Bis[5-(2-ammonioethyl)imidazole-N^3]tetrakis(isothiocyanato)nickel(II), [Ni(C$_5$H$_{10}$N$_3$)$_2$(NCS)$_4$]

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Abstract. $M_r = 515.4$, monoclinic, $P2_1/n$, $a = 10.584$ (1), $b = 8.8187$ (8), $c = 11.588$ (2) Å, $\beta = 89.975$ (8)°, $V = 1081.6$ (2) Å^3, $Z = 2$, $D_m = 1.59$ (1), $D_x = 1.58$ Mg m^{-3}, λ(Mo $K\alpha$)=0.71069 Å, μ(Mo $K\alpha$) = 1.29 mm^{-1}, $F(000) = 532$, $T = 292$ K, $R = 0.035$ for 1455 observed reflexions. The complex has $\bar{1}$ symmetry with Ni^{2+} located at the center of symmetry. The six N atoms coordinated to Ni^{2+} form a distorted octahedron. The histaminium ligand is a monocation protonated at the side-chain N atom. The side chain has the *gauche* form. All N$^\pi$–H and ammonium groups and all S atoms are involved in H bonds.

Introduction. Containing three N atoms, histamine can, depending on pH, act as a mono-, bi- or tridentate ligand. Physiological activity of histamine derivatives depends on both their composition and geometry. Structural investigations of these derivatives are helpful in studying the role histamine plays in tissues. Although the structures of several histamine derivatives have been determined so far (Bonnet & Jeannin, 1970*a,b,c,*1972*a,b*; Bonnet & Ibers, 1973; Bonnet, Jeannin & Laaonini, 1975; Dahan, 1976; Główka, Gałdecki, Kazimierczak & Maśliński, 1980; Prout, Critchley & Ganellin, 1974; Veidis, Palenik, Schaffrin & Trotter, 1969; Yamane, Ashida & Kakudo, 1973), none is known to contain histamine ligands in mono-cationic form. On the other hand, the histamine monocation is known to be the most important form of histamine in a physiological environment. Structural investigations of the title complex containing histamine monocation ligands have thus been undertaken to study this form of histamine. IR and Raman spectra of the complex suggested that it is also stable in water solution and that it contains non-equivalent isothiocyanate groups (Wojtczak, 1982). Another aim of this study was to verify these suggestions.

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Experimental. Crystals from water, density by flotation method, $0.5 \times 0.4 \times 0.25$ mm, Syntex $P2_1$ diffractometer, graphite monochromator, 1833 independent hkl with $2\theta \leq 50°$, 1455 with $I \geq 1.96\sigma$ (I); Patterson method, $\sum w(\Delta F)^2$ minimized, anisotropic full matrix, H (from ΔF map) fixed, final $R = 0.035$,† $R_w = 0.033$, $w = \sigma^{-2}(F)$ from counting statistics; scattering factor for Ni^{2+} from *International Tables for X-ray Crystallography* (1974), programs described by Jaskólski (1982), RIAD-32 computer.

Discussion. The atomic parameters are given in Table 1. Bond lengths and angles and the atom numbering scheme are shown in Fig. 1. Histamine exists in the monocationic form protonated at N(18) of the side chain. The Ni^{2+} cation is surrounded by six N atoms forming a distorted octahedron. The coordination

† Lists of structure factors and anisotropic thermal parameters and details of the H-bonding scheme and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38304 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and* B_{eq} (*Willis & Pryor,* 1975) *for non-hydrogen atoms*

