Inorganica Chimica Acta, 155 (1989) 85–89

Bis(imidazolidine-2-thione)(thiocyanato-*N*)copper(I): Preparation, Thermal Analysis and Crystal Structure

ERIC S. RAPER*, JAMES R. CREIGHTON, JOHN D. WILSON

Department of Chemical and Life Sciences, The Polytechnic, Newcastle upon Tyne NE1 7ST, U.K.

WILLIAM CLEGG*

Department of Inorganic Chemistry, The University, Newcastle upon Tyne NE1 7RU, U.K.

and ALEX MILNE

International Paint, Stoneygate Lane Felling, Gateshead, Tyne and Wear NE10 0JY, U.K.

(Received May 30, 1988)

Abstract

Reaction between copper(I) thiocyanate and imidazolidine-2-thione ($imdtH_2$) in ethanol–acetonitrile solution produced a compound of formula $[Cu(imdtH_2)_2(NCS)]$, which has been characterised by a combination of spectroscopic, thermal and crystal structure analysis.

The crystal structure of the compound consists of neutral mononuclear molecules in which the central metal and the thiocyanate atoms occupy crystallographic mirror planes in the monoclinic unit cell ($a = 6.081(3)$, $b = 14.583(7)$, $c = 7.351(2)$ Å, $\beta = 103.46(4)°$, space group $P2_1/m$, $Z = 2$). The complex contains a CuS_2N arrangement formed from two monodentate S-donating $imdtH_2$ ligands (Cu–S = 2.221(1) Å) and an N-donating thiocyanate anion (Cu–N = 1.956(4) Å). Angles at the Cu(I) atom (119.2(1); 121.6(1)°) are consistent with a relatively undistorted trigonal arrangement at the metal. The CuS_2N arrangement in the complex is further stabilised by NH...N(thiocyanate) H bonds (N...N = 3.060 Å; N–H...N = 160°). The final conventional R index is 0.057 for 1308 observed reflections ($F \geqslant 4\sigma(F)$).

The IR spectrum of the complex is indicative of a CuS_2N arrangement with ν(CuS) at 245 cm^{-1}. Thermal decomposition of the complex in air (150–740 °C) involves desulphurisation of the $imdtH_2$ ligands and thiocyanate anions together with *in situ* copper sulphide production (150–560 °C) followed by degradation to copper(II) oxide (620–740 °C).

Introduction

The ability of imidazolidine-2-thione ($imdtH_2$) to coordinate to a wide range of elements is well established [1]. The dominant coordination mode of $imdtH_2$ is monodentate-S but with Cu(I) the ligand is also μ_2-S bridging towards the tetrahedrally and trigonally coordinated metal [2]. Copper(I) thiocyanate forms addition compounds with many nitrogen bases. The resultant stoichiometries of these reactions are mostly 1:1 or 1:2 in which the anion bridges metal nuclei with the production of single or double-stranded polymeric chains [3, 4]. Similar structural studies with heterocyclic thioamides are relatively scarce although a silver complex $[Ag(imdtH_2)_2(SCN)]$ has been reported to contain trigonal AgS_3 units which produce distorted pyramidal coordination at the metal through additional long Ag–S contacts [5].

Structural studies of the ligand 1-methylimidazoline-2-thione (mimtH) with a variety of copper salts have produced a range of complexes with varying stoichiometries and structures. These range from mononuclear $[Cu(mimtH)_3](NO_3)$ [6], to dinuclear $[Cu_2(mimtH)_4Cl_2]$ [7], $[Cu_2(mimtH)_5](SO_4)\cdot 3H_2O$ [8], $[Cu_2(mimtH)_6(BF_4)_2$ [9] and polymeric species $[Cu(mimtH)(CN)]$ [10]. A tetranuclear complex has also been obtained from benzimidazoline-2-thione ($bzimtH_2$) and copper perchlorate, $[Cu_4(bzimtH_2)_{10}]\cdot(ClO_4)_2\cdot 14H_2O$ [11].

