Behaviour of Thiocarbonohydrazidium Cation as a Ligand. Crystal and Molecular Structure of Dichloro($1H^+$-thiocarbonohydrazidium-*NS*)-copper(II) Chloride

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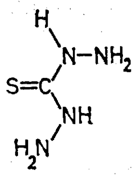
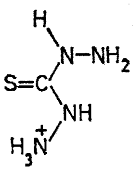
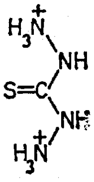
Crystals of the title compound are triclinic, space group $P\bar{1}$, with $Z = 2$ in a unit cell of dimensions: $a = 8.310(6)$ $b = 8.566(5)$, $c = 5.902(5)$ Å, $\alpha = 103.9(2)$, $\beta = 99.2(2)$, $\gamma = 83.1(2)°$. The structure was solved from diffractometer data by Patterson and Fourier methods and refined by block-diagonal least-squares to R 0.046 for 1 454 observed reflections. The structure consists of complex cations consisting of copper, two chlorine atoms, and one chelating monoprotonated thiocarbonohydrazide molecule, and chloride anions. Copper is approximately square-planar co-ordinated, the corners being occupied by two co-ordinated chlorines, and by one sulphur and one nitrogen of a chelating ligand, which is in a *cis,cis*-conformation. By taking into account a long interaction between copper and the chloride ion Cl(3) [Cu $\cdots$ Cl(3) 3.051 Å] the co-ordination polyhedron around copper can be considered as an elongated square pyramid.

RESEARCH on thiocarbonohydrazide (tcaz) and its derivatives both in solution and in the solid state has demonstrated the presence in aqueous acidic solutions of neutral, mono-, and di-protonated species,[1,2] having conformations (I)—(III) in the crystal state.


cis,trans
(I)


cis,trans
(II)


cis,cis
(III)

Species (I) was identified in the crystal structures of the neutral compound [3,4] and its metal chelates (*NS*).[5-7] Species (II) is present in the crystals of tcaz·0.5HCl)[4] and species (III) in the crystals of tcaz·2HCl·$2H_2O$ [8] and tcaz·H_2SO_4.[9]

Transformation from the neutral or monoprotonated to the diprotonated species is associated with a change of conformation from *cis,trans* to *cis,cis*. Both steric hindrance between $-\overset{+}{N}H_3$ and $>$NH of the opposite group and electrostatic attraction between the $-\overset{+}{N}H_3$ groups and the electron cloud associated with the C–S bond are probably responsible for stabilizing the *cis,cis*-conformation.

From a systematic structural study, it became apparent that protonation of the $-NH-NH_2$ group causes its rotation around the C–N bond, to assume a *cis*-position with respect to the sulphur atom. Moreover, chelation to the metal also requires that the other $-NH_2$ group be rotated to a *cis*-position; the species Htcaz$^+$ must therefore behave as a chelating agent with a *cis,cis*-conformation. The crystal structure determination of the title compound confirms this conclusion.

EXPERIMENTAL

Preparation.—Green prismatic crystals were obtained by evaporating solutions of copper dichloride and tcaz in aqueous hydrochloric acid solution.

Crystal Data.—$CH_7Cl_3CuN_4S$, $M = 277.1$, Triclinic, $a = 8.310(6)$, $b = 8.566(5)$, $c = 5.902(5)$ Å, $\alpha = 103.9(2)$, $\beta =$

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[1] A. Braibanti, E. Leporati, F. Dallavalle, and M. A. Pellinghelli, *Inorg. Chim. Acta*, 1968, **2**, 449.

[2] A. Braibanti, F. Dallavalle, and E. Leporati, *Inorg. Chim. Acta*, 1969, **3**, 459.

[3] A. Braibanti, A. Tiripicchio, and M. Tiripicchio Camellini, *Acta Cryst.*, 1969, **B25**, 2286.

[4] A. Braibanti, A. Tiripicchio, and M. Tiripicchio Camellini, *J.C.S. Perkin II*, 1972, 2116.