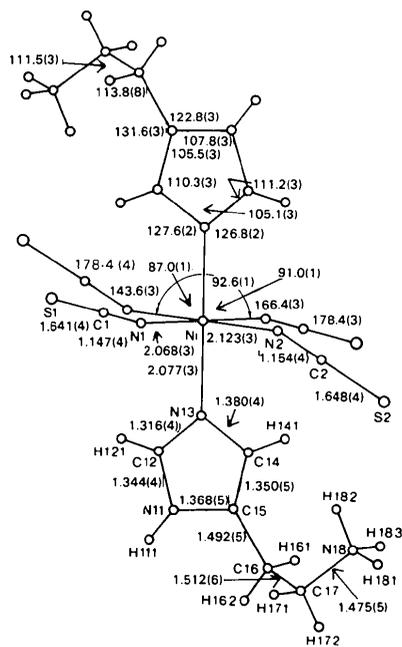|	x	y	z	B_{eq}(Å^2)
Ni	0	0	10000	2.03 (2)
S(1)	−2890 (1)	3931 (1)	8812 (1)	3.38 (3)
C(1)	−1817 (3)	2643 (4)	9106 (3)	2.11 (9)
N(1)	−1054 (3)	1767 (4)	9328 (3)	2.71 (9)
S(2)	4047 (1)	1995 (1)	10531 (1)	3.91 (3)
C(2)	2510 (4)	1708 (4)	10586 (3)	2.50 (9)
N(2)	1435 (3)	1484 (4)	10603 (3)	3.00 (9)
N(11)	1629 (3)	189 (4)	6676 (2)	2.61 (9)
C(12)	678 (3)	304 (4)	7442 (3)	2.37 (9)
N(13)	1028 (3)	−167 (3)	8474 (2)	2.24 (9)
C(14)	2271 (3)	−608 (4)	8345 (3)	2.50 (9)
C(15)	2651 (3)	−403 (4)	7242 (3)	2.26 (9)
C(16)	3898 (4)	−646 (5)	6668 (3)	3.00 (9)
C(17)	4729 (4)	748 (5)	6652 (4)	3.5 (1)
N(18)	5184 (3)	1133 (4)	7821 (4)	4.5 (1)

Fig. 1. Numbering scheme in the chemical unit and bond lengths (Å) and angles (°) with their e.s.d.'s.
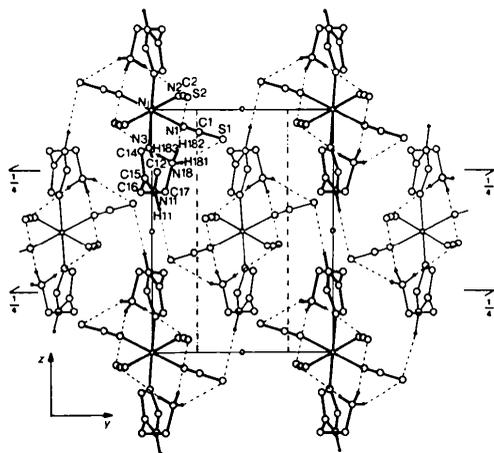

Fig. 2. Projection of the structure down the *a* axis. All H atoms attached to C atoms have been omitted.

sphere includes four NCS⁻ anions and two histamine monocations coordinated to Ni^{2+} via their N^τ atoms.* The two Ni–NCS distances [2·068 (3), 2·123 (3) Å] are similar to those found by Bonnet & Jeannin (1970c,1972b). The difference between these two distances [0·055 (4) Å] is consistent with the non-equivalence of the Ni–NCS bonds deduced from oscillation spectra (Wojtczak, 1982).

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* Following the IUPAC–IUB Commission on Biochemical Nomenclature recommendations for histidine, the imidazole N nearer the side chain is designated N^π, and the one farther from it is N^τ (Black & Ganellin, 1974).

The structure contains a three-dimensional network of H bonds (Fig. 2) with N^π–H and ammonium groups as the donors. The acceptors are the isothiocyanate S atoms, each being an acceptor for two bonds. The four H bonds are relatively weak and very similar. One of them, N(18)···S(2), is intramolecular and may contribute to the appreciable bend of the N(2)C(2)S(2) isothiocyanate group [Ni–N(2)–C(2) is 143·6 (3)° while the usual values are 155–175°] and it probably also stabilizes this histamine monocation complex in solution (see *Introduction*).

