from the plane being 0·090, −0·021, −0·057, 0·099 and −0·111 Å ($\sigma = 0{\cdot}002$ Å) respectively, atom O(1) being 0·272 (1) Å from the plane. Ring (11) is highly distorted with deviations from the plane as great as 0·33 and −0·31 Å for C(5) and C(9′) respectively, and torsional angles as large as 51·8 (2)° (Table 2). The angles between the normals to the pairs of planes (8) and (9), (8) and (11), (9) and (11) are 27·3, 18·3 and 20·3° ($\sigma = 0{\cdot}3°$) respectively. Thermal anisotropy is moderate in the central rings but significant in some of the attached phenyl rings. There is a marked tendency for the various planar sections of the molecule to be parallel to one another and/or to some significant repeat direction such as a cell axis. All intermolecular contacts are above van der Waals distances.

Thanks are due to Professor M. J. Gallagher (School of Chemistry, The University of New South Wales) for suggesting the problem, for providing crystals and for helpful discussions, to Mr D. C. Craig for data collection and assistance in computing, to Mrs C. Faust for drawing the diagrams computed by *ORTEP* (Johnson, 1976), and to the University for computing time on the CDC-171. Bond lengths and angles were computed using *FANDEB*, a local version of *ORFFE* (Busing, Martin & Levy, 1964).

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# Thiocarbonohydrazide Dihydrochloride Hemihydrate, $CH_8N_4S^{2+}.2Cl^-.0{\cdot}5H_2O$: A Triclinic Structure which Exhibits a Monoclinic Subcell

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**Abstract.** $M_r = 188{\cdot}08$, triclinic, $P\bar{1}$, $a = 9{\cdot}936$ (7), $b = 19{\cdot}108$ (9), $c = 9{\cdot}421$ (6) Å, $\alpha = 104{\cdot}5$ (1), $\beta = 118{\cdot}4$ (1), $\gamma = 90{\cdot}9$ (1)°, $V = 1504$ (2) Å$^3$, $Z = 8$, $D_x = 1{\cdot}66$ g cm$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·71069 Å, $\mu$(Mo $K\alpha$) = 10·58 cm$^{-1}$, $F(000) = 776$, $T = 295$ K, $R = 0{\cdot}0322$ for 3884 independent observed reflections. There are four crystallographically independent units in the cell, approximately related by pseudo symmetry centres and twofold screw axes, so a monoclinic subcell can be recognized. The structure consists of diprotonated cations, in the expected *cis,cis* conformation, of $Cl^-$ anions and of water molecules. The structural parameters in the four independent units are practically equal. Several >NH···Cl, $-NH_3^+\cdots Cl$, $-NH_3^+\cdots O$ and OH···Cl hydrogen bonds determine the packing of the cations and anions in the crystal.

**Introduction.** Thiocarbonohydrazide (tcaz), $SC(NHNH_2)_2$, and its protonated species can assume either a *cis,trans* conformation, *i.e.* with one hydrazinic group bent toward the C—S bond and the other toward the opposite side, or a *cis,cis* conformation, *i.e.* with both groups bent toward the C—S bond. The former has been found in the neutral molecule (Braibanti, Tiripicchio & Tiripicchio Camellini, 1969, 1972), in its metal chelates (*N,S*) (Bigoli, Braibanti, Manotti Lanfredi, Tiripicchio & Tiripicchio Camellini, 1971; Bigoli, Pellinghelli, Tiripicchio & Tiripicchio Camellini, 1975; Bigoli, Pellinghelli & Tiripicchio, 1975) and when tcaz is monoprotonated (Braibanti, Tiripicchio & Tiripicchio Camellini, 1972); the latter is assumed when tcaz is diprotonated (Braibanti, Pellinghelli, Tiripicchio & Tiripicchio Camellini, 1971; Bigoli, Braibanti, Manotti

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Lanfredi & Tiripicchio, 1972) and when the monoprotonated species Htcaz$^+$ behaves as chelating ligand (Manotti Lanfredi, Tiripicchio & Tiripicchio Camellini, 1975; Lanfranchi, Manotti Lanfredi, Tiripicchio & Tiripicchio Camellini, 1978). From the results of these structural studies, 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 S atom, and, moreover, that chelation to the metal also requires that the other $-NH_2$ group be rotated to a *cis* position.