[5] F. Bigoli, A. Braibanti, A. M. Manotti Lanfredi, A. Tiripicchio, and M. Tiripicchio Camellini, *Inorg. Chim. Acta*, 1971, **5**, 392.

[6] F. Bigoli, M. A. Pellinghelli, A. Tiripicchio, and M. Tiripicchio Camellini, *Acta Cryst.*, 1975, **B31**, 55.

[7] F. Bigoli, M. A. Pellinghelli, and A. Tiripicchio, *Cryst. Struct. Comm.*, 1975, **4**, 123.

[8] A. Braibanti, M. A. Pellinghelli, A. Tiripicchio, and M. Tiripicchio Camellini, *Inorg. Chim. Acta*, 1971, **5**, 523.

[9] F. Bigoli, A. Braibanti, A. M. Manotti Lanfredi, and A. Tiripicchio, *J.C.S. Perkin II*, 1972, 2121.

99.2(2), $\gamma = 83.1(2)°$, $U = 401.1$ Å^3, $D_c = 2.29$, $Z = 2$, $F(000) = 274$. Mo-K_α radiation, $\lambda = 0.71069$ Å; μ(Mo-K_α) $= 39.8$ cm^{-1}. Space group $P\bar{1}$ from systematic absences and from structure determination.

Unit-cell parameters were determined from rotation and Weissenberg photographs and refined on an automated single-crystal diffractometer.

Intensity Data.—Intensity data were collected on a Siemens AED single-crystal diffractometer, by use of Zr-filtered radiation and the ω–2θ scan technique. An elongated crystal of dimensions *ca.* $0.037 \times 0.050 \times 0.300$ mm^3 was aligned with its [001] axis along the ϕ axis of the diffractometer and all the reflections with $2\theta < 58°$ were measured. Of 2 119 independent reflections, 1 454 having $I > 2\,\sigma(I)$ were used in the analysis. The usual corrections for Lorentz and polarization factors were made, but no correction was applied for absorption effects. The first absolute scaling and the overall isotropic temperature factor were obtained by Wilson's method.[10]

TABLE 1

Fractional atomic co-ordinates ($\times 10^4$ for non-hydrogen, $\times 10^3$ for hydrogen atoms), with estimated standard deviations in parentheses

	x/a	y/b	z/c
Cu	1 806(1)	3 307(1)	355(1)
Cl(1)	1 625(2)	817(2)	−2 021(3)
Cl(2)	409(2)	2 834(2)	3 027(3)
Cl(3)	4 792(2)	2 104(2)	3 405(3)
S	1 891(2)	5 913(2)	2 395(3)
N(1)	3 305(6)	5 621(6)	−1 423(9)
N(2)	2 802(7)	4 031(6)	−2 112(10)
N(3)	3 176(7)	8 133(6)	934(10)
N(4)	2 500(7)	9 251(6)	2 785(10)
C	2 816(7)	6 582(7)	516(11)
H(1)	373(9)	589(9)	−259(13)
H(21)	352(11)	308(11)	−226(16)
H(22)	218(10)	400(10)	−362(15)
H(3)	341(9)	856(9)	−17(13)
H(41)	298(9)	914(9)	414(13)
H(42)	140(9)	940(9)	268(14)
H(43)	268(10)	1 026(10)	271(15)

TABLE 2

Thermal parameters (Å^2), with their estimated standard deviations in parentheses *