In order to extend the range of counter ions used in the above series a number of imidazole-thione derivatives have been reacted with copper(I) thiocyanate. The most successful preparation, involving $imdtH_2$, yielded a colourless crystalline diamagnetic product which is the subject of this report.

Experimental

Starting Materials

Copper(I) thiocyanate and the ligand, $imdtH_2$, as 2-imidazolidinethione, were supplied by the Aldrich Chemical Company, and were used as supplied.

---

*Authors to whom correspondence should be addressed.

0020-1693/89/$3.50

Preparation and Analysis of [Cu(imdtH$_2$)$_2$NCS]

Copper(I) thiocyanate (0.244 g; 2 mmol) and imdtH$_2$ (0.816 g; 8 mmol), were added to 50 ml of an ethanol/acetonitrile mixture (25:75; *v*:*v*) in a round bottomed flask (250 ml). The reaction mixture was refluxed until the solid reactants dissolved (*ca.* 1 h), then set aside. Colourless crystals developed slowly and after ten weeks they were removed by filtration, washed with absolute ethanol (20 ml), dried and stored *in vacuo*. Yield 60%.

Anal. Calc. for $CuC_{13}H_{12}N_5S_3$: C 25.80; H 3.68; N 21.5; Cu 19.87. Found: C 25.85; H 3.65; N 21.65; Cu 20.80%.

Physical Methods

Perkin-Elmer infrared grating spectrophotometer, 4000–200 cm^{-1}, CsI discs. Stanton-Redcroft TG 750 thermal analyser (TG, DTG) with ceramic furnace, column dried flowing air, Pt crucibles. Stanton-Redcroft DTA 673/4, flowing N$_2$, quartz crucibles. Sample masses 5–8 mg. Heating rates 10 to 20 °C min^{-1} (TG, DTG); 20 °C min^{-1} (DTA). Quantitative DTA method [12]. Stanton-Redcroft hot stage microscope, HSM-5, Hitachi DK81 video camera, JVC TM/90 PSN colour monitor. Room temperature, Newport Instruments, Gouy magnetic balance. Guinier-Hagg parafocussing X-ray camera, Cu Kα_1 monochromatised radiation, (λ = 1.5405 Å), Kodirex single coated X-ray film, Siemens microdensitometer.

Crystal Structure Determination

Unit cell data together with intensity data collection and processing details are summarised in Table 1. A Siemens AED2 diffractometer was used for the unit cell determination and intensity data collection. The coordinates of the non-H atoms were obtained by direct methods and refined by blocked-cascade least-squares methods on F to a minimum of $\Sigma w\Delta^2$, ($\Delta = |F_o| - |F_c|$) with anisotropic thermal parameters.

Coordinates of the imido (NH) H atoms were obtained from difference Fourier methods and refined freely, other H atom coordinates were constrained (C–H = 0.96 Å; H–C–H = 109.5°), $U(\mathrm{H}) = 1.2U_{eq}(\mathrm{C})$). Final conventional $R = 0.057$ R_w-$[=(\Sigma w^{1/2}|\Delta|/(\Sigma w^{1/2}|F_o|)] = 0.047$ with $w^{-1} = \sigma^2(F) = \sigma^2_c(F) + 22 - 161G + 319G^2 - 35S + 17S^2 + 62GS$ ($G = F_o/F_{max}$; $S = \sin\theta/\sin\theta_{max}$) [13].

Neutral atom scattering factors were taken from ref. 14. Final refined coordinates are in Table 2, bond lengths and angles are in Table 3. SHELXTL and related programs were used in the analysis [15]. See also 'Supplementary Material'.

