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Structure of the *NS*-Donor Ligand 4-(Ethylthiomethyl)-5-methylimidazole

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Abstract. $C_7H_{12}N_2S$, $M_r = 156.25$, monoclinic, $P2_1/n$, $a = 9.684$ (6), $b = 11.459$ (3), $c = 15.834$ (4) Å, $\beta = 92.62$ (3)°, $V = 1755.2$ Å³, $Z = 8$, $D_x = 1.18$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.710730$ Å, $\mu = 2.88$ cm⁻¹, $F(000) = 672.92$, $T = 293$ K, final $R = 0.060$ for 1914 significant reflections. The asymmetric unit contains two molecules of 4-(ethylthiomethyl)-5-methylimidazole (*memi*). The molecules are coupled in chains parallel to the a axis by hydrogen from the N—H of one molecule to the pyridine-type N atom of the next molecule. The imidazole rings are planar. The least-squares plane through the imidazole ring and the plane through the thioether S and its adjacent C atoms make dihedral angles of 103.9 (2) and 87.1 (3)° in the two independent *memi* molecules. The corresponding angle in *memi* ligands coordinated to transition-metal ions is close to 90°, which implies that the conformation of the free ligand is favourable for coordination.

Introduction. As part of a research program to synthesize low-molecular-weight analogues of the active sites of metalloproteins we are designing ligands which contain chromophores similar to those in certain metalloenzymes. Several reports describing the preparation and spectroscopic characterization of transition-metal coordination compounds containing

these ligands have been published by our group (see for instance: Ochocki, Driessen, de Graaff & Reedijk, 1988; Bouwman & Driessen, 1988). Most of these reports also include X-ray crystal structures of one or two of the complexes. Hitherto, the crystal structures of the free ligands themselves have not been determined. The conformation of a free ligand is not necessarily identical to the conformation of the complexed ligand (Driessen, Groeneveld & van der Weij, 1970).

The *NS*-donor ligand 4-(ethylthiomethyl)-5-methylimidazole (*memi*) has been designed to obtain MN_2S_2 chromophores which may serve as models for the active site in plastocyanine (Colman, Freeman, Guss, Murata, Norris, Ramshaw & Venkappa, 1978). Several coordination compounds of the ligand *memi* have been prepared and characterized (Bouwman, Westheide, Driessen & Reedijk, 1989). To gain insight into the precise stereochemistry of the uncomplexed ligand its X-ray crystal structure has been determined.

Experimental. Colorless needle, grown from ethanol at room temperature, with approximate dimensions 0.5 × 0.3 × 0.3 mm. Enraf-Nonius CAD-4 four-circle diffractometer, graphite-monochromatized Mo $K\alpha$. Cell constants from setting angles of 24 reflections, $10 < \theta < 12^\circ$. Corrections for Lorentz and polarization effects. Transmission coefficients 0.97 to

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1.03; absorption correction not applied. $2.0 < \theta < 27.5^\circ$, $h -12$ to 12 , $k 0$ to 14 , $l 0$ to 20 . Standard reflections $25\bar{3}$, $3\bar{3}\bar{6}$, $\bar{1}37$, intensity variation 5.45%. 4384 measured reflections, 4235 independent, $R_{\text{int}} = 0.022$, 2321 reflections with $I < 2\sigma(I)$ were classified as unobserved. Structure solved by direct methods. F used in LS refinement. Most H atoms found in difference Fourier syntheses, some [H(172), H(173), H(273)] placed at 0.95 Å from parent atom. Least-squares refinement of positional and anisotropic thermal parameters of non H atoms. For H atoms a common isotropic displacement parameter, B , was refined, final value: 9.8 \AA^2 ; positional parameters of H atoms coupled to parent atom. $S = 3.620$, $w = 1/\sigma^2(F)$, $R = 0.060$, $wR = 0.070$; $(\Delta/\sigma)_{\text{max}} < 0.30$. Max., min. $\Delta\rho$ values in final difference synthesis 0.30, -0.43 e \AA^{-3} . Scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). Leiden University Computer (IBM 3083); *MULTAN* (Main, Lessinger, Woolfson, Germain & Declercq, 1978) and programs written or modified by S. Gorter, R. A. G. de Graaff and E. W. Rutten-Keulemans.

