are free to form hydrogen bonds and, in the crystal structure of (—)-*mer*-[Co(L-Ala)$_3$].H$_2$O, H(1) and H(14) participate in the bonds connecting molecules of the complex and molecules of water in one sheet. The connexion between the adjacent sheets is realized through an N(2)—H(8)···O(12) interaction. It is considered that the conformation of the chelate rings and the ability of the axial H atoms to form hydrogen bonds are mutually dependent (Raymond, Corfield & Ibers, 1967). The hydrogen-bond interactions of axial amine H atoms in the crystal structure of Co(L-Ala)$_3$.H$_2$O, if they exist, are too weak to affect the conformation of the chelate rings.

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The Crystal and Molecular Structure of Trichloro(1*H*$^+$-thiocarbonohydrazidium-*N*,*S*)-copper(II) Monohydrate

By Maurizio Lanfranchi, Anna Maria Manotti Lanfredi, Antonio Tiripicchio*
and Marisa Tiripicchio Camellini

Istituto di Chimica Generale, Università di Parma, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Parma, Italy

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$CH_9Cl_3CuN_4OS$ is triclinic, space group $P\bar{1}$, with $a = 8{\cdot}188$ (7), $b = 8{\cdot}778$ (7), $c = 7{\cdot}219$ (7) Å, $\alpha = 93{\cdot}0$ (1), $\beta = 96{\cdot}5$ (1), $\gamma = 117{\cdot}3$ (1)°, $Z = 2$. The structure was refined to $R = 0{\cdot}067$ for 1535 counter reflexions. It consists of Cu complexes, $CuCl_3(NH_2NHCSNHN^+H_3)$, where one monoprotonated thiocarbonohydrazide molecule acts as a chelating ligand, and water molecules which link the complexes by hydrogen bonding. The Cu coordination polyhedron is a square pyramid whose base is formed by two Cl [Cu–Cl(1) = 2·257, Cu–Cl(2) = 2·342 Å], one S (Cu–S = 2·263 Å) and one N [Cu–N(2) = 2·052 Å] from the ligand, which is in a *cis–cis* conformation. The apex of the pyramid is occupied by a third Cl atom [Cu–Cl(3) = 2·628 Å].

Introduction

In crystals thiocarbonohydrazide (tcaz), $SC(NHNH_2)_2$, and its protonated species can assume either a *cis–trans* (I,II) or a *cis–cis* conformation (III,IV). The *cis–trans* conformation (I) has been found in the neutral molecule (Braibanti, Tiripicchio & Tiripicchio Camellini, 1969, 1972) and its metal chelates (*N*,*S*) (Bigoli, Braibanti, Manotti Lanfredi, Tiripicchio & Tiripicchio Camellini, 1971; Bigoli, Pellinghelli, Tiripicchio & Tiripicchio Camellini, 1975; Bigoli, Pellinghelli & Tiripicchio, 1975) and conformation II is found when

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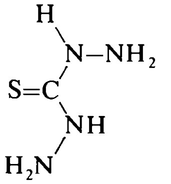
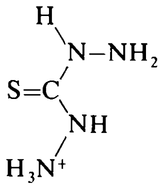
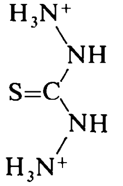
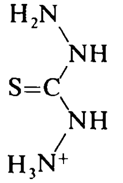
* To whom correspondence should be addressed.

tcaz is monoprotonated (Braibanti, Tiripicchio & Tiripicchio Camellini, 1972). The *cis–cis* conformation (III) is assumed when tcaz is diprotonated (Braibanti, Pellinghelli, Tiripicchio & Tiripicchio Camellini, 1971; Bigoli, Braibanti, Manotti Lanfredi & Tiripicchio, 1972) and conformation IV is found when the species $Htcaz^+$ behaves as a chelating agent (Manotti Lanfredi, Tiripicchio & Tiripicchio Camellini, 1975). Protonation of the $-NH-NH_2$ group seems to be responsible for its rotation around the C–N bond to assume a *cis* position with respect to S, while chelation to metal requires the other $-NH_2$ group to be rotated to assume a *cis* position, resulting in conformation IV. This last behaviour of $Htcaz^+$ is found again in the title compound.