TABLE 1. Crystallographic Data

Formula	$CuC_7H_{12}N_5S_3$
M_r	325.5
a (Å)	6.081(3)
b (Å)	14.583(7)
c (Å)	7.351(2)
β (°)	103.46(4)
V (Å^3)	633.98
Reflection conditions	*hkl*:none
	0kl:*k* = 2*n*
Space group	$P2_1/m$
Crystal size (mm)	0.31 × 0.38 × 0.46
Radiation, λ (Å)	Cu, 1.54184
No. reflections for cell parameters	32(20–35°, 2θ)
D_x (g cm^{-3})	1.707
Z	2
F(000)	332
μ (mm^{-1})	6.83
$2\theta_{max}$ (°)	155
h ranges	−7 to 7
k ranges	−18 to 18
l ranges	−8 to 8
Scan width	1.7° + α-doublet separation
Scan time (s)	14–56
T (K)	298
Standard reflections	3; *ca.* 2.5% decay
Transmission factors	0.055–0.185
Absorption correction	semi-empirical
Total data	4977
Unique data	1335
R_{int}	0.13
Observed data ($F > 4\sigma(F)$)	1309

TABLE 2. Fractional Atomic Coordinates (×10^4) for Refined Atoms[a]

Atom	*x*	*y*	*z*
Cu(1)	3318(1)	7500	2366(1)
N(99)	6533(6)	7500	3614(6)
C(99)	7997(7)	7500	4947(6)
S(99)	9964(2)	7500	6869(2)
S(2)	1527(1)	6170(1)	1717(1)
C(2)	3538(5)	5324(2)	2167(4)
N(1)	3131(5)	4459(3)	1928(5)
H(1)	2155(76)	4203(35)	1669(50)
N(3)	5740(5)	5454(3)	2799(5)
H(3)	6237(58)	5900(28)	3004(45)
C(4)	6993(5)	4602(3)	2973(4)
C(5)	5156(5)	3878(3)	2393(5)

[a] e.s.d.s given in parentheses.

Results and Discussion

Positive shifts to ν(NH) (3320 cm^{-1}), ν(CN) (1340, 1515 cm^{-1}) and negative shifts to ν(CS) (910, 495 cm^{-1}) and δ(CS) (370 cm^{-1}) coupled with ν(CuS) (245 cm^{-1}) suggest S-donation to the metal by imdtH$_2$ [16. 17]. Thiocyanate bands occur at 2040 ν(CN) and 805 ν(CS) cm^{-1}; unfortunately the δ(NCS) bands of the anion (470–490 cm^{-1})

TABLE 3. Bond Lengths (Å) and Angles (°)[a]

Bond lengths (Å)			
Cu(1)–N(99)	1.956(4)	Cu(1)–S(2)	2.221(1)
N(99)–C(99)	1.161(5)	C(99)–S(99)	1.625(4)
S(2)–C(2)	1.714(3)	C(2)–N(1)	1.290(5)
C(2)–N(3)	1.324(4)	N(1)–H(1)	0.689(48)
N(1)–C(5)	1.468(5)	N(3)–H(3)	0.719(39)
N(3)–C(4)	1.447(5)	C(4)–C(5)	1.524(5)
Bond angles (°)			
N(99)–Cu(1)–S(2)	119.2(1)	S(2)–Cu(1)–S(2')	121.6(1)
Cu(1)–N(99)–C(99)	151.9(4)	N(99)–C(99)–S(99)	177.4(5)
Cu(1)–S(2)–C(2)	107.1(1)	S(2)–C(2)–N(1)	124.9(2)
S(2)–C(2)–N(3)	125.6(3)	N(1)–C(2)–N(3)	109.5(3)
C(2)–N(1)–H(1)	133.8(40)	C(2)–N(1)–C(5)	114.1(3)
H(1)–N(1)–C(5)	112.0(40)	C(2)–N(3)–H(3)	123.0(29)
C(2)–N(3)–C(4)	112.2(3)	H(3)–N(3)–C(4)	124.8(29)
N(3)–C(4)–C(5)	103.5(3)	N(1)–C(5)–C(4)	100.7(3)

Symmetry operator for S(2'): $x, \frac{3}{2} - y, z$. [a]e.s.d.s given in parentheses.