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	1.85(3)	1.03(2)	2.09(3)	−0.36(2)	0.79(2)	−0.01(2)
Cl(1)	2.76(6)	1.15(5)	2.18(6)	−0.16(4)	0.49(5)	0.04(4)
Cl(2)	1.47(5)	1.77(5)	2.16(6)	−0.28(4)	0.53(4)	0.40(4)
Cl(3)	1.59(5)	2.18(6)	2.91(7)	−0.49(4)	0.77(5)	0.53(5)
S	2.00(6)	1.24(5)	1.87(6)	−0.39(4)	0.76(5)	0.19(4)
N(1)	1.48(19)	1.61(18)	2.03(20)	−0.52(15)	0.68(16)	0.04(15)
N(2)	2.00(21)	1.47(18)	2.30(22)	−0.54(16)	0.84(17)	−0.32(16)
N(3)	2.32(22)	1.45(19)	2.31(22)	−0.47(16)	0.63(18)	0.43(16)
N(4)	2.24(22)	0.92(17)	2.82(24)	−0.16(15)	0.65(19)	−0.16(16)
C	1.41(21)	1.56(21)	1.63(22)	0.10(17)	0.00(17)	0.14(17)
	B					
H(1)	2.5(1.6)					
H(21)	4.7(2.2)					
H(22)	3.5(1.9)					
H(3)	2.5(1.6)					
H(41)	2.3(1.5)					
H(42)	3.0(1.7)					
H(43)	3.4(1.8)					

* Anisotropic thermal parameters in the form: $\exp[-0.25(h^2a^{*2}B_{11} + \ldots + 2klb^*c^*B_{23})]$.

Structure Determination and Refinement.—The structure was solved by Patterson and Fourier methods and refined by block-diagonal least-squares, at first with isotropic, then with anisotropic thermal parameters. Hydrogen atoms were located directly from a difference synthesis calculated after several cycles of least squares. Further least-squares cycles were computed including the hydrogen atoms with isotropic thermal parameters. Unit weights were chosen in every stage of the refinement by analysing the variation of $|\Delta F|$ with $|F|$. The final R was 0.046.

Atomic scattering factors for non-hydrogen atoms were taken from ref. 11, and for hydrogen from ref. 12. Final atomic co-ordinates and thermal parameters are given in Tables 1 and 2. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21378 (12 pp., 1 microfiche).*

All the calculations were performed on a CDC 6 600 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale (Bologna), with programs written by Immirzi.[13]

DISCUSSION

The crystal structure (Figure 1) consists of complex copper cations containing monoprotonated tcaz, and chloride ions. Interatomic distances and angles are given in Table 3.

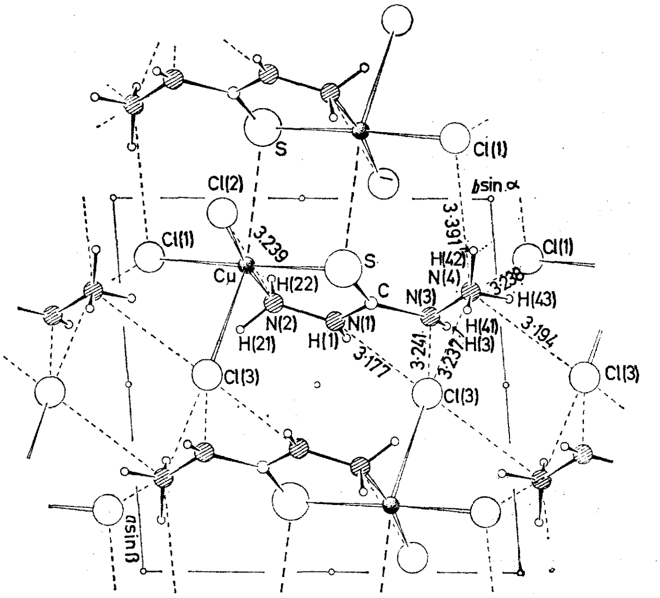

FIGURE 1 Projection of the structure down c

Copper is approximately square planar co-ordinated, the corners of the square being occupied by two chlorine

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

[10] A. J. C. Wilson, *Nature*, 1942, **150**, 152.

