The copper promoted oxidation of 1-methylimidazoline-2(3*H*)-thione to bis(1-methylimidazol-2-yl)sulfide

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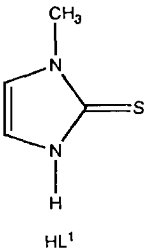
Abstract

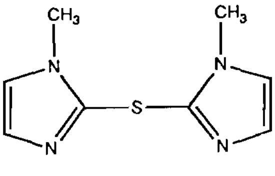
The interaction of 1-methylimidazoline-2(3*H*)-thione (HL^1) in nitromethane solution with copper(II) perchlorate or nitrate yields the complexes $[Cu(L^2)_2(H_2O)_2]X_2 \cdot nH_2O$ ($X^- = ClO_4^-$, $n = 2$; $X^- = NO_3^-$, $n = 0$) where L^2 is the chelate N-donor ligand bis(1-methylimidazol-2-yl)sulfide. The single crystal structure of the complex $[Cu(L^2)_2(H_2O)_2](ClO_4)_2 \cdot 2H_2O$ has been determined. Crystals of the complex are monoclinic, space group $P2_1/n$ with $a = 7.696(2)$, $b = 13.875(3)$, $c = 13.186(2)$ Å, $\beta = 95.98(2)°$ and $Z = 2$. The coordination around the copper is approximately tetragonal with the imino nitrogen atoms from the L^2 ligands equatorial (Cu–N 1.990(3) and 2.004(3) Å) and the water molecules axial (Cu–O 2.501(4) Å). Evidence presented, indicates that the sulfur extruded from the coupling of two HL^1 molecules, during the formation of L^2, is ultimately oxidised to the sulfate ion.

Introduction

Reports of the reactions of heterocyclic thioamides with copper salts have in general concentrated on the isolation of copper(I) complexes. For example, with 1-methylimidazoline-2(3*H*)-thione (HL^1), the characterisation of compounds such as $[Cu(HL)_3]NO_3$ [1], $Cu_2(HL^1)_4Cl_2$ [2], $[Cu_2(HL^1)_5]SO_4 \cdot 3H_2O$ [3], $[Cu_2(HL)_6](BF_4)_2$ [4], and $[Cu(HL^1)CN]_n$ [5] has been described. However HL^1 is unusual in that it forms a mixed-valence cluster, $[Cu^I_{10}Cu^{II}_2(L^1)_{12}(H_2O)_4]X_2$ ($X^- = ClO_4^-$, PF_6^- or $MeCO_2^-$), directly from copper(II) salts [6], and as well, its oxidation to the monosulfide, bis(1-methylimidazol-2-yl)sulfide (L^2) is promoted by copper(II) [6–8]. This last reaction affords L^2 bound to copper(II) as an N-donor bidentate in the complexes $Cu_2(L^2)_2Cl_4$ (prepared from the reaction of HL^1 with $CuCl_2 \cdot H_2O$ in methanol [8] or nitromethane [6] and $[Cu(L^2)_2(H_2O)_2](MeOSO_3)_2$ (from HL^1 and $CuSO_4 \cdot 5H_2O$ in methanol [7]). In this paper, in an attempt to gain further information on the copper promoted oxidation of HL^1 to L^2, we focus on the reaction of HL^1 with $Cu(ClO_4)_2 \cdot 6H_2O$ and the fate of the 'extruded' sulfur.



HL^1



L^2

Experimental

Physical measurements were made as previously described [9].

Preparation of $[Cu(L^2)_2(H_2O)_2](ClO_4)_2 \cdot 2H_2O$

To a solution $Cu(ClO_4)_2 \cdot 6H_2O$ (0.37 g, 1 mmol) in ethanol (5 cm^3) was added HL^1 (0.46 g, 1 mmol) dissolved in nitromethane (30 cm^3). The resulting dark green solution was filtered and upon standing for 3 days with slow evaporation, pale blue microcrystals (A) (~ 0.07 g) deposited. These were removed by filtration and after a week dark blue needles of the product crystallised. Yield 0.28 g (40%). *Anal.* Calc. for $C_{16}H_{28}Cl_2CuN_8O_{12}S_2$: C 26.6; H 3.9; N 15.5. Found: C 26.9; H 4.15; N 15.2%.