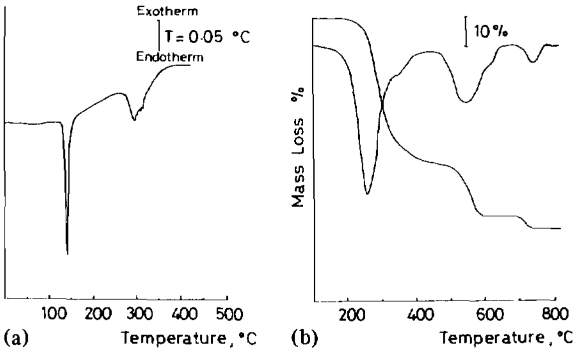

Fig. 1. Thermal analysis curves: (a) TG/DTG in flowing air, heating rate 20 °C min^{-1}; (b) DTA inflowing dinitrogen, heating rate 20 °C min^{-1}.

are obscured by ligand bands. These observations satisfy some of the criteria for *N*-thiocyanate coordination [18]. Consequently the IR spectra suggest a S_2N-donor set for the complex.

Thermal analysis, in flowing air, Fig. 1a, shows that the complex decomposes over the temperature range 150–740 °C to copper(II) oxide. The agreement between experimental (75.5%) and theoretical mass loss (75.4%) is within experimental error (±2.0%) and confirms the empirical formula of the complex. Both TG and DTG curves show the decomposition to be a three stage process. The first two major, and contiguous, stages (150–290 °C, 49.0% mass loss; 290–560 °C, 22.0% mass loss; Fig. 1a) involve desulphurisation of $imdtH_2$ and thiocyanate, respectively, and concomitant production of copper(II) sulphide. Room temperature X-ray powder diffraction studies of the cooled melt, initially obtained at about 500 °C, as well as hot-stage microscopy, confirmed copper(II) sulphide formation. The final stage (680–740 °C; 4.5% mass loss) accounts for the conversion of copper(II) sulphide to copper(II) oxide.

The DTA curve, in dinitrogen (Fig. 1b), shows two well resolved endotherms, the first of which is a melting endotherm (107–157 °C; ΔH_m 56.4 ± 4 kJ mol^{-1}) and the second is a decomposition endotherm (250–370 °C; ΔH_D 47.7 ± 6 kJ mol^{-1}). Such modest enthalpy requirements suggest that the decomposition involves a combination of endothermic ligand desulphurisation and exothermic metal sulphide formation. The alternative scheme, of unchanged ligand evolution, requires at least 140 kJ mol^{-1} for the $imdtH_2$ molecules alone [12].

The neutral mononuclear complex consists of a copper(I) atom trigonally coordinated by two S-donating $imdtH_2$ ligands and one N-donating thiocyanate anion (Fig. 2). The constituent atoms of the Cu–N–C–S moiety occupy crystallographic mirror planes in the unit cell (Fig. 3).

Bond lengths and angles (Table 3) are consistent with trigonally coordinated copper(I). The Cu–S distance is within the range reported (2.191 to 2.282 Å) for related systems [6, 8, 19–21] and the Cu_2SN

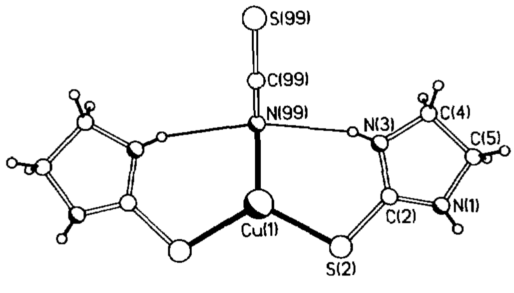

Fig. 2. Perspective view of the complex with intramolecular H-bonding and numbering of atoms.