The results of the structural analysis of thiocarbonohydrazide dihydrochloride hemihydrate are here reported. Its crystals separate rapidly as white needles from aqueous solutions of tcaz and hydrochloric acid, at very low values of pH ($\sim$ 0·5). They transform in a short time in solution into crystals of thiocarbonohydrazide dihydrochloride dihydrate, whose structure has already been reported (Braibanti, Pellinghelli, Tiripicchio & Tiripicchio Camellini, 1971).

**Experimental.** Crystal approximately 0·07 × 0·08 × 0·25 mm. Siemens AED diffractometer, Nb-filtered Mo $K\alpha$ radiation. 27 reflections ($12 < \theta < 15°$) for accurate unit-cell parameters. 5937 independent reflections with $\theta < 26°$, $-10 \leq h \leq 10$, $-23 \leq k \leq 22$, $0 \leq l \leq 11$. 3884 reflections with $I \geq 2\sigma(I)$ considered observed. The standard reflection 322 remeasured every 20 reflections showed a significantly decreasing intensity (max. variation 14%); correction for this crystal decay applied taking the intensity of the standard reflection as internal scaling for the data set. Lp correction. Absorption ignored because of the very low absorbance of the sample. After several attempts structure solved by *MULTAN* (Germain, Main & Woolfson, 1971) and refined first by isotropic full-matrix then by anisotropic blocked full-matrix least squares (*SHELX*76, Sheldrick, 1976). All H atoms clearly located from a $\Delta F$ synthesis. Final cycle computed including H atoms with isotropic thermal parameters: the parameters were refined in two blocks, each containing positional and thermal parameters of two pseudorelated units (observation-to-parameter ratio in the final cycle $3884/452 = 8{\cdot}6$). $\sum w|\Delta F|^2$ minimized; final $R = 0{\cdot}0322$, $wR = 0{\cdot}0474$. Unit weights in first cycles of refinement then $w = k[\sigma^2(F_o) + gF_o^2]^{-1}$ ($k = 0{\cdot}0310$, $g = 0{\cdot}005$) in last cycles. $(\Delta/\sigma)_{\max} = 0{\cdot}16$. Max. height in final difference map 0·34 e Å$^{-3}$. Atomic scattering factors and anomalous-scattering corrections from *International Tables for X-ray Crystallography* (1974). Calculations performed on the CYBER76 computer of the Consorzio per la Gestione del Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Casalecchio, Bologna, with financial support from the University of Parma. Atomic coordinates and equivalent isotropic thermal parameters (Hamilton, 1959) for nonhydrogen atoms are given in Table 1.*

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* (*Hamilton,* 1959) *for the nonhydrogen atoms, with e.s.d.'s in parentheses*