(I)


(II)


(III)


(IV)

Experimental

Green crystals were obtained by evaporation of aqueous hydrochloric solutions of $CuCl_2$ and tcaz.

Crystal data

$CH_9Cl_3CuN_4OS$, M_r = 295·1, triclinic, a = 8·188 (7), b = 8·778 (7), c = 7·219 (7) Å, α = 93·0 (1), β = 96·5 (1), γ = 117·3 (1)°, V = 454·9 (8) Å^3, D_c = 2·15 g cm^{-3}, Z = 2, $F(000)$ = 294, Cu $K\alpha$ radiation, λ = 1·54178 Å, μ(Cu $K\alpha$) = 135·0 cm^{-1}. Space group $P\bar{1}$ was obtained from the structure determination; unit-cell parameters were determined from rotation and Weissenberg photographs and were refined on an automated diffractometer.

Intensities were collected on a Siemens AED single-crystal diffractometer with Ni-filtered Cu $K\alpha$ radiation and the ω–2θ scan technique. A crystal 0·025 × 0·065 × 0·230 mm was aligned with [001] along the φ axis of the diffractometer and all reflexions with $2\theta < 140°$ were measured. Of the 1695 independent reflexions, 1535 with $I > 2\sigma(I)$ were used in the analysis. Corrections for Lorentz and polarization factors were made, but no correction was applied for absorption. An absolute scale and overall temperature factor were obtained by Wilson's method.

Structure determination and refinement

The structure was solved by Patterson and Fourier methods and was refined by block-diagonal least squares, first with isotropic, then anisotropic thermal parameters. The H atoms were located from a ΔF

Table 1. *Final atomic coordinates for the non-hydrogen atoms* ($\times 10^4$) *and for the hydrogen atoms* ($\times 10^3$) *with e.s.d.'s in parentheses*

	x	y	z
Cu	1492 (2)	2453 (2)	1963 (2)
Cl(1)	2232 (3)	4664 (3)	206 (3)
Cl(2)	−1531 (3)	2000 (3)	2157 (4)
Cl(3)	2632 (3)	4429 (3)	5190 (3)
S	614 (3)	−259 (3)	2706 (4)
O(*W*)	5973 (10)	8031 (10)	2539 (12)
N(1)	4133 (11)	1031 (10)	2204 (13)
N(2)	4012 (11)	2549 (10)	1738 (13)
N(3)	2814 (11)	−1723 (10)	2986 (13)
N(4)	1172 (11)	−3263 (10)	3170 (12)
C	2640 (12)	−318 (11)	2581 (14)
H(1)	503 (13)	100 (12)	229 (13)
H(21)	491 (13)	371 (12)	247 (13)
H(22)	434 (13)	265 (12)	59 (13)
H(3)	347 (13)	−198 (12)	262 (13)
H(41)	83 (13)	−310 (12)	400 (13)
H(42)	39 (13)	−391 (12)	229 (13)
H(43)	143 (13)	−400 (12)	333 (13)
H(5)	623 (13)	723 (12)	283 (13)
H(6)	672 (13)	923 (12)	285 (13)

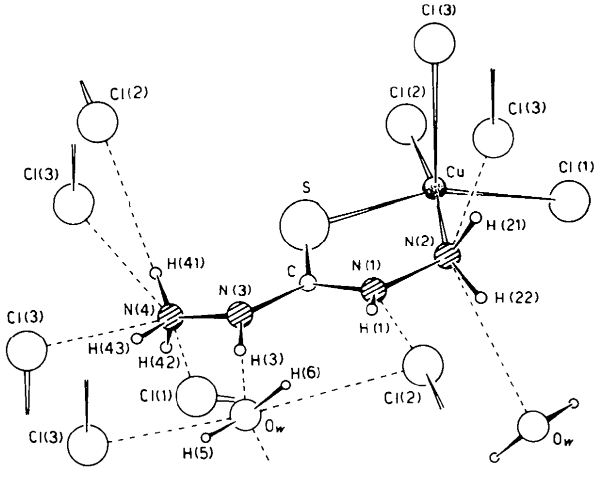


Fig. 1. Clinographic projection of the structure.

synthesis after anisotropic refinement. Further cycles were computed including the H atoms with isotropic thermal parameters. The analysis of the variation of $|\Delta F|$ with respect to $|F|$ showed that unit weights were satisfactory at all stages. The final R was 0·067 (observed reflexions only). Scattering factors for non-hydrogen atoms were taken from Cromer & Mann (1968) and for H from Stewart, Davidson & Simpson (1965). Final atomic coordinates are given in Table 1.*

All calculations were performed on the CDC 6600 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale (Bologna) with programs written by Immirzi (1967).