The imidazole ring of the histamine residue is planar ($\chi^2 = 2\cdot49$). Coordination to Ni^{2+} does not have any effect on the imidazole-ring geometry. Comparison with 5-(2-aminoethyl)imidazole (Bonnet & Ibers, 1973) reveals that the differences in bond distances and angles of the imidazole moieties are less than $2\cdot6\sigma$.

In solids, histamine and its salts are known so far in the *trans* form only, although in solution both *trans* and *gauche* forms have comparable stabilities (Prout, Critchley & Ganellin, 1974). In the present compound histamine has the *gauche* form, the torsion angle C(15)–C(16)–C(17)–N(18) being 69·4 (4)°. The C(14)–C(15)–C(16)–C(17) torsion angle is −92·1 (4)° and the dihedral angle between the planes through the side chain and the imidazole ring is 71·1 (4)°. The histamine conformation has usually been described in terms of these two planes. It should be noted, however, that it may not be adequate to compare the above dihedral angle with the values reported for other histamine entities since in all previous cases the side chain had the *trans* form while in the present structure it is *gauche*. Thus an adequate description of the histamine conformation requires the two torsion angles at the side chain {N(18)–C(17)–C(16)–C(15) and C(17)–C(16)–C(15)–C(14)[N(11)]}.

It was found (Durrant, Ganellin & Parsons, 1975) that biological activity of histamine is associated with its N^τ–H tautomeric form (H_1-receptor) while the N^π–H form is inactive. In the present compound histamine has the inactive N^π–H form, stabilized by the coordinative Ni–N(13) bond.

References

BLACK, J. W. & GANELLIN, C. R. (1974). *Experientia*, **30**, 111–113.
BONNET, J. J. & IBERS, J. A. (1973). *J. Am. Chem. Soc.* **95**, 4829–4833.
BONNET, J. J. & JEANNIN, Y. (1970a). *Acta Cryst.* **B26**, 318–326.
BONNET, J. J. & JEANNIN, Y. (1970b). *C. R. Acad. Sci. Sér. C*, **270**, 1329–1333.
BONNET, J. J. & JEANNIN, Y. (1970c). *Bull. Soc. Fr. Minéral. Cristallogr.* **93**, 287–299.

BONNET, J. J. & JEANNIN, Y. (1972a). *Acta Cryst.* B28, 1079–1085.

BONNET, J. J. & JEANNIN, Y. (1972b). *Bull. Soc. Fr. Minéral. Cristallogr.* 95, 61–67.

BONNET, J. J., JEANNIN, Y. & LAAONINI, M. (1975). *Bull. Soc. Fr. Minéral. Cristallogr.* 98, 208–213.

DAHAN, F. (1976). *Acta Cryst.* B32, 2472–2475.

DURRANT, G. J., GANELLIN, C. R. & PARSONS, M. E. (1975). *J. Med. Chem.* 18, 905–909.

GŁÓWKA, M. L., GAŁDECKI, Z., KAZIMIERCZAK, W. & MAŚLIŃSKI, C. (1980). *Acta Cryst.* B36, 2148–2150.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

JASKÓLSKI, M. (1982). *Collected Abstracts of the Fourth Symposium on Organic Crystal Chemistry,* Poznań, September 1982, edited by Z. KALUSKI, pp. 70–71. A. Mickiewicz Univ., Poznań.

PROUT, K., CRITCHLEY, S. R. & GANELLIN, C. R. (1974). *Acta Cryst.* B30, 2884–2886.

VEIDIS, M. V., PALENIK, G. J., SCHAFFRIN, R. & TROTTER, J. (1969). *J. Chem. Soc.* (A), pp. 2659–2666.

WILLIS, B. T. M. & PRYOR, A. W. (1975). *Thermal Vibrations in Crystallography,* pp. 101–102. Cambridge Univ. Press.

WOJTCZAK, J. (1982). In preparation.

YAMANE, T., ASHIDA, T. & KAKUDO, M. (1973). *Acta Cryst.* B29, 2884–2891.