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The nitrate analogue $[Cu(L^2)_2(H_2O)_2](NO_3)_2$ was prepared in a similar manner. *Anal.* Calc. for $C_{16}H_{24}CuN_{10}O_8S_2$: C 31.4; H 3.9. Found: C 31.2; H 4.6%.

Crystal data for $[Cu(L^2)_2(H_2O)_2](ClO_4)_2 \cdot 2H_2O$

$C_{16}H_{28}Cl_2CuN_8O_{12}S_2$, $M = 723.0$. Monoclinic, $a = 7.696(2)$, $b = 13.875(3)$, $c = 13.186(2)$ Å, $\beta = 95.98(2)°$, $V = 1400.3(5)$ Å^3, space group $P2_1/n$, $Z = 2$, $D_c = 1.69$ g cm^{-3}. Crystal size 0.20×0.27×0.20 mm. μ(Mo Kα) = 12.0 cm^{-1}. Nicolet R3m diffractometer, $\omega/2\theta$ scan type, graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å), temperature 143 K, 2685 reflections measured ($5° \leq 2\theta \leq 52°$, $\pm h$, $+k$, $+l$) 2205 unique with $I > 3\sigma(I)$, empirical absorption correction [10] (max., min. transmission factors = 0.884, 0.478). Refinement [11] non-hydrogen atoms anisotropic, hydrogen atoms isotropic, R (R_w) 0.039 (0.050), weighting scheme $w = 1/[\sigma^2 F_o + 0.0004 F_o^2]$.

Results and discussion

The dark blue compound which finally crystallises out from the reaction of HL^1 and $Cu(ClO_4)_2 \cdot 6H_2O$ in nitromethane/ethanol is formulated as $[Cu(L^2)_2(H_2O)_2](ClO_4)_2 \cdot 2H_2O$. Its IR spectrum does not show characteristic thioamide bands and other spectroscopic results indicate the presence of copper(II) (λ_{max}(nujol) 570 nm (d–d band); ESR (nitromethane, 113 K) $g_{\parallel} = 2.249$, $|A_{\parallel}| = 195 \times 10^{-4}$ cm^{-1}; $g_{\perp} = 2.055$). A similar complex, $[Cu(L^2)_2(H_2O)_2](NO_3)_2$, was obtained from copper(II) nitrate. The single crystal X-ray structure of the perchlorate complex shows the coordination environment around the copper to be tetragonally distorted octahedral with the imino nitrogen atoms from the L^2 ligands forming a square plane (Cu–N(1) 1.990(3) and Cu–N(3) 2.004(3) Å) and the water molecules axial (Cu–O(5) 2.501(4) Å) (Table 1). The geometry of the $[Cu(L^2)_2(H_2O)_2]^{2+}$ species (Fig. 1) is very similar to that found for the same cation in $[Cu(L^2)_2(H_2O)_2](MeOSO_3)_2$ [7]. The non-coordinated perchlorate ions participate in a hydrogen bonding network with the coordinated and lattice water molecules.

TABLE 1. Bond lengths (Å) and angles (°) for $[Cu(L^2)_2(H_2O)_2](ClO_4)_2 \cdot 2H_2O$ with e.s.d.s in parentheses

