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Copper Promoted Reactions of the Heterocyclic Thioamide, 2-Thiazolidinethione

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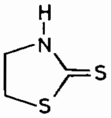
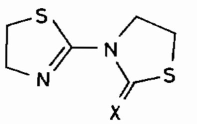
Interest in the interaction of heterocyclic thioamides with transition metal ions has focussed primarily on the isolation of complexes in which the thioamide ligand remains intact [1]. One exception is the reaction of benzothiazoline-2-thione in chloroform with solid copper(II) perchlorate hexahydrate which yields a complex containing an oxidised form of the thioamide, RSSSR, in which an additional sulphur atom has been inserted [2]. Thermal desulphurization of the coordinated heterocyclic thioamido ligand, L^1, has also been reported [3]. In a recent review [4] it has been stated that only rarely does ring fusion occur with heterocyclic thiones in the presence of metal ions.

This paper reports on a new type of reaction which is promoted by copper ions and results in an apparent loss of the elements of H_2S from two molecules of 2-thiazolidinethione (L^1H) with concomitant formation of a new C–N bond.



L^1H

Recently we reported that cleavage of the exocyclic carbon–sulphur bond readily occurs when heterocyclic thioamide complexes of copper are dissolved in pyridine, the sulphato complex, $[Cu(py)_4SO_4]\cdot 2H_2O$, being isolated [5]. We now report a different reactivity pattern when nitromethane is used as the solvent. The ligand L^1H in the presence of copper ions yields coordinated L^2 or L^3.



L^2 X = O

L^3 X = S

For example, when $CuCl_2\cdot 2H_2O$ in ethanol was added dropwise to L^1H dissolved in nitromethane, a green solution formed and green needle like crystals started to appear after 1 h. The same product was also obtained when the thioamide complex, $[Cu(L^1H)_3Cl_2]$, was dissolved in nitromethane. Spectroscopic results indicated the presence of copper(II) (λ_{max} (nujol) 415(sh) and 720 nm; ESR (nitromethane, 77 K) $g_\parallel = 2.229$, $A_\parallel = 152 \times 10^{-4}$ cm^{-1}, $g_\perp = 2.050$) although the infrared spectrum was different from that expected for coordinated thioamide ligands in that bands assignable to N–H stretching frequencies and other principal thioamide absorptions were absent. Microanalytical data indicated the loss of sulphur. An X-ray structural analysis* confirmed that the thioamide L^1H had reacted to form the new ligand L^3 and the complex was in fact $[(CuL^3Cl_2)_n]$ (Fig. 1). This complex has a polymeric structure with each (CuL^3Cl_2) unit being linked into infinite chains by a chlorine atom bridging to an adjacent copper atom. The geometry around the copper(II) is distorted square pyramidal with L^3 being attached via the thione sulphur and the imino nitrogen. Dissolution of the copper(II) bromide complex, $[Cu(L^1H)_3Br_2]$, in nitromethane yielded dark brown needles of a diamagnetic copper(I) complex, $[CuL^3Br]$, which was identified on the basis of analytical results, spectroscopic data and an X-ray structural analysis*.