Structures of Two Complexes of Copper(II) Chloride and 1,4-Oxathiane. The Two-Dimensional Polymers Poly[di-μ-chloro-μ-(1,4-oxathiane-*O*,*S*)-copper(II)], [Cu₃(C₄H₈OS)₂Cl₆]ₙ, and Poly[dichlorobis-μ-(1,4-oxathiane-*O*,*S*)-copper(II)], [Cu(C₄H₈OS)₂Cl₂]ₙ

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Abstract. (I) $[CuCl_2]_3[C_4H_8OS]_2$, $M_r = 611\cdot68$, triclinic, $P\bar{1}$, $a = 9\cdot375$ (5), $b = 7\cdot370$ (5), $c = 7\cdot821$ (4) Å, $\alpha = 112\cdot17$ (12), $\beta = 112\cdot56$ (11), $\gamma = 76\cdot18$ (5)°, $U = 459\cdot3$ Å³, $Z = 1$, $D_x = 2\cdot212$ Mg m⁻³; Cu $K\alpha$ radiation, $\lambda = 1\cdot5418$ Å, $\mu = 13\cdot6$ mm⁻¹, $F(000) = 301$, $T = 293$ K; $R = 0\cdot060$ for 1077 reflexions. (II) $[CuCl_2][C_4H_8OS]_2$, $M_r = 342\cdot80$, orthorhombic, *Abma* (a non-standard setting of *Cmca*, No. 64), $a = 10\cdot86$ (1), $b = 12\cdot63$ (1), $c = 9\cdot64$ (1) Å, $U = 1322\cdot2$ Å³, $Z = 4$, $D_x = 1\cdot723$ Mg m⁻³; Cu $K\alpha$ radiation, $\lambda = 1\cdot5418$ Å, $\mu = 8\cdot5$ mm⁻¹, $F(000) = 700$, $T = 293$ K; $R = 0\cdot047$ for 390 reflexions. In (I) stepped chains $(CuCl_2)_n$ are crosslinked by (S···O)-bridging 1,4-oxathiane ligands to give five-coordinate ($CuCl_4S$) and six-coordinate ($CuCl_4O_2$) environments. In (II) linear $CuCl_2$ units are joined into layers normal to **b** by (S···O)-bridges to give a six-coordinate environment with no chloride bridges.

Introduction. There has been renewed interest in the structures of metal complexes of thioether ligands (Murray & Hartley, 1981; Walton, 1980). Until recently, 1,4-oxathiane (tx) was known only as a monodentate ligand giving monomeric complexes (McEwen & Sim, 1967; Barnes, Hunter & Lown, 1977). This ligand is now known to give polymeric complexes with Cuᴵ and Agᴵ using S—, O— and

S···O—bridges (Barnes & Paton, 1982, 1983; Barnes, Blyth & Paton, 1982). The reaction of CuCl with tx has been reinvestigated. In addition to green CuCl₂.2tx (II) (Walton, 1966), red (CuCl₂)₃.2tx (I) and white CuCl.tx (III) have been obtained. (III) is not isomorphous with CuBr.tx (Barnes & Paton, 1982) but no crystals suitable for structure determination have been obtained.

Experimental. 1,4-Oxathiane vapour was allowed to diffuse into anhydrous CuCl₂ in ethanol at room temperature. The usual product was (II) but microscopic examination of some batches revealed red plates (I) and occasionally a few white plates (III). The compounds were separated under the microscope. They deteriorate in air but could be stored indefinitely in sealed vials when dry.

The structures of (I) and (II) were determined using intensities from equi-inclination Weissenberg photographs scanned by the SERC Microdensitometer Service, Daresbury Laboratory. All calculations were performed on the Dundee University DEC10 computer using the *SHELX* 76 (Sheldrick, 1976), *XANADU* (Roberts & Sheldrick, 1975) and *PLUTO* (Motherwell & Clegg, 1978) program packages. Atomic scattering parameters were from *International Tables for X-ray Crystallography* (1974). All crystals were mounted in Lindemann-glass capillaries.

Compound (I). Data were collected for layers (0–8)*kl* and *h*(0–5)*l*. The γ angle was measured by

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