[11] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[12] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[13] A. Immirzi, *Ricerca Sci.*, 1967, **37**, 743.

atoms and by one sulphur and one nitrogen of a chelating monoprotonated tcaz ligand. The conformation of the ligand is *cis,cis* as expected (Figure 2). The two Cu–Cl bond lengths (2.237 and 2.261 Å) correspond well to a covalent bond (calc. 2.27 Å). Cu–S and Cu–N bonds, involving Htcaz$^+$, are 2.271 and 2.033 Å. The four atoms of the co-ordination square show a very slight tetrahedral distortion [deviations Cl(1) 0.02, Cl(2) −0.01, S 0.02, and N(2) −0.04 Å out of the mean plane

TABLE 3

Main interatomic bond distances (Å) and angles (°), with estimated standard deviations in parentheses

(*a*) In the co-ordination polyhedron

(i) Distances

Cu–Cl(1)	2.261(5)	Cu–S	2.271(5)
Cu–Cl(2)	2.237(4)	Cu–Cl(3)	3.051(7)
Cu–N(2)	2.033(7)		

(ii) Angles

Cl(1)–Cu–Cl(2)	94.7(1)	Cl(3)–Cu–Cl(1)	91.2(1)
Cl(2)–Cu–S	89.2(1)	Cl(3)–Cu–Cl(2)	84.3(1)
S–Cu–N(2)	85.3(2)	Cl(3)–Cu–S	93.9(1)
N(2)–Cu–Cl(1)	90.2(2)	Cl(3)–Cu–N(2)	103.2(2)

(*b*) In the thiocarbonohydrazide molecule

(i) Distances

C–S	1.683(8)	N(1)–N(2)	1.418(8)
C–N(1)	1.330(8)	N(3)–N(4)	1.411(8)
C–N(3)	1.353(8)		
N(1)–H(1)	0.91(9)	N(4)–H(41)	0.86(8)
N(2)–H(21)	0.94(9)	N(4)–H(42)	0.90(7)
N(2)–H(22)	0.95(8)	N(4)–H(43)	0.91(9)
N(3)–H(3)	0.88(9)		

(ii) Angles

S–C–N(1)	122.8(5)	C–N(3)–N(4)	117.6(5)
S–C–N(3)	121.9(5)	C–S–Cu	97.6(2)
N(1)–C–N(3)	115.2(6)	N(1)–N(2)–Cu	115.1(4)
C–N(1)–N(2)	118.0(5)		
H(1)–N(1)–C	129(5)	H(3)–N(3)–N(4)	114(5)
H(1)–N(1)–N(2)	112(5)	H(41)–N(4)–H(42)	114(7)
H(21)–N(2)–H(22)	107(8)	H(41)–N(4)–H(43)	105(7)
H(21)–N(2)–Cu	89(6)	H(41)–N(4)–N(3)	112(5)
H(21)–N(2)–N(1)	125(6)	H(42)–N(4)–N(3)	118(5)
H(22)–N(2)–Cu	119(5)	H(42)–N(4)–H(43)	97(7)
H(22)–N(2)–N(1)	103(5)	H(43)–N(4)–N(3)	109(5)
H(3)–N(3)–C	123(5)		

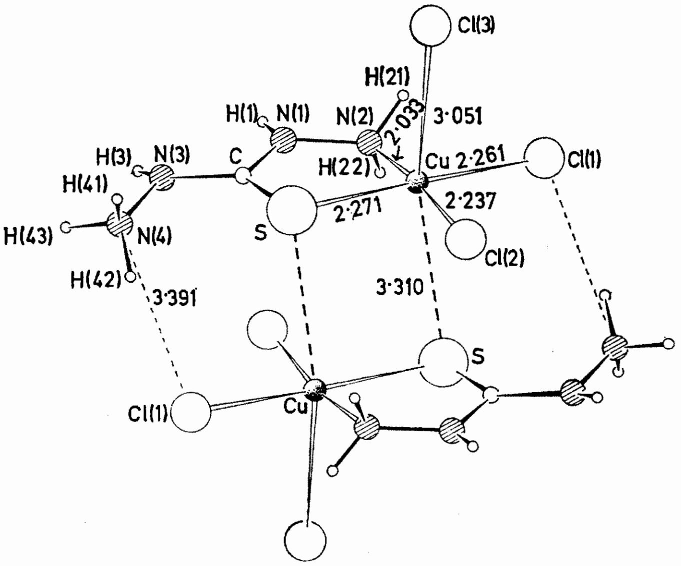

FIGURE 2 Co-ordination around the copper atom

TABLE 4

Equations of least-squares planes are in the form: $AX + BY + CZ = D$, where X, Y, and Z are co-ordinates in Å referred to orthogonal axes, and obtained from fractional ones by applying the matrix: $\|a\sin\gamma, 0, -c\sin\alpha\cos\beta^*|a\cos\gamma, b, c\cos\alpha|0, 0, c\sin\alpha\sin\beta^*\|$. Deviations (Å) of relative atoms from the planes are in square brackets