Cu–N(1)	1.990(3)	Cu–N(3)	2.004(3)
S(1)–C(1)	1.755(3)	Cu–O(5)	2.501(4)
N(1)–C(1)	1.327(4)	S(1)–C(5)	1.756(3)
N(2)–C(1)	1.343(4)	N(1)–C(2)	1.383(4)
N(2)–C(4)	1.460(5)	N(2)–C(3)	1.368(4)
N(3)–C(6)	1.384(4)	N(3)–C(5)	1.333(4)
N(4)–C(7)	1.368(5)	N(4)–C(5)	1.352(4)
C(2)–C(3)	1.348(5)	N(4)–C(8)	1.465(5)
C(6)–C(7)	1.341(5)		
N(3)–Cu–N(1)	88.7(1)	C(5)–S(1)–C(1)	97.1(2)
C(1)–N(1)–Cu	126.3(2)	C(2)–N(1)–Cu	128.4(2)
C(2)–N(1)–C(1)	105.2(3)	C(3)–N(2)–C(1)	107.0(3)
C(4)–N(2)–C(1)	127.0(3)	C(4)–N(2)–C(3)	126.0(3)
C(5)–N(3)–Cu	126.1(2)	C(6)–N(3)–Cu	128.5(2)
C(6)–N(3)–C(5)	105.2(3)	C(7)–N(4)–C(5)	106.4(3)
C(8)–N(4)–C(5)	126.8(3)	C(8)–N(4)–C(7)	126.7(3)
N(1)–C(1)–S(1)	125.8(3)	N(2)–C(1)–S(1)	122.7(2)
N(2)–C(1)–N(1)	111.4(3)	C(3)–C(2)–N(1)	109.4(3)
C(2)–C(3)–N(2)	107.0(3)	N(3)–C(5)–S(1)	125.4(2)
N(4)–C(5)–S(1)	123.3(2)	N(4)–C(5)–N(3)	111.3(3)
C(7)–C(6)–N(3)	109.4(3)	C(6)–C(7)–N(4)	107.7(3)

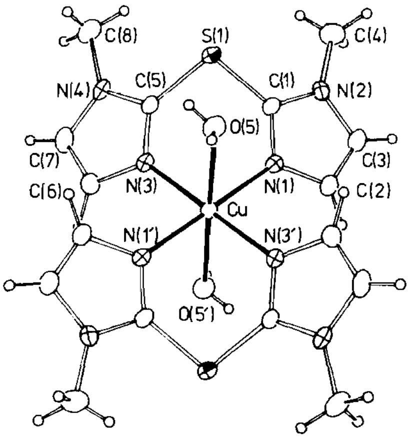

Fig. 1. Structure of the $[Cu(L^2)_2(H_2O)_2]^{2+}$ ion showing 50% probability envelopes for thermal parameters for non-hydrogen atoms.

The production of a molecule of the monosulfide of L^2 from two molecules of the thione, HL^1, formally requires the loss of two atoms of hydrogen and one of sulfur. The initial mixing of HL^1 with copper(II) perchlorate or nitrate, in a 4:1 molar ratio, affords a dark green solution which exhibits an ESR spectrum indicating the formation of the $[Cu(HL^1)_4]^{2+}$ cationic species with coordination of the thione sulfur to Cu(II). The observed parameters ($g_{\parallel} = 2.123$, $|A_{\parallel}| = 124 \times 10^{-4}$ cm^{-1}; $g_{\perp} = 2.021$) are similar to $[CuL_4]^{2+}$ thiourea species (e.g. for L = *N,N*-dimethyl-*N*-*p*-tolylthiourea $g_{\parallel} = 2.126$, $|A_{\parallel}| = 125 \times 10^{-4}$ cm^{-1}; $g_{\perp} = 2.031$) [12] and the point arising from the $g_{\parallel} - |A_{\parallel}|$ values lies close to the 'CuS_4' delineator [13, 14] on a Blumberg–Peisach plot [15]. Moreover the spectral profile also corresponds to an 'S_4' donor set bound to copper(II) including the characteristic resolution of the $I_{Cu} = 3/2$ coupling due to ^{63}Cu and ^{65}Cu isotopes on the $g_{\parallel}$ line [14]. The subsequent oxidation of HL^1 to its disulfide by copper(II) would be expected to occur, as is typical for such thiones [16]. For example, thiourea is oxidised by copper(II) perchlorate, in acetonitrile, to the α,α'-dithiobis(formadinium) ion, $[(H_2N)_2CSSC(NH_2)_2]^{2+}$, which has been isolated as the perchlorate salt. The reoxidation of Cu(I) with the concomitant loss of sulfur would allow the formation of the $[Cu(L^2)_2]^{2+}$ cationic complex. This latter species is the only ESR detectable copper(II) complex when the pale blue solid **A**, which is initially formed, starts crystallising out. This initial solid **A** is of variable composition but IR spectroscopy shows it contains copper(II) sulfate pentahydrate and at least one other sulfur–oxygen compound. For some samples the IR spectrum was identical to an authentic sample of $CuSO_4 \cdot 5H_2O$. The reaction was repeated a number of times but microanalyses were not reproducible between samples. The low carbon figures (*c.* 7%) and absence of nitrogen, along with the IR spectral results, suggest the presence of RSO_x^{n-} species. Copper(II) is known to oxidatively cleave disulfides to sulfinates [17, 18] and, as mentioned in the 'Introduction', the $MeOSO_3^-$ anion is formed when HL^1 reacts with $CuSO_4 \cdot 5H_2O$ in methanol [7]. Although it is not clear whether the source of the $MeOSO_3^-$ sulfur is the thione or the copper sulfate, the former is more likely on the basis of the present results. In conclusion, therefore, it appears that in the reaction of HL^1 with copper(II) perchlorate to give L^2, the extruded sulfur is oxidised ultimately to the sulfate ion. In this respect the reaction parallels the copper promoted oxidation of the thioamide, benzothiazoline-2-thione, and its 6-ethoxy derivative, in pyridine solvent, where the products are the appropriate monosulfide and $[Cu(pyridine)_4]SO_4 \cdot 2H_2O$ [19].