| | $x$ | $y$ | $z$ | $B_{eq}$(Å$^2$) |
|---|---|---|---|---|
| Cl(1) | 2350 (1) | 106 (1) | 4098 (1) | 2·66 (3) |
| Cl(2) | 5795 (1) | 1675 (1) | 851 (1) | 2·52 (3) |
| Cl(3) | 4082 (1) | 3222 (1) | 3301 (1) | 2·73 (3) |
| Cl(4) | 7734 (1) | 4894 (1) | 1675 (1) | 2·74 (3) |
| Cl(5) | 2528 (1) | 5132 (1) | 4051 (1) | 2·63 (3) |
| Cl(6) | 5882 (1) | 6649 (1) | 1666 (1) | 2·57 (3) |
| Cl(7) | 4085 (1) | 8264 (1) | 4012 (1) | 2·76 (3) |
| Cl(8) | 7569 (1) | 9890 (1) | 1490 (1) | 2·65 (3) |
| S(1) | 549 (1) | 1805 (1) | −437 (1) | 2·22 (4) |
| S(2) | 9245 (1) | 3032 (1) | 1719 (1) | 2·19 (3) |
| S(3) | 482 (1) | 6856 (1) | 2734 (1) | 2·33 (3) |
| S(4) | 9378 (1) | 8023 (1) | 5575 (1) | 2·24 (3) |
| O(1) | 4758 (3) | 60 (2) | 2442 (4) | 3·32 (12) |
| O(2) | 4758 (4) | 5044 (2) | 2341 (4) | 3·53 (11) |
| N(11) | 1949 (4) | 1081 (2) | 1795 (4) | 2·43 (13) |
| N(21) | 3368 (4) | 1427 (2) | 2102 (5) | 2·43 (13) |
| N(31) | −647 (4) | 810 (2) | 349 (4) | 2·55 (12) |
| N(41) | −2095 (4) | 1009 (2) | −655 (5) | 2·79 (13) |
| N(12) | 7946 (4) | 3585 (2) | 3576 (4) | 2·22 (11) |
| N(22) | 6496 (4) | 3385 (2) | 2071 (4) | 2·49 (12) |
| N(32) | 10520 (4) | 3851 (2) | 4900 (4) | 2·48 (10) |
| N(42) | 11966 (4) | 3758 (2) | 4997 (5) | 2·48 (14) |
| N(13) | 1935 (3) | 6094 (2) | 1275 (4) | 2·34 (10) |
| N(23) | 3347 (4) | 6466 (2) | 2726 (4) | 2·55 (12) |
| N(33) | −661 (4) | 5813 (2) | −194 (4) | 2·57 (11) |
| N(43) | −2130 (4) | 6006 (2) | −486 (5) | 2·78 (13) |
| N(14) | 8003 (3) | 8592 (2) | 3007 (4) | 2·17 (11) |
| N(24) | 6577 (4) | 8378 (2) | 2890 (4) | 2·31 (12) |
| N(34) | 10591 (3) | 8831 (2) | 4439 (4) | 2·56 (11) |
| N(44) | 12041 (4) | 8743 (2) | 5677 (4) | 2·49 (12) |
| C(1) | 635 (4) | 1223 (2) | 619 (4) | 1·79 (12) |
| C(2) | 9226 (4) | 3515 (2) | 3434 (4) | 1·81 (12) |
| C(3) | 606 (4) | 6247 (2) | 1227 (4) | 1·82 (11) |
| C(4) | 9314 (4) | 8508 (2) | 4307 (4) | 1·78 (11) |

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

| | | | |
|---|---|---|---|
| C(1)—S(1) | 1·646 (5) | S(1)—C(1)—N(11) | 124·6 (6) |
| C(1)—N(11) | 1·338 (5) | S(1)—C(1)—N(31) | 123·2 (4) |
| C(1)—N(31) | 1·367 (6) | N(11)—C(1)—N(31) | 112·1 (5) |
| N(11)—N(21) | 1·413 (6) | C(1)—N(11)—N(21) | 118·0 (6) |
| N(31)—N(41) | 1·418 (5) | C(1)—N(31)—N(41) | 116·1 (5) |
| C(2)—S(2) | 1·657 (4) | S(2)—C(2)—N(12) | 124·9 (3) |
| C(2)—N(12) | 1·346 (6) | S(2)—C(2)—N(32) | 123·4 (6) |
| C(2)—N(32) | 1·347 (5) | N(12)—C(2)—N(32) | 111·6 (5) |
| N(12)—N(22) | 1·414 (5) | C(2)—N(12)—N(22) | 117·6 (4) |
| N(32)—N(42) | 1·413 (6) | C(2)—N(32)—N(42) | 118·1 (5) |
| C(3)—S(3) | 1·652 (4) | S(3)—C(3)—N(13) | 124·8 (3) |
| C(3)—N(13) | 1·339 (6) | S(3)—C(3)—N(33) | 123·1 (6) |
| C(3)—N(33) | 1·369 (5) | N(13)—C(3)—N(33) | 112·1 (6) |
| N(13)—N(23) | 1·414 (5) | C(3)—N(13)—N(23) | 118·4 (4) |
| N(33)—N(43) | 1·424 (6) | C(3)—N(33)—N(43) | 116·2 (6) |
| C(4)—S(4) | 1·666 (5) | S(4)—C(4)—N(14) | 124·5 (6) |
| C(4)—N(14) | 1·345 (5) | S(4)—C(4)—N(34) | 122·7 (4) |
| C(4)—N(34) | 1·339 (6) | N(14)—C(4)—N(34) | 112·7 (5) |
| N(14)—N(24) | 1·413 (6) | C(4)—N(14)—N(24) | 118·1 (5) |
| N(34)—N(44) | 1·404 (5) | C(4)—N(34)—N(44) | 118·4 (4) |

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, and details of hydrogen bonds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39315 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

**Discussion.** Preliminary rotation and Weissenberg photographs, both around [001], the elongation direction of the crystal, showed that the reflections of the layers with $l$ even were much more intense that those with $l$ odd and that, neglecting some weak reflections, approximate monoclinic symmetry could be assigned to the reflections of the $l$-even layers with quasi-systematic absences compatible with the space group $P2_1/b$ requiring the presence of glides and twofold screw axes.

