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Structure of Thiomorpholin-3-one: Comments on the Geometry of Monocoordinated Metal Complexes

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Abstract. Perhydro-1,4-thiazin-3-one, C_4H_7NOS, $M_r = 117{\cdot}2$, monoclinic, $P2_1/c$, $a = 10{\cdot}642\,(2)$, $b = 6{\cdot}089\,(1)$, $c = 9{\cdot}133\,(1)$ Å, $\beta = 111{\cdot}48\,(1)°$, $V = 550{\cdot}7\,(2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}413$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 41{\cdot}6$ cm^{-1}, $F(000) = 248$, room temperature, $R = 0{\cdot}038$, $wR = 0{\cdot}054$ for 830 observed [$I > 3\sigma(I)$] reflections. The molecule adopts a half-chair conformation with the S atom 0·918 (2) Å from the best plane passing through the rest of the atoms in the molecule. The crystal structure is stabilized by a sequence of N—H···O hydrogen bonds resulting in a helical arrangement of molecules about an axis parallel to the *b* axis.

Introduction. Many of the *p*-block elements [*p*-block elements are defined as those whose *p* orbital is filling (Addison, 1961)] such as S, Se and halogens, have been shown to exhibit a characteristic pattern of secondary interactions (Rosenfield, Parthasarathy & Dunitz, 1977; Guru Row & Parthasarathy, 1981; Ramasubbu, Parthasarathy & Murray-Rust, 1986; Ramasubbu & Parthasarathy, 1987) which may be understood in terms of frontier molecular orbitals. Non-bonded interactions of S (and Se) with other atoms in a molecule have been analyzed in terms of electrophile–nulceophile interactions and have been categorized as Type I (involving electrophiles), Type II (involving nucleophiles), Type I–II pairing and Type III (interactions involving two atoms of one kind – for example S···S, Se···Se *etc.*) on the basis of spherical polar coordinates θ and φ, specifying the direction of the S(Se)···X vector, where X is the contacting atom, with respect to the plane of the sulfide (selenide), Y—S(Se)—Z (Rosenfield *et al.*, 1977; Guru Row & Parthasarathy, 1981). The angle θ ($0 < \theta < 90°$) is defined as the angle between the normal to the plane [Y—S(Se)—Z] and the vector S(Se)···X, and the angle φ ($0 < |\varphi| < 180°$) as the angle between the bisector of Y—S(Se)—Z and the direction of S(Se)···X projected onto the plane (Rosenfield *et al.*, 1977). To obtain more insight into the nature of such contacts we have undertaken crystallographic determinations of many S- and Se-containing compounds. In this paper we report the crystal structure of thiomorpholin-3-one which has a Type III contact.

Experimental. Crystals of the title compound were obtained from ethanol solutions by slow evaporation; crystal dimensions 0·3 × 0·3 × 0·1 mm; data collected on a CAD-4 diffractometer; Cu $K\alpha$ radiation; lattice parameters refined using 17 centered reflections ($16 < 2\theta < 32°$); 1622 reflections measured of which 1162 were unique; $R_{symm} = 0{\cdot}033$; reflections measured to the limit of Cu sphere using $\omega/2\theta$ scan; range of *hkl*: h 0→13, k 0→7 and l −11→11; 830 reflections were significant with $I > 3\sigma(I)$; three reflections monitored every hour of X-ray exposure and showed no significant variation in intensity during the course of data collection; Lorentz and polarization, and anisotropy of absorption using φ-scan corrections applied; the average, maximum and minimum transmissions are 0·85, 0·99 and 0·64 respectively.

Structure was solved using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); structural parameters refined by full-matrix least-squares refinement; difference density maps cal-

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culated at $R = 0{\cdot}078$ to locate all H-atom positions which were then included in the refinement with individual isotropic thermal parmeters; final R for 830 observed reflections is 0·038; wR is 0·054; function minimized in the least squares $\sum w(|F_o|^2 - |F_c|^2)$ where $w = 1/\sigma^2$; $(\Delta/\sigma)_{max} < 0{\cdot}01$ for all atoms; largest feature in the difference map was 0·36 and −0·26 e Å^{-3}; $S = 2{\cdot}4$; atomic scattering factors from *International Tables for X-ray Crystallography* (1974); programs for structure determination and refinement, Fourier analysis and *ORTEP* (Johnson, 1976) as in *SDP* (Frenz, 1982).

