Multiple nitrene insertions into the copper–sulfur bonds of dithiocarbamate ligands: synthesis and molecular structure of the tetraamido complex $[Cu\{\eta^2\text{-}RNSC(NMe_2)SNR\}_2]$ (R = $SO_2C_6H_4Me$-*p*)

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During the aziridination of styrene with PhI=NR (R = $SO_2C_6H_4Me$-*p*) the copper(III) catalyst $[Cu(\eta^2\text{-}S_2CNMe_2)_2][FeCl_4]$ is converted into the crystallographically characterised tetraamido complex $[Cu\{\eta^2\text{-}RNSC(NMe_2)SNR\}_2]$, a result of nitrene insertion into all four copper–sulfur bonds.

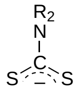
Recent work, primarily by the groups of Evans[1] and Jacobsen,[2] has revealed that a wide range of copper complexes can act as homogeneous catalysts towards the aziridination of alkenes. Although the nature of this catalytic process is not well understood, preliminary results from the Jacobsen group are strongly suggestive of the formation of a copper–nitrene complex.[3] While this would appear to be a sensible proposal, the nitrene (imido) ligand is a strong π donor and is generally associated with high-valent metal centres, that is those with low d electron counts.[4] Thus, while complexes with d^0–d^2 centres are abundant, those with electron counts of d^3–d^6 are extremely rare and there are no well authenticated examples of mononuclear complexes of this type with higher electron counts.[4]

Our work in this area has been concerned with gaining a better understanding of the catalytic process with a view to developing new, more efficient and selective, aziridination catalysts.[5] As part of this effort, and in an attempt to elucidate the oxidation state of the active catalyst, we have shown that, under the correct reaction conditions, copper(I)–(III) dithiocarbamate complexes are all highly active catalysts. After a number of these catalytic runs we noted the formation of a small amount of a new green solid which we sought to characterise in order to gain insight into the catalytic process. Herein we report details of the structure of the novel tetraamido complex $[Cu\{\eta^2\text{-}RNSC(NMe_2)SNR\}_2]$ **1**, formally resulting from the insertion of nitrene groups into all four sulfur–copper bonds of the catalyst.

While carrying out the aziridination of styrene using PhI=NR as a nitrene source and the copper(III) dithiocarbamate complex $[Cu(\eta^2\text{-}S_2CNMe_2)_2][FeCl_4]$ as catalyst, after the reaction was complete, extraction into dichloromethane and layering with toluene resulted in the deposition of green paramagnetic crystals characterised by X-ray crystallography as the tetraamido copper(II) complex $[Cu\{\eta^2\text{-}RNSC(NMe_2)SNR\}_2]$ **1** as shown in Fig. 1.†

The molecule consists of a four-coordinate copper(II) centre bound by two new chelating ligands, formed as a result of nitrene insertion into the copper–sulfur bonds of the dithiocarbamate ligand. It has overall D_{2d} symmetry, the copper centre being a compressed tetrahedron, with a dihedral angle of 35.4° between CuN_2 planes. The ligand has a bite angle of 87.4(2)° and an angle of 97.7(2)° separates the two. The six-membered ring is puckered with the tosyl (Tos) groups on nitrogen adopting an alternating up–down configuration, and copper–nitrogen distances of 2.016(4) and 2.005(4) Å are similar to those found in related copper(II) complexes.[6]

Resonance forms I and II are commonly used to explain the ability of the dithiocarbamate ligand to stabilise both low- and high-valent metal centres, respectively,[7] and similar structures



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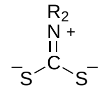

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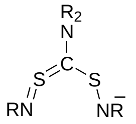

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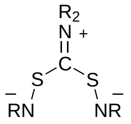
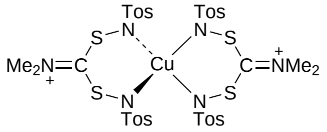


IV



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III and IV can be considered for the new ligand in **1**. Close inspection of the structural parameters of the ring reveal that only the diamido form IV contributes to any extent. Thus, while the ring itself is severely puckered, the dithiocarbamate unit is quite flat [max. deviation 0.008 Å by C(30)] and planar about N(3). Further, the backbone carbon–nitrogen bond, C(30)–N(3), at 1.330(6) Å is short and similar to those found in related dithiocarbamate complexes.[7,8] That resonance form III does not contribute significantly is also shown by the relatively long sulfur–carbon [S(3)–C(30) 1.579(5), S(4)–C(30) 1.781(5)