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*Crystal data for $[(CuL^3Cl_2)_n]$: $C_6H_8Cl_2CuN_2S_3$, M = 338.55. Monoclinic, $a = 9.560(2)$, $b = 14.866(3)$, $c = 7.658(4)$ Å, $\beta = 90.25(1)°$, $V = 1088.3$ Å^3 (by least-squares refinement of the positions of 12 diffractometer measured reflections, $\lambda = 1.5418$ Å), space group $P2_1/c$ from systematic absences, $Z = 4$, $D_m = 1.99(1)$ g cm^{-3} (by flotation), $D_c = 2.06$ g cm^{-3}, μ(Cu Kα) = 127.6 cm^{-1} (the crystal size precluded the need to apply absorption corrections), 1146 observed reflections, 619 reflections $> 5\sigma(F)$ used for refinement, $2\theta_{max} = 110°$, $R = 0.096$, non-hydrogen atoms anisotropic, hydrogen atoms isotropic. For $[CuL^3Br]$: $C_6H_8BrCuN_2S_3$, M = 347.79. Triclinic, $a = 7.496(1)$, $b = 8.574(1)$, $c = 10.421(1)$ Å, $\alpha = 120.55(1)$, $\beta = 105.56(1)$, $\gamma = 95.76(1)°$, $V = 532.6$ Å^3 (by least-squares refinement of the positions of 20 reflections with $32.0° < 2\theta < 40.4°$, $\lambda = 0.7107$ Å), space group $P\bar{1}$, $Z = 2$, $D_c = 2.17$ g cm^{-3}, μ(Mo-Kα) = 66.2 cm^{-1} (absorption by empirical corrections, minimum, maximum transmission 0.46, 0.35), 2026 observed reflections, $2\theta_{max} = 60°$, $R(R_w)$ 0.039 (0.048), non-hydrogen atoms anisotropic, hydrogen atoms isotropic. For $[CuL^2_2(H_2O)_2](ClO_4)_2$: $C_{12}H_{20}Cl_2CuN_4O_{12}S_4$, M = 674.55. Monoclinic, $a = 8.088(1)$, $b = 11.124(1)$, $c = 15.517(3)$ Å, $\beta = 120.14(1)°$, $V = 1207.3$ Å^3 (by least-squares refinement of the positions of 12 diffractometer measured reflections, $\lambda = 1.5418$ Å), space group $P2_1/c$ from systematic absences, $Z = 2$, $D_m = 1.85(1)$ g cm^{-3} (by flotation), $D_c = 1.87$ g cm^{-3}, μ(Cu Kα) = 72.4 cm^{-1} (the crystal size precluded the need to apply absorption corrections), 1209 observed reflections, 828 reflections $> 5\sigma(F)$ used for refinement, $2\theta_{max} = 110°$, $R = 0.082$, non-hydrogen atoms anisotropic, hydrogen atoms isotropic.

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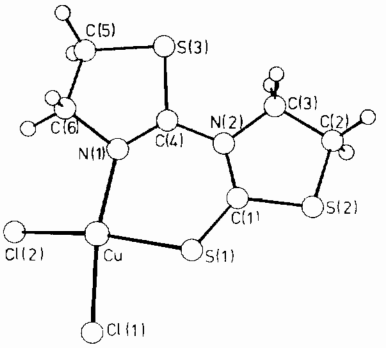


Fig. 1. Structure of one CuL^3Cl_2 unit in the polymeric complex $[(CuL^3Cl_2)_n]$. Significant bond lengths and angles are: Cu–Cl(1) = 2.275(9), Cu–Cl(2) = 2.999(9), Cu–S(1) = 2.294(10), Cu–N(1) = 2.00(3) Å; Cl(1)–Cu–Cl(2) = 92.4(4), Cl(1)–Cu–S(1) = 81.4(3), Cl(2)–Cu–S(1) = 161.5(4), N(1)–Cu–S(1) = 89.1(8), N(1)–Cu–Cl(1) = 169.1(8), N(1)–Cu–Cl(2) = 95.0(9)°. The Cu atom also binds apically to a Cl atom of an adjacent molecule [Cu–Cl(2^{I}) = 2.727(10) Å] thus forming a linear polymer.

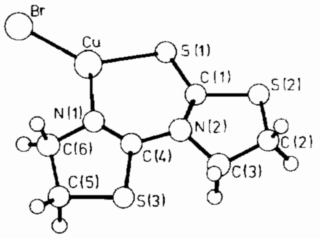


Fig. 2. Structure of $[CuL^3Br]$. Significant bond lengths and angles are: Cu–Br = 2.280(1), Cu–S(1) = 2.193(1), Cu–N(1) = 1.980(3) Å; Br–Cu–S(1) = 134.2(1), S(1)–Cu–N(1) = 98.9(1), N(1)–Cu–Br = 126.9(1)°.

The copper(I) is three coordinate with an approximately trigonal planar environment (Fig. 2). Characterized terminal Cu(I)–Br bonds are not common but the Cu–Br distance of 2.280(1) Å compares well with the Cu–Br bond length of 2.281(3) Å in $[MoS_4(CuBr)_4]^{2-}$ [7] where the sulphur atoms bridge the copper and molybdenum atoms. Other complexes which contain three coordinated copper(I) have longer Cu–Br distances, for example: $[Cu(PPh_3)_2Br]$ (2.346(2) Å) [8]; $[(t\text{-}BuNC)_4Mo(\mu\text{-}t\text{-}BuS)_2CuBr]$ (2.317(2) Å) [9]; and $[Cu_2Br_4]^{2-}$ (2.328(2) Å) [10].