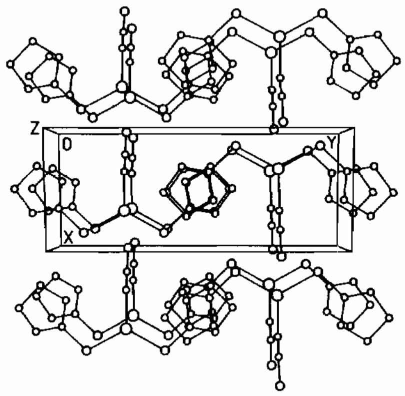

Fig. 3. Perspective view of unit cell contents.

coordination sphere is relatively undistorted with the copper(I) atom only slightly displaced (−0.021 Å) from the plane formed with the donor atoms. Thiocyanate dimensions (Table 2) are consistent with other instances in which the anion is N-donating [22, 23].

Changes in the dimensions of the imdtH$_2$ ligand upon coordination are limited to a modest lengthening of the C(2)–S(2) distance (1.694(4) to 1.714(3) Å), and to a significant decrease in the thioamido C(2)–N(1,3) distances (1.349(3) to 1.317(mean) Å) [1]. These observations reflect changes in electronic distribution within the thioamide component of the ligand upon coordination. The Cu–S–C angle (107.1(1)°) is typical of terminally coordinated imidazolethione donors [1, 8]. Twisting of imdtH$_2$ about the Cu–S–C plane is modest (0.7°), and only slight 'tilting' of imdtH$_2$ about the CuS$_2$N plane (8.4°) occurs, while the plane of the Cu–NCS unit is virtually normal (94.0°) to that of imdtH$_2$. The complexes [Cu(imdtH$_2$)$_2$(NCS)] and [Ag(imdtH$_2$)$_2$(SCN)] [5] form an interesting pair: both cations are 'soft', and the ligands are identical and S-bonded. The major difference between the complexes is the coordinating mode of the thiocyanate ion. The Ag(I) complex has the expected AgS$_3$ arrangement, which is also reported for [Ag(thiourea)$_2$(SCN)] [24], the CuS$_2$N arrangement in the Cu(I) complex is novel. Thiocyanate linkage isomerism is known to be affected by steric and electronic effects in the solid state [25]. Although such effects are generally difficult to distinguish from one another in specific cases, the relative donor–acceptor behaviour of the ligands is recognised as a major source of electronic effects [26]. Relative lengthening of the C_{sp^2}–S_{exo} and shortening of the C_{sp^2}–N_{sp^2} distance, of imdtH$_2$ in [Cu(imdtH$_2$)$_2$(NCS)] (Table 3) are indicative of ligand σ-donor and π-acceptor behaviour. Such effects will certainly modify the relative 'softness' of the central metal and may account, at least in part, for the presence of N-donating thiocyanate.

Differing packing arrangements are also manifest between the two complexes under discussion. In the Ag(I) complex, neighbouring AgS$_3$ units form weak centrosymmetric dimers which contain Ag$_2$S$_2$ rings (Ag...S = 3.105(2) Å); similar packing arrangements are also reported for (Ag(thiourea)$_2$(SCN)] [24]. Additional non-bonded interactions in [Ag(imdtH$_2$)$_2$(SCN)] include intramolecular N–H...S-(thiocyanate), and intermolecular N–H...N(thiocyanate), H bonds [5]. The presence of H-bonding between the imido (NH) H atom of imdtH$_2$ and the thiocyanate N atom [N(3)–H(3)$\cdots$N(99) = 160°] is the major non-bonded interaction in [Cu(imdtH$_2$)$_2^-$(NCS)]. Because of the inherent symmetry of the complex the N-donating thiocyanate ion is stabilised by such H-bonding from both of the imdtH$_2$ ligands (Fig. 3).