The structure therefore presents an extensive pseudosymmetry, with a pseudohalving of the unit cell at $z = \frac{1}{2}$; each half has the pseudo space group $P2_1/b$, with pseudocentres at $z = \frac{1}{4}$ and $\frac{3}{4}$ and pseudo screw axes. In Fig. 1 the relation between the triclinic cell and the halved monoclinic subcell is shown. The monoclinic cell and indices can be obtained by the matrix $//10\frac{1}{2}/01\frac{1}{2}/00\frac{1}{2}//$ from the triclinic ones. The parameters of the pseudomonoclinic cell are: $a = 8{\cdot}74$, $b = 18{\cdot}50$, $c = 4{\cdot}71$ Å, $\alpha = 90{\cdot}2$, $\beta = 90{\cdot}1$, $\gamma = 99{\cdot}1°$.

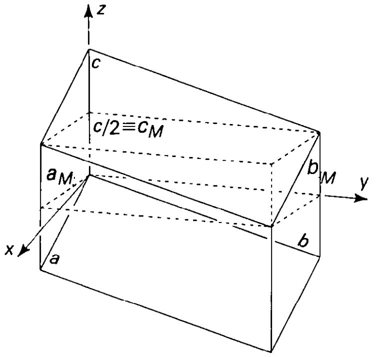

Fig. 1. Relation between the triclinic cell and the halved monoclinic subcell. The monoclinic cell can be obtained from the triclinic cell by the matrix $//10\frac{1}{2}/01\frac{1}{2}/00\frac{1}{2}//$.

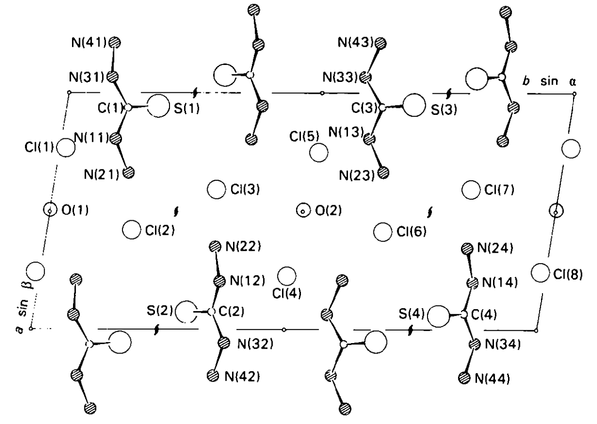

Fig. 2. Projection of the structure along **c** showing the contents of a half-cell (monoclinic subcell). Only the pseudocentres at $z = \frac{1}{4}$ and pseudo screw axes relating the four independent units are represented.

The crystal structure consists of $H_2tcaz^{2+}$ cations, in a *cis,cis* conformation typical of the diprotonated species, of $Cl^-$ anions and of water molecules. There are four crystallographically independent tcaz.-2HCl.0·5$H_2O$ units in the cell, but related by pseudosymmetry (pseudocentres at 0,0,$\frac{1}{4}$ and 0,0,$\frac{3}{4}$ and pseudo twofold screw axes). This is clearly shown in Fig. 2 in which a projection of the structure along **c** is presented. For clarity only the contents of a half-cell are shown and the units generated by the true centres are omitted. The O atoms of the water molecules are almost on the pseudocentres. The $C_{2v}$ symmetry and the hydrogen bonding of the water molecules do not allow the presence of true centres and are probably responsible for the lack of monoclinic symmetry.