Discussion

The structure consists of trichlorothiocarbonohydrazidiumcopper(II) complexes and water molecules, linked by hydrogen bonds (Fig. 1). Bond distances and angles are given in Table 2. The Cu coordination polyhedron is a square pyramid whose base is occupied by two Cl atoms and by one S and one N from a chelating monoprotonated tcaz ligand which shows a *cis–cis* conformation. The two Cu—Cl lengths in the basal plane correspond well to the values usually found in similar configurations. Cu—S and Cu—N(2) bonds (2·263 and 2·052 Å) involving Htcaz^+ are in good agreement with those found in dichloro($1H^+$-thiocarbonohydrazidium)copper(II) chloride (Manotti Lanfredi, Tiripicchio & Tiripicchio Camellini, 1975). The four atoms forming the base of the pyramid show a tetrahedral distortion from their mean plane; the Cu atom is displaced towards the apex of the pyramid (Table 3). The apex of the pyramid is occupied by Cl(3) at a much shorter distance (2·628 Å) than that (3·051 Å) found in dichloro($1H^+$-thiocarbonohydrazidium)-copper(II) chloride (Manotti Lanfredi, Tiripicchio & Tiripicchio Camellini, 1975). The sixth octahedral site of Cu is occupied by the S atom from an adjacent complex at a distance ($\text{Cu}\cdots\text{S}^{\text{i}}$ = 3·606 Å), much longer than those usually considered as bond interactions. The angles formed by the $\text{Cu}\cdots\text{S}^{\text{i}}$ direction with the other bonds in the coordination polyhedron are: S—Cu—S^{i} 83·2, $\text{N(2)—Cu—S}^{\text{i}}$ 94·1, $\text{Cl(1)—Cu—S}^{\text{i}}$ 77·5, $\text{Cl(2)—Cu—S}^{\text{i}}$ 82·6 and $\text{Cl(3)—Cu—S}^{\text{i}}$ 167·6°. As a consequence of this long interaction and of the hydrogen bonding between the $\text{—N}^+\text{H}_3$ group and $\text{Cl(1}^{\text{i}})$ [$\text{N(4)—H(42)—Cl(1}^{\text{i}}) = 21°$], loosely bound dimers are formed.

Table 2. *Bond distances* (Å) *and angles* (°)

Cu–Cl(1)	2·257 (4)	N(1)–H(1)	0·74 (12)
Cu–Cl(2)	2·342 (4)	N(2)–H(21)	1·01 (8)
Cu–Cl(3)	2·628 (5)	N(2)–H(22)	0·90 (10)
Cu–S	2·263 (4)	N(3)–H(3)	0·74 (12)
Cu–N(2)	2·052 (10)	N(4)–H(41)	0·72 (11)
S–C	1·696 (11)	N(4)–H(42)	0·82 (8)
C–N(1)	1·324 (11)	N(4)–H(43)	0·78 (12)
C–N(3)	1·348 (15)	O(*W*)–H(5)	0·85 (12)
N(1)–N(2)	1·435 (14)	O(*W*)–H(6)	0·94 (9)
N(3)–N(4)	1·430 (10)		
Cl(1)–Cu–Cl(2)	95·9 (1)	H(1)–N(1)–C	119 (8)
Cl(1)–Cu–N(2)	88·9 (3)	H(1)–N(1)–N(2)	121 (8)
N(2)–Cu–S	85·7 (3)	H(21)–N(2)–N(1)	120 (6)
S–Cu–Cl(2)	88·3 (1)	H(21)–N(2)–Cu	102 (6)
Cl(1)–Cu–S	159·6 (1)	H(21)–N(2)–H(22)	103 (9)
Cl(2)–Cu–N(2)	173·5 (3)	H(22)–N(2)–N(1)	102 (7)
Cl(3)–Cu–Cl(1)	94·7 (1)	H(22)–N(2)–Cu	116 (6)
Cl(3)–Cu–Cl(2)	88·7 (1)	H(3)–N(3)–C	125 (8)
Cl(3)–Cu–S	105·5 (1)	H(3)–N(3)–N(4)	108 (8)
Cl(3)–Cu–N(2)	95·4 (3)	H(41)–N(4)–N(3)	108 (8)
Cu–S–C	98·4 (4)	H(41)–N(4)–H(42)	117 (10)
Cu–N(2)–N(1)	114·2 (6)	H(41)–N(4)–H(43)	108 (11)
S–C–N(1)	122·0 (8)	H(42)–N(4)–N(3)	125 (7)
S–C–N(3)	120·4 (7)	H(42)–N(4)–H(43)	87 (11)
N(1)–C–N(3)	117·5 (9)	H(43)–N(4)–N(3)	109 (7)
C–N(1)–N(2)	119·6 (8)	H(5)–O(*W*)–H(6)	128 (9)
C–N(3)–N(4)	118·3 (8)		