Supplementary Material

H atom coordinates with isotropic thermal parameters, anisotropic thermal parameters and structure factor tables are available from the authors.

References

1 L. P. Battaglia, A. Bonamartini Corradi and M. Nardelli, *Croat. Chim. Acta, 57* (1984) 5215.
2 L. P. Battaglia, A. Bonamartini Corradi, M. Nardelli and M. E. Vidoni Tani, *J. Chem. Soc., Dalton Trans.*, (1976) 143.
3 P. C. Healy, C. Pakawatchai, R. I. Papasergio, V. A. Patrick and A. H. White, *Inorg. Chem., 23* (1984) 3769.
4 G. O. Morpurgo, G. Dessy and V. Fares, *J. Chem. Soc., Dalton Trans.*, (1984) 785.
5 M. Belicchi Ferrari, G. Gasparri Fava and M. E. Vidoni Tani, *Cryst. Struct. Commun., 10* (1981) 571.
6 E. R. Atkinson, D. J. Gardiner, A. R. W. Jackson and E. S. Raper, *Inorg. Chim. Acta, 98* (1985) 35.
7 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.
8 E. R. Atkinson, E. S. Raper, D. J. Gardiner, H. M. Davies, N. P. C. Walker and A. R. W. Jackson, *Inorg. Chim. Acta, 100* (1985) 285.
9 E. S. Raper, J. R. Creighton, D. Robson, J. D. Wilson, W. Clegg and A. Milne, *Inorg. Chim. Acta, 143* (1988) 95.
10 E. S. Raper, J. R. Creighton, J. D. Wilson, W. Clegg and A. Milne, *Inorg. Chim. Acta, 155* (1988) 77.
11 E. S. Raper, J. R. Creighton, J. D. Wilson, W. Clegg and A. Milne, *Inorg. Chim. Acta, 149* (1988) 265.
12 E. S. Raper, *J. Therm. Anal., 25* (1982) 463.
13 W. Hong and B. E. Robertson, in A. J. C. Wilson (ed.), *Structure and Statistics in Crystallography*, Adenine Press, New York, 1985, p. 125.
14 *International Tables for X-ray Crystallography*, Vol. IV, Birmingham, Kynoch Press, 1974, pp. 99, 149.
15 G. M. Sheldrick, *SHELXTL*, an integrated system for solving, refining and displaying crystal structures from diffraction data, Revision 5, University of Göttingen, 1985.

16 K. Dwarakanath and D. N. Sathyanarayana, *Bull. Chem. Soc. Jpn., 52* (1979) 2699.

17 K. Dwarakanath and D. N. Sathyanarayana, *Indian J. Chem., 18A* (1979) 302.

18 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, New York, 3rd edn., 1978, pp. 270–274.

19 M. S. Weininger, G. W. Hunt and E. L. Amma, *J. Chem. Soc., Chem. Commun.*, (1972) 1140.

20 L. P. Battaglia, A. Bonamartini Corradi, F. A. Devillanova and G. Verani, *Transition Met. Chem., 4* (1979) 264.

21 F. A. Devillanova, G. Verani, L. P. Battaglia and A. Bonamartini Corradi, *Transition Met. Chem., 5* (1980) 362.

22 E. S. Raper, J. R. Creighton, R. E. Oughtred and I. W. Nowell, *Inorg. Chim. Acta, 87* (1984) 19.

23 E. S. Raper, R. E. Oughtred, J. R. Creighton and I. W. Nowell, *Inorg. Chim. Acta, 87* (1984) 201.

24 M. R. Udupa, G. Henkel and B. Krebs, *Inorg. Chim. Acta, 18* (1976) 173.

25 J. L. Burmeister in A. A. Newman (ed.), *The Chemistry and Biochemistry of Thiocyanic Acid and its Derivatives'*, Academic Press, London, 1976, pp. 68–130.

26 R. J. Balahura and N. A. Lewis, *Coord. Chem. Rev., 20* (1976) 109.