All the diprotonated cations have approximate $C_{2v}$ symmetry (with the twofold axis along the C–S bond) with structural parameters practically equal (Table 2) and in good agreement with those reported in the other diprotonated cations (Braibanti, Pellinghelli, Tiripicchio & Tiripicchio Camellini, 1971; Bigoli, Braibanti, Manotti Lanfredi & Tiripicchio, 1972). All thioureide

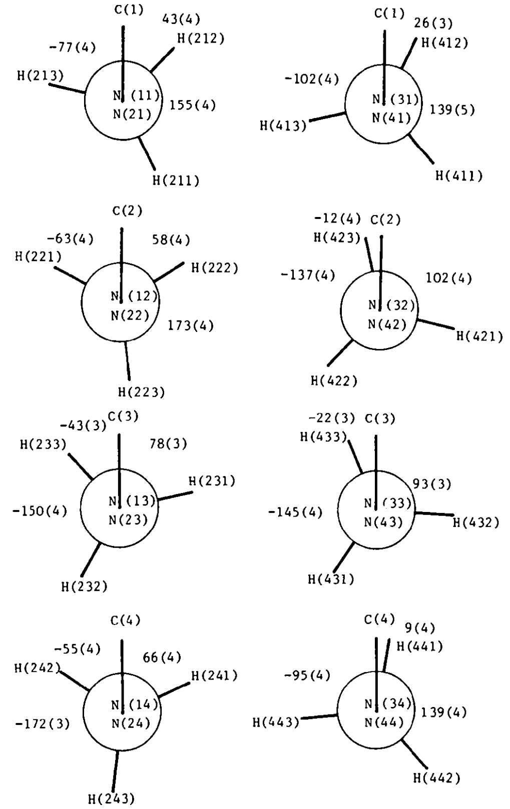

Fig. 3. Newman projections along the N–N bonds of the four independent molecules showing the conformations of the terminal H atoms (angles in deg).

moieties are nearly planar, constituting the rigid parts of the cations, with the terminal $-NH_3^+$ groups on opposite sides. In each cation the H atoms of the two $-NH_3^+$ groups are in different conformations (*gauche* and eclipsed) with respect to the C—N bond, as shown in Fig. 3 where the Newman projections along the N—N bonds are depicted for both $NH_3^+$ groups of the four independent cations. In each eclipsed group an H atom is involved in an intramolecular hydrogen bond with the S.

The packing of the cations, anions and water molecules in the crystal is determined by an extensive network of NH···Cl, $-NH_3^+\cdots Cl$, $-NH_3^+\cdots O$ and OH···Cl hydrogen bonds.

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# Structure of 5-Azatricyclo[4.3.1.$0^{3,8}$]decan-4-one Hemihydrate, $C_9H_{13}NO.\frac{1}{2}H_2O$

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**Abstract.** $M_r = 160{\cdot}22$, monoclinic, $P2_1/c$, $a = 12{\cdot}375\ (3)$, $b = 12{\cdot}695\ (3)$, $c = 12{\cdot}521\ (3)$ Å, $\beta = 119{\cdot}29\ (2)°$, $V = 1715{\cdot}6\ (8)$ Å$^3$, $Z = 8$, $D_m = 1{\cdot}27\ (2)$, $D_x = 1{\cdot}24$ g cm$^{-3}$, $\lambda(\text{Cu}\ K\alpha) = 1{\cdot}5418$ Å, $\mu = 6{\cdot}29$ cm$^{-1}$, $F(000) = 696$, $T = 295$ K. Final $R = 0{\cdot}079$ for 1494 unique observed reflections. The constraints of the tricyclic system result in a significantly non-planar character of the amide group. In the unit cell, there are two symmetric independent molecules of the lactam. These two molecules are of two conformational types: *A*, where the non-planarity of the amide group is caused mostly by a torsion around the C′—N bond, and *B*, in which there is a pyramidal arrangement of the bonds at N.

**Introduction.** The structure of 5-azatricyclo[4.3.1.$0^{3,8}$]-decan-4-one hemihydrate was determined as a part of studies on potential occurrence of non-planar amide groups in amides and peptides (Ealick & van der Helm, 1977; Bláha *et al.*, 1978; Bláha & Maloň, 1980). This lactam is a model compound in which the *cis*-amide group is embedded in a rigid tricyclic skeleton. Determination of properties characteristic for a non-planar amide group, *e.g.* dependence of chiroptical parameters on the extent and character of deviation from planarity, could be a starting point for finding other similar deviations in flexible amides (peptides) in solution (Bláha & Maloň, 1980). The synthesis of the compound (I) as well as results of the chiroptical studies in solution are reported elsewhere (Tichý, Farag, Maloň, Kálal & Bláha, 1984).

**Experimental.** Colorless prismatic crystals grown by slow evaporation from a hexane/benzene/ether mixture at room temperature; molecular formula of title compound confirmed by elemental analysis; crystal

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