Discussion. Positional parameters and equivalent isotropic thermal parameters for the non-H atoms are listed in Table 1.* Atomic distances and intramolecular bond angles for the non-H atoms are listed in Table 2. An *ORTEP* projection (Johnson, 1965) of the asymmetric unit and the atomic labeling are given in Fig. 1.

The asymmetric unit consists of two memi molecules. The asymmetric unit itself seems rather symmetrical (see Fig. 1): a close inspection of the fractional coordinates (Table 1) reveals that the two molecules can almost be generated from one another when a twofold screw axis parallel to the a axis is assumed.

The positions of the H atoms associated with the imidazole N atoms have been located from difference syntheses. The N—H distances (see Table 2) indicate that H(11) and H(21) are bonded to N(11) and N(21) respectively, and hydrogen bonded to N(23) and N(13) respectively. The memi molecules are linked together through these hydrogen bonds, as depicted in Fig. 2.

The two imidazole rings are planar. The methyl C atoms, C(16) and C(26), and the methylene C atoms, C(10) and C(20), lie in the respective planes of the imidazole rings to within 0.06 Å. The imidazole

Table 1. Atomic coordinates ($\times 10^5$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10$) of the non-H atoms

	x	y	z	B_{eq}
C(10)	30214 (5)	64549 (4)	93908 (3)	47 (1)
N(11)	2114 (3)	45442 (3)	86552 (3)	39 (1)
C(12)	13608 (4)	39321 (4)	85173 (3)	45 (1)
N(13)	24844 (3)	45108 (3)	87499 (3)	42 (1)
C(14)	20267 (4)	55534 (3)	90602 (3)	35 (1)
C(15)	6157 (4)	55941 (3)	90040 (3)	35 (1)
C(16)	-3916 (5)	65051 (4)	92227 (3)	51 (2)
C(17)	60390 (8)	80464 (8)	93508 (6)	132 (4)
C(18)	47225 (7)	83668 (6)	91207 (5)	87 (3)
S(19)	37533 (2)	72304 (2)	85432 (1)	63 (1)
C(20)	78879 (5)	16529 (4)	80887 (3)	42 (1)
N(21)	51801 (3)	37794 (3)	84613 (2)	35 (1)
C(22)	63485 (4)	44157 (4)	85130 (3)	38 (1)
N(23)	74504 (3)	37745 (3)	83819 (3)	37 (1)
C(24)	69532 (4)	26590 (3)	82329 (3)	33 (1)
C(25)	55527 (4)	26459 (4)	82823 (3)	36 (1)
C(26)	44948 (4)	17010 (4)	81741 (4)	54 (2)
C(27)	109242 (6)	1592 (6)	85503 (4)	70 (2)
C(28)	94984 (5)	-1840 (4)	88046 (3)	53 (2)
S(29)	84489 (1)	10414 (1)	91095 (1)	55 (1)

Table 2. Bond lengths (\AA) and bond angles ($^\circ$) involving non-H atoms

C(10)—C(14)	1.491 (6)	C(20)—C(24)	1.490 (6)
C(10)—S(19)	1.783 (5)	C(20)—S(29)	1.822 (5)
N(11)—C(12)	1.342 (5)	N(21)—C(22)	1.345 (5)
N(11)—C(15)	1.373 (5)	N(21)—C(25)	1.381 (5)
C(12)—N(13)	1.312 (5)	C(22)—N(23)	1.319 (5)
N(13)—C(14)	1.373 (5)	N(23)—C(24)	1.382 (5)
C(14)—C(15)	1.366 (5)	C(24)—C(25)	1.362 (5)
C(15)—C(16)	1.480 (6)	C(25)—C(26)	1.495 (6)
C(17)—C(18)	1.360 (9)	C(27)—C(28)	1.507 (7)
C(18)—S(19)	1.826 (6)	C(28)—S(29)	1.812 (5)
N(11)—N(23)	2.829 (5)	N(21)—N(13)	2.798 (5)
N(11)—H(11)	0.923	N(21)—H(21)	1.016
N(23)—H(11)	1.909	N(13)—H(21)	1.804
C(14)—C(10)—S(19)	110.7 (3)	C(24)—C(20)—S(29)	108.7 (3)
C(12)—N(11)—C(15)	107.5 (4)	C(22)—N(21)—C(25)	107.2 (3)
N(11)—C(12)—N(13)	111.9 (4)	N(21)—C(22)—N(23)	111.8 (4)
C(12)—N(13)—C(14)	105.3 (4)	C(22)—N(23)—C(24)	105.3 (3)
C(10)—C(14)—N(13)	121.0 (4)	C(20)—C(24)—N(23)	122.2 (4)
C(10)—C(14)—C(15)	128.9 (4)	C(20)—C(24)—C(25)	127.9 (4)
N(13)—C(14)—C(15)	110.1 (4)	N(23)—C(24)—C(25)	109.9 (4)
N(11)—C(15)—C(14)	105.2 (4)	N(21)—C(25)—C(24)	105.7 (4)
N(11)—C(15)—C(16)	122.2 (4)	N(21)—C(25)—C(26)	121.4 (4)
C(14)—C(15)—C(16)	132.6 (4)	C(24)—C(25)—C(26)	132.9 (4)
C(17)—C(18)—S(19)	113.3 (6)	C(27)—C(28)—S(29)	113.6 (4)
C(10)—S(19)—C(18)	101.0 (3)	C(20)—S(29)—C(28)	102.1 (2)