Supplementary material

This is available from the Cambridge Crystallographic Data Centre.

Acknowledgements

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References

1 E. R. Atkinson, D. J. Gardiner, A. R. W. Jackson and E. S. Raper, *Inorg. Chim. Acta, 98* (1985) 35.

2 J. R. Creighton, D. J. Gardiner, A. C. Gorvin, C. Gutteridge, A. R. W. Jackson, E. S. Raper and P. M. A. Sherwood, *Inorg. Chim. Acta, 103* (1985) 195.

3 E. R. Atkinson, E. S. Raper, D. J. Gardiner, H. M. Dawes, N. P. C. Walker and A. R. W. Jackson, *Inorg. Chim. Acta, 100* (1985) 285.

4 E. S. Raper, J. R. Creighton, D. Robson, J. D. Wilson, W. Clegg and A. Milne, *Inorg. Chim. Acta, 143* (1988) 95.

5 E. S. Raper, J. R. Creighton, J. D. Wilson, W. Clegg and A. Milne, *Inorg. Chim. Acta, 155* (1989) 77.

6 E. W. Ainscough, E. N. Baker, A. G. Bingham and A. M. Brodie, *J. Chem. Soc., Dalton Trans.*, (1989) 39.

7 D. A. Baldwin, J. C. A. Boeyens, R. G. Copperthwaite, J. H. N. Loubser and A. J. Markwell, *J. Cryst. Spectrosc. Res., 14* (1984) 157.

8 D. A Baldwin, J. C. A Boeyens, L. Denner and A. J. Markwell, *J. Cryst. Spectrosc. Res., 16* (1986) 763.

9 E. W. Ainscough, A. M. Brodie, J. M. Husbands, G. J. Gainsford, E. J. Gabe and N. F. Curtis, *J. Chem. Soc., Dalton Trans.*, (1985) 151.

10 G. M. Sheldrick, *SHELX-76*, program for crystal structure determination, University of Cambridge, U.K., 1976.

11 G. M. Sheldrick, *SHELXTL*, Revision 4.1, Nicolet XRD Corporation, Madison, Wisconsin, CA, U.S.A., 1984.

12 D. A. Zatko and B. Kratochvil, *Anal. Chem., 40* (1968) 2120.

13 U. Sakaguchi and A. W. Addison, *J. Chem. Soc., Dalton Trans.*, (1979) 600.

14 E. W. Ainscough, A. G. Bingham and A. M. Brodie, *Inorg. Chim. Acta, 138* (1987) 175.

15 J. Peisach and W. E. Blumberg, *Arch. Biochem. Biophys., 165* (1974) 691.

16 E. W. Ainscough and A. M. Brodie, *Coord. Chem. Rev., 27* (1978) 59.

17 A. Odari, T. Maruyama, O. Yamauchi, T. Fujiwara and K. Tomita, *J. Chem. Soc., Chem. Commun.*, (1982) 646.

18 L. S. Higashi, M. Lundeen, E. Hilti and K. Seff, *Inorg. Chem., 16* (1977) 310.

19 E. W. Ainscough, A. G. Bingham and A. M. Brodie, *Inorg. Chim. Acta, 96* (1985) L47.