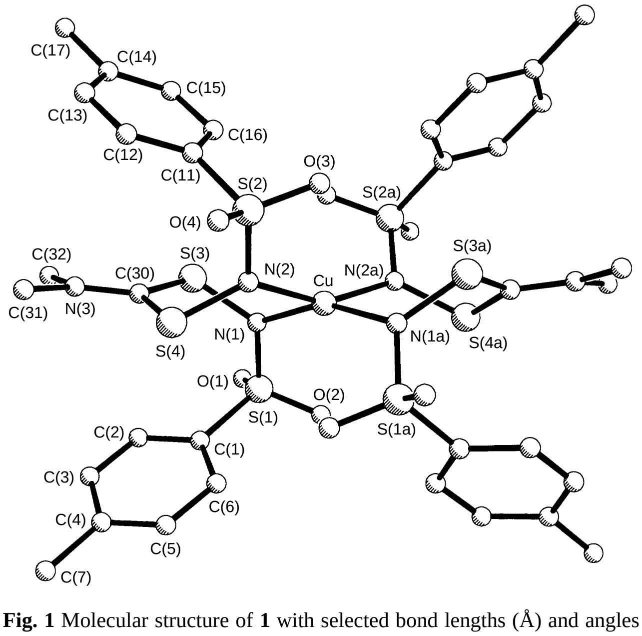

Fig. 1 Molecular structure of **1** with selected bond lengths (Å) and angles (°): Cu–N(1) 2.005(4), Cu–N(2) 2.016(4), S(1)–N(1) 1.642(4), S(2)–N(2) 1.649(4), S(3)–N(1) 1.687(4), S(4)–N(2) 1.694(4), S(3)–C(30) 1.759(5), S(4)–C(30) 1.781(5), N(3)–C(30) 1.330(6); N(1)–Cu–N(2) 87.4(2), N(1)–Cu–N(2A) 97.7(2), N(1)–Cu–N(1A) 157.0(2), N(2)–Cu–N(2A) 154.5(2), Cu–N(1)–S(3) 124.3(2), N(1)–S(3)–C(30) 103.5(2), S(3)–C(30)–S(4) 119.3(3), C(30)–S(4)–N(2) 103.5(2), S(4)–N(2)–Cu 124.1(2)

Å] and sulfur–nitrogen [N(1)–S(3) 1.687(4), N(2)–S(4) 1.694(4) Å] bonds within the ring, the former being considerably longer than those in related copper(II) dithiocarbamate complexes,[8] while the latter are longer than the sulfur–nitrogen bonds to the tosyl groups [N(1)–S(1) 1.642(4), N(2)–S(2) 1.649(4) Å]. Thus, the zwitterionic diamido formulation **IV** is the most apt ligand description. Further, the ring nitrogens N(1) and N(2) are essentially planar as shown by the sum of the bond angles at each of 359.3 and 358.9°, respectively.

As far as we are aware, the chelating ligand found in **1** has not previously been characterised although it appears to be quite stable. The mode of formation of **1** is also unknown. While a number of novel rearrangements[9] and insertions into the dithiocarbamate backbone[9,10] have been reported, we are unaware of examples of nitrene or related insertions into the metal–sulfur bonds. What is clear, however, from the isolation of **1** is that nitrene coordination to the copper centre must be facile and this supports Jacobsen's recent observations.[3] We have previously reacted known copper aziridination catalysts with the nitrene source and, while in all cases a rapid reaction takes place (as evidenced by the dissolution of the nitrene source), we have previously been unable to characterise the product(s).[5] Copper-catalysed aziridination reactions are generally carried out in the presence of an excess of the alkene, which is known to bind to the copper centre.[11] We speculate, then, that during the normal course of catalysis, nitrene transfer to the precoordinated alkene from the highly reactive copper–nitrene species is facile, giving rise to aziridines. However, in the absence of the alkene, the copper-bound nitrene moiety may react with other metal-bound ligands as is found in **1**.

Since formation of **1** involves the multiple insertion of nitrene fragments we are currently trying to determine whether this is a stepwise process and we are also assessing the ability of **1** to act as an aziridination catalyst. Direct addition of an excess of the nitrene source to [Cu(η^2-S_2CNMe_2)$_2$][$FeCl_4$] initially affords a red solution and later a green precipitate. While neither contains **1**, the latter appears to combine nitrene, copper and dithiocarbamate fragments and its identity and relationship to **1** are under investigation.

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Footnotes

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† *Crystal data* for **1**·$2CH_2Cl_2$: crystal dimensions 0.36 × 0.26 × 0.24 mm, $C_{36}H_{44}Cl_4CuN_6O_8S_8$, monoclinic, space group $C2/c$ (no. 15), M = 1150.59, a = 12.457(2), b = 22.648(5), c = 19.224(4) Å, β = 106.59(3)°, U = 5198(2) Å^3, Z = 4, D_c = 1.470 g cm^{-3}, μ(Mo-Kα) = 9.98 cm^{-1}, $F(000)$ = 2364. Data were obtained at 25 ± 1 °C on a Nicolet R3mV diffractometer using graphite-monochromated Mo-Kα radiation. A total of 4469 reflections (4274 unique) were collected using the ω scan method within a 2θ range 5–50°. The structure was solved by direct methods and refined by full-matrix least-squares methods using 3086 reflections [$I_o > 2\sigma(I)$]. The final refinement converged to R = 0.0624 and R_w = 0.1462. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this mnaterial should quote the full literature citation and the reference number 182/450.

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