Table 3. *Least-squares planes*

Equations of least-squares planes are in the form $AX + BY + CZ = D$, where X, Y, and Z are coordinates in Å referred to orthogonal axes, and are obtained from the fractional coordinates 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 atoms from the planes are in square brackets.

	A	*B*	*C*	*D*
Plane 1: Cl(1), Cl(2), S, N(2)	−0·2696	−0·3382	−0·9016	−1·7766
[Cl(1) 0·114, Cl(2) −0·004, S 0·189, N(2) −0·299, Cu −0·231, Cl(3) −2·831]				
Plane 2: Cu, S, C, N(1), N(2)	−0·1576	−0·1922	−0·9686	−1·7824
[Cu −0·001, S 0·001, C 0·007, N(1) −0·033, N(2) 0·026]				
Plane 3: S, C, N(1), N(2), N(3)	−0·1558	−0·2063	−0·9660	−1·7677
[S −0·001, C 0·020, N(1) −0·028, N(2) 0·010, N(3) −0·001, N(4) 0·215]				

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* Lists of structure factors and thermal parameters are available from the authors and have also been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32901 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 4. *Hydrogen bonds and short intermolecular contacts* (Å)

(*a*) Hydrogen-bond distances (Å)

N(4)···Cl(1$^{\mathrm{i}}$)	3·198 (9)	N(1)···Cl(2$^{\mathrm{iv}}$)	3·254 (10)
H(42)···Cl(1$^{\mathrm{i}}$)	2·45 (9)	H(1)···Cl(2$^{\mathrm{iv}}$)	2·55 (10)
N(4)···Cl(3$^{\mathrm{ii}}$)	3·130 (11)	N(2)···Cl(3$^{\mathrm{v}}$)	3·290 (9)
H(43)···Cl(3$^{\mathrm{ii}}$)	2·41 (12)	H(21)···Cl(3$^{\mathrm{v}}$)	2·34 (8)
N(4)···Cl(2$^{\mathrm{iii}}$)	3·432 (10)	N(2)···O(W^{vi})	3·105 (13)
H(41)···Cl(2$^{\mathrm{iii}}$)	2·79 (9)	H(22)···O(W^{vi})	2·26 (9)
N(4)···Cl(3$^{\mathrm{iii}}$)	3·192 (10)	O(W)···Cl(2$^{\mathrm{vii}}$)	3·176 (9)
H(41)···Cl(3$^{\mathrm{iii}}$)	2·67 (10)	H(6)···Cl(2$^{\mathrm{vii}}$)	2·30 (9)
N(3)···O(W^{ii})	2·745 (14)	O(W)···Cl(3$^{\mathrm{v}}$)	3·296 (11)
H(3)···O(W^{ii})	2·05 (12)	H(5)···Cl(3$^{\mathrm{v}}$)	2·49 (12)

(*b*) Hydrogen-bond angles (°)