When $Cu(ClO_4)_2 \cdot 6H_2O$ is the copper(II) source, the ligand L^3 is once again formed but is bound to copper(I). In a typical reaction the thioamide L^1H dissolved in nitromethane was added to $Cu(ClO_4)_2 \cdot 6H_2O$ in ethanol. The initially green colored solution turned to yellow then to brown and after two weeks dark brown crystals of the diamagnetic copper(I) complex, $[CuL^3_2]ClO_4$, were deposited. However, if this latter complex was left in the mother liquor, the whole solution turned green and bright green diamond shaped crystals of the copper(II) complex of the carbonyl ligand L^2 appeared. Characterization by X-ray diffraction* showed the complex to be $[CuL^2_2(H_2O)_2](ClO_4)_2$ (Fig. 3). The geometry around the copper(II) is distorted octahedral with short Cu–N and Cu–O bonds in a square plane and longer axial bonds to the two coordinated water molecules. The ESR parameters in frozen nitromethane ($g_{\parallel} = 2.301$, $A_{\parallel} = 149 \times 10^{-4}$ cm^{-1}, $g_{\perp} = 2.088$) are consistent with a CuN_2O_2 equatorial coordination. Moreover, the presence of the coordinated carbonyl chromophore was confirmed by the observation of a strong band in the infrared spectrum at 1634 cm^{-1} attributable to a C=O stretching frequency. The formation of the L^2 complex may be considered as a hydrolysis product of the L^3 complex.

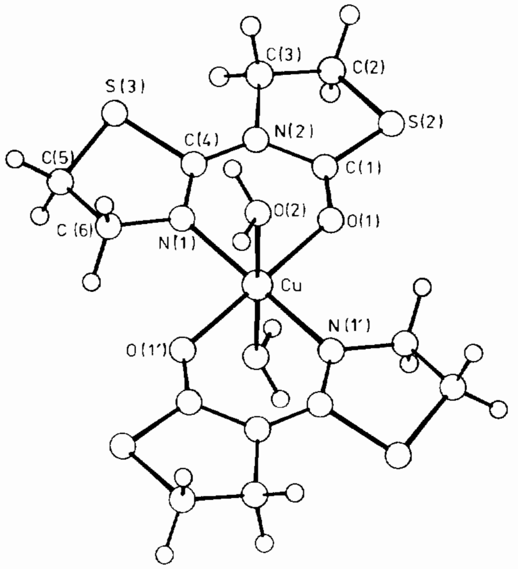
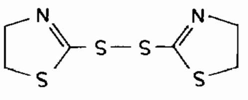


Fig. 3. Structure of the $[CuL^2_2(H_2O)_2]^{2+}$ ion. Significant bond lengths and angles are: Cu–O(1) = 2.01(1), Cu–N(1) = 1.98(1), Cu–O(6) = 2.36(1) Å; N(1)–Cu–O(1) = 91.9(5), N(1)–Cu–O(1') = 88.1(5), N(1)–Cu–O(6) = 93.1(5), O(1)–Cu–O(6) = 90.5(5)°.

Initially the interaction of the thioamide, L^1H, with copper(II) would be expected to lead to its oxidation to the disulphide, L^4, and the reduction of the metal to copper(I). A subsequent intramolecular nucleophilic attack [11] (either proton or copper catalysed) of the imino nitrogen of one ring onto the



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*See footnote p. L5.

trigonal (C^2) carbon of the other ring would give L^3 on elimination of sulphur. Nitromethane would enhance such a reaction by virtue of its high polarity. It is also a potential proton source (from its aci-tautomer) as would be the original thione, L^1H, on oxidation. Experiments which subject L^4 to the same reaction conditions, to test the mechanism, could not be performed because L^4 is unstable. The reactions discussed above are not typical for all thioamides, in fact these are exceptional cases. The factors determining their reactivity are still being studied.

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