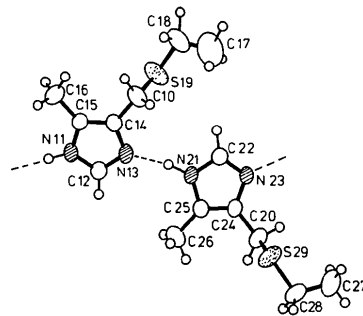


Fig. 1. *ORTEP* projection (Johnson, 1965) with 50% probability contours (non-H atoms) and atomic labeling of the asymmetric unit of 4-(ethylthiomethyl)-5-methylimidazole.

* Lists of H-atom coordinates, atomic distances involving the H atoms, anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52054 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

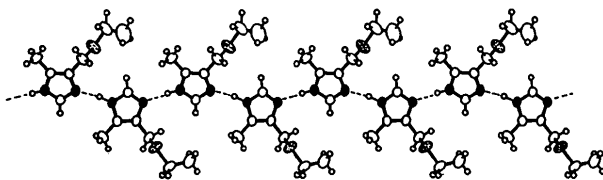


Fig. 2. Molecules of 4-(ethylthiomethyl)-5-methylimidazole linked by hydrogen bonds along the *a* axis.

plane through N(11)—C(12)—N(13)—C(14)—C(15) and the plane through C(10)—S(19)—C(18) make an angle of 103.9 (2)° with one another, while the imidazole plane through N(21)—C(22)—N(23)—C(24)—C(25) and the plane through C(20)—S(29)—C(28) make an angle of 87.1(3)° with one another. The angles formed by the corresponding planes in the coordinated ligand are also close to 90°. In [Co(memi)₂(NCS)₂] this angle is 91.6 (1)°, in [Ni(memi)₂(H₂O)₂](NO₃)₂ it is 90.3 (2)° and in [Cu(memi)₂(H₂O)₂](NO₂) it is 86.5 (3)° (Bouwman, Westheide, Driessen & Reedijk, 1989). The conformations of the free ligand and the coordinated ligand are thus hardly different. This means that the conformation of the free ligand is favorable for coordination.

There is no intermolecular stacking of the aromatic rings. The packing of the molecules is dictated

by normal van der Waals contacts and the hydrogen bonding noted above.

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Structure of Strychnine Hydrochloride Sesquihydrate

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Abstract. C₂₁H₂₃N₂O₂⁺.Cl⁻.1.5H₂O, *M_r* = 397.90, monoclinic, *P*2₁, *a* = 7.617 (1), *b* = 32.463 (2), *c* = 7.849 (1) Å, β = 90.40 (2)°, *V* = 1940.8 (4) Å³, *Z* = 4, *D_m* = 1.39, *D_x* = 1.36 g cm⁻³, λ(Cu Kα) = 1.5418 Å,

μ = 19.724 cm⁻¹, *F*(000) = 844, final *R* = 0.047 for 3368 observed reflections. Strychnine hydrochloride is a naturally occurring alkaloid in its protonated form. One of the N atoms accepts the proton from hydrochloric acid changing its hybridization to *sp*³. The indole N atom is *sp*² hybridized with its lone-

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