H(42)–N(4)···Cl(1$^{\mathrm{i}}$)	21 (8)	H(1)–N(1)···Cl(2$^{\mathrm{iv}}$)	17 (8)
N(4)–H(42)···Cl(1$^{\mathrm{i}}$)	153 (10)	N(1)–H(1)···Cl(2$^{\mathrm{iv}}$)	158 (11)
H(43)–N(4)···Cl(3$^{\mathrm{ii}}$)	19 (7)	H(21)–N(2)···Cl(3$^{\mathrm{v}}$)	18 (6)
N(4)–H(43)···Cl(3$^{\mathrm{ii}}$)	154 (9)	N(2)–H(21)···Cl(3$^{\mathrm{v}}$)	155 (9)
H(41)–N(4)···Cl(2$^{\mathrm{iii}}$)	25 (7)	H(22)–N(2)···O(W^{vi})	17 (6)
N(4)–H(41)···Cl(2$^{\mathrm{iii}}$)	148 (9)	N(2)–H(22)···O(W^{vi})	157 (9)
H(41)–N(4)···Cl(3$^{\mathrm{iii}}$)	40 (8)	H(6)–O(W)···Cl(2$^{\mathrm{vii}}$)	19 (6)
N(4)–H(41)···Cl(3$^{\mathrm{iii}}$)	130 (9)	O(W)–H(6)···Cl(2$^{\mathrm{vii}}$)	154 (8)
H(3)–N(3)···O(W^{ii})	18 (7)	H(5)–O(W)···Cl(3$^{\mathrm{v}}$)	16 (6)
N(3)–H(3)···O(W^{ii})	156 (10)	O(W)–H(5)···Cl(3$^{\mathrm{v}}$)	159 (9)

(*c*) Short intermolecular contacts (Å)

N(4)···Cl(1$^{\mathrm{ii}}$)	3·179 (11)	Cl(1)···Cl(3$^{\mathrm{viii}}$)	3·676 (5)
N(3)···Cl(1$^{\mathrm{ii}}$)	3·470 (10)	Cl(1)···Cl(2$^{\mathrm{ix}}$)	3·696 (5)
N(2)···Cl(1$^{\mathrm{vi}}$)	3·442 (10)	Cl(3)···Cl(3$^{\mathrm{v}}$)	3·581 (5)
O(W)···S$^{\mathrm{vii}}$	3·369 (9)	S···S$^{\mathrm{iii}}$	3·634 (6)
O(W)···Cl(1)	3·311 (9)		

Roman numeral superscripts denote the following equivalent positions

(i)	$-x, -y, -z$	(vi)	$1-x, 1-y, -z$
(ii)	$x, -1+y, z$	(vii)	$1+x, 1+y, z$
(iii)	$-x, -y, 1-z$	(viii)	$x, y, -1+z$
(iv)	$1+x, y, z$	(ix)	$-x, 1-y, -z$
(v)	$1-x, 1-y, 1-z$		

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 [1·696 (11) Å] and the N–C–N angle [117·5 (9)°], are closer to the corresponding values found in the *cis–trans* derivatives (Braibanti, Tiripicchio & Tiripicchio Camellini, 1969, 1972) than those observed in the other *cis–cis* species (Braibanti, Pellinghelli, Tiripicchio & Tiripicchio Camellini, 1971; Bigoli, Braibanti, Manotti Lanfredi & Tiripicchio, 1972). This has already been observed in dichloro(1H^{+}-thiocarbonohydrazidium)copper(II) chloride (Manotti Lanfredi, Tiripicchio & Tiripicchio Camellini, 1975).

The penta-atomic chelate ring is nearly planar (Table 3), the maximum displacement for N(1) and N(2) being 0·03 Å. In the Htcaz^{+} ligand only the N(1)N(2)-CSN(3) group of atoms is planar (Table 3), the terminal N(4) protonated atom being out of the plane by 0·22 Å.

Packing is determined by a dense network of intermolecular hydrogen bonds [one of which, N(4)–H(41)···Cl(2$^{\mathrm{iii}}$), N(4)–H(41)···Cl(3$^{\mathrm{iii}}$), is bifurcated] involving the Cl atoms, the water molecules and the N atoms of the Htcaz^{+} ligand (Table 4).

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