molecules (the closest such H · · · Cl approach being 2.68 Å in **1b** compared to 6.26 Å in **1a**; both have, of course, some degree of *intra*-molecular interaction, with H · · · Cl distances of 2.65 and 2.68 Å for **1a** and **1b** respectively).

The two forms of complex **1** do not interconvert in the solid state at room temperature and melt at effectively the same temperature (157 °C) decomposing in the process. As far as interconverting in solution goes, we have been able to show that pure crystalline **1a** can be redissolved and used to generate crystalline **1b**; indeed in such situations it is common to obtain a mixture of intergrown crystals of *both* forms. As for ascertaining the ability of **1b** to generate **1a** this has been made harder to prove by the limited amounts of the former at our disposal (crystallisation of **1b** only occurs from relatively dilute solutions, precluding the isolation of much more than 5–10 mg from any one batch). We *can* say, however, that slow evaporation of a solution of **1b** does not seem to yield any blue crystals of **1a**, and that the UV/VIS spectrum of such a solution lacks a band (λ_{max} 385 nm, $\varepsilon_{mol} = 1700$ mol^{-1} dm^3 cm^{-1}) that appears in solutions of **1a** [note that an additional band at λ_{max} 235 nm (ε_{mol} 15 000) is common to both while a broad d–d band centred on 730 nm in **1a** envelopes the area covered by a sharper band at 620 nm in solutions of **1b**]. Both these observations leave open the possibility that **1b** could be the most thermodynamically stable of the two forms and that, once formed, it cannot regenerate **1a**. We hope that future work will shed more light on this question.

In conclusion we can say that the appearance of two such isomeric forms appears to be unprecedented for a *neutral* copper(II) complex. Given that it is likely to be some feature of **I** as a ligand that is inducing such effects, it follows that these results suggest that the ligand properties of the whole family of sulfimides deserve far more attention than they have so far been afforded.

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