	A	*B*	*C*	*D*
Plane (1): Cl(1), Cl(2), S, N(2)	−0.8237	0.2949	−0.4843	−0.3162

[Cl(1) −0.023, Cl(2) 0.002, S −0.025, N(2) 0.046, Cu −0.112, Cl(3) −3.128]

	A	*B*	*C*	*D*
Plane (II): S, C, N(1), N(3)	−0.8268	0.2424	−0.5076	−0.6335

[S −0.001, C 0.015, N(1) −0.006, N(3) −0.008, N(2) 0.172, N(4) 0.191]

	A	*B*	*C*	*D*
Plane (III): S, C, N(1), N(2)	−0.8241	0.3155	−0.4705	−0.2178

[S −0.003, C 0.043, N(1) −0.054, N(2) 0.014, Cu −0.147, N(3) 0.126, N(4) 0.408]

TABLE 5

Hydrogen bonds and short intermolecular contacts (Å)

(*a*) Hydrogen bonds

(i) Distances (Å)

N(2) ··· Cl(2$^{\mathrm{I}}$)	3.239(9)	H(3) ··· Cl(1$^{\mathrm{III}}$)	2.64(8)
H(22) ··· Cl(2$^{\mathrm{I}}$)	2.35(8)	N(4) ··· Cl(3$^{\mathrm{IV}}$)	3.237(9)
N(1) ··· Cl(3$^{\mathrm{II}}$)	3.177(8)	H(41) ··· Cl(3$^{\mathrm{IV}}$)	2.47(7)
H(1) ··· Cl(3$^{\mathrm{II}}$)	2.41(9)	N(4) ··· Cl(1$^{\mathrm{V}}$)	3.391(7)
N(3) ··· Cl(3$^{\mathrm{II}}$)	3.241(8)	H(42) ··· Cl(1$^{\mathrm{V}}$)	2.51(8)
H(3) ··· Cl(3$^{\mathrm{II}}$)	2.53(8)	N(4) ··· Cl(3$^{\mathrm{III}}$)	3.194(8)
N(3) ··· Cl(1$^{\mathrm{III}}$)	3.238(9)	H(43) ··· Cl(3$^{\mathrm{III}}$)	2.43(9)

(ii) Angles (°)

H(22)–N(2) ··· Cl(2$^{\mathrm{I}}$)	18(5)	N(3)–H(3) ··· Cl(1$^{\mathrm{III}}$)	127(6)
N(2)–H(22) ··· Cl(2$^{\mathrm{I}}$)	154(7)	H(41)–N(4) ··· Cl(3$^{\mathrm{IV}}$)	22(5)
H(1)–N(1) ··· Cl(3$^{\mathrm{II}}$)	27(5)	N(4)–H(41) ··· Cl(3$^{\mathrm{IV}}$)	150(6)
N(1)–H(1) ··· Cl(3$^{\mathrm{II}}$)	143(6)	H(42)–N(4) ··· Cl(1$^{\mathrm{V}}$)	9(5)
H(3)–N(3) ··· Cl(3$^{\mathrm{II}}$)	31(5)	N(4)–H(42) ··· Cl(1$^{\mathrm{V}}$)	168(7)
N(3)–H(3) ··· Cl(3$^{\mathrm{II}}$)	139(6)	H(43)–N(4) ··· Cl(3$^{\mathrm{III}}$)	27(5)
H(3)–N(3) ··· Cl(1$^{\mathrm{III}}$)	41(5)	N(4)–H(43) ··· Cl(3$^{\mathrm{III}}$)	143(7)

(*b*) Short intermolecular contacts (Å)

N(1) ··· Cl(2$^{\mathrm{V}}$)	3.295(10)	N(3) ··· Cl(3$^{\mathrm{IV}}$)	3.535(9)
N(4) ··· Cl(1$^{\mathrm{VI}}$)	3.198(8)	Cu ··· S$^{\mathrm{V}}$	3.310(6)
N(4) ··· Cl(2$^{\mathrm{III}}$)	3.324(8)	Cl(2) ··· S($^{\mathrm{VII}}$)	3.445(7)
N(4) ··· Cl(1$^{\mathrm{III}}$)	3.363(8)	N(2) ··· Cl(3$^{\mathrm{I}}$)	3.332(9)
N(3) ··· Cl(2$^{\mathrm{V}}$)	3.530(10)		

Roman numeral superscripts denote the following equivalent positions:

I $x, y, -1 + z$
II $1 - x, 1 - y, -z$
III $x, 1 + y, z$
IV $1 - x, 1 - y, 1 - z$
V $-x, 1 - y, -z$
VI $x, 1 + y, 1 + z$
VII $-x, 1 - y, 1 - z$

through them] and the copper atom is a little displaced (0.11 Å) from the same towards the chloride ion Cl(3). The distance Cu $\cdots$ Cl(3) (3.051 Å) is much longer than for an ionic bond, corresponding to a very weak interaction. Taking this contact into account, the co-ordination polyhedron can best be considered as an elongated square pyramid. The sixth octahedral co-ordination site of copper is occupied by the sulphur atom from an adjacent complex at a distance (Cu $\cdots$ S 3.310 Å) much longer than those usually considered as bond interactions. The angles formed by the Cu $\cdots$ S direction with the other bonds in the co-ordination polyhedron are: S–Cu–S^{V} 91.6, N(2)–Cu–S^{V} 89.6, Cl(1)–Cu–S^{V} 84.2, Cl(2)–Cu–S^{V} 83.4, and Cl(3)–Cu–S^{V} 166.5°. As a consequence of this long interaction and of the hydrogen bonding between the $-\overset{+}{N}H_3$ group and Cl(1) [N(4)–H(42) $\cdots$ Cl(1^{V}) 9°] dimers are formed in the structure.

A comparison of bond distances and angles in tcaz in different conformations and different crystals shows that the main variations involve the C–S bond and the N–C–N angle. The C–S bond in diprotonated *cis,cis*-species [1.645(3) (ref. 8) and 1.663(4) Å (ref. 9)] is always shorter than in neutral or monoprotonated *cis,trans*-species [1.724(10),[3] 1.705(2),[4] and 1.694(2) Å (ref. 4)] and the N–C–N angle in *cis,cis*-species [111.1(2) (ref. 8) and 113.1(3) (ref. 9)] is narrower than in *cis,trans*-species [117.5(7),[3] 117.5(2),[4] and 115.8(2) (ref. 4)]. The greater double-bond character of the C–S bond, apparent in the diprotonated species, can be explained by field effects of the positive charge on the electron distribution of the conjugated thioureide group. Although the conformation of the ligand in the present compound is *cis,cis*, bond distances and angles in it, in particular the C–S bond [1.683(2) Å] and the N–C–N angle [115.2(6)°], are closer to those found in the *cis,trans*- than in the other *cis,cis*-species. The lengthening of the C–S bond observed in the present analysis can be explained by the co-ordinating behaviour of sulphur.

Considering non-hydrogen atoms only, the ligand is not perfectly planar (Table 4): the thioureide group is planar, containing some π conjugation, and constitutes the rigid portion of the molecule, the terminal N(2) and N(4) atoms being out of the plane, on the same side, by 0.17 and 0.19 Å respectively.

Packing is determined by a dense network of intermolecular hydrogen bonds (one of which is bifurcated) involving the chlorine atoms and the nitrogen atoms of the $Htcaz^+$ ligand (Table 5).

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