Discussion. The final positional and isotropic equivalent thermal parameters for all atoms are listed in Table 1.* The bond lengths and angles are given in Table 2. The thiomorpholinone ring adopts a half-chair conformation with the S atom 0·918 (2) Å from the best plane passing through the remaining non-hydrogen atoms. The atomic numbering scheme and molecular structure are depicted in Fig. 1. The molecules are held together by a helical arrangement of N—H···O hydrogen bonds as shown in Fig. 2. There are both right-handed and left-handed helical columns whose helical axis are parallel to the b axis. The two columns run antiparallel to each other. The parameters defining the hydrogen bond are: N(4)—H(N4) = 0·73 (2); N(4)···O(3) = 2·896 (3); H(N4)···O(3) = 2·21 (3) Å and N(4)—H(N4)···O(3) = 156 (3)°. There are no significant intermolecular contacts involving S atoms except for an $S_{(x,y,z)}\cdots S_{(1-x,-y,1-z)}$ contact distance of 3·670 (1) Å. Considering the van der Waals radius for S to be 1·80 Å (Bondi, 1964), we find that this contact is just outside the limiting distance of 3·60 Å considered in our studies (Guru Row & Parthasarathy, 1981). This contact belongs to the Type III class of contacts since

* Lists of structure factors, anisotropic thermal parameters and results of least-squares-plane calculations have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51142 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

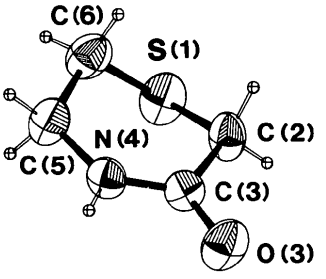

Fig. 1. A perspective view of the molecule showing the atomic numbering scheme used. The thermal ellipsoids were drawn at 50% probability level.

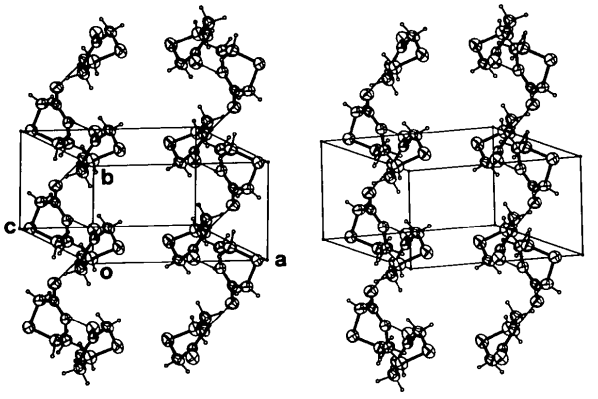

Fig. 2. A stereoscopic view of the packing of the molecules showing the helical arrangement of N—H···O hydrogen bonds.

Table 1. *Fractional atomic coordinates with equivalent isotropic thermal parameters for non-hydrogen atoms and isotropic thermal parameters for hydrogen atoms (e.s.d.'s are given in parentheses)*

$$B_{eq} = \tfrac{4}{3}[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}].$$

	x	y	z	B_{eq}/B_{iso}(Å^2)
S(1)	0·58895 (5)	0·0752 (1)	0·36901 (8)	4·70 (2)
C(2)	0·6881 (2)	−0·1585 (4)	0·4643 (3)	4·13 (6)
C(3)	0·8209 (2)	−0·1027 (4)	0·5918 (3)	3·22 (5)
O(3)	0·8683 (2)	−0·2322 (3)	0·7028 (2)	4·93 (5)
N(4)	0·8843 (2)	0·0790 (3)	0·5792 (2)	3·48 (4)
C(5)	0·8407 (3)	0·2539 (5)	0·4635 (3)	4·36 (6)
C(6)	0·7226 (3)	0·1951 (5)	0·3199 (3)	4·56 (6)
H(C2)1	0·636 (2)	−0·235 (4)	0·502 (3)	2·0 (6)*
H(C2)2	0·709 (3)	−0·258 (5)	0·382 (3)	2·8 (7)*
H(N4)	0·943 (3)	0·102 (5)	0·651 (3)	3·1 (7)*
H(C5)1	0·918 (3)	0·312 (5)	0·430 (3)	2·3 (6)*
H(C5)2	0·817 (4)	0·388 (6)	0·514 (4)	5·4 (9)*
H(C6)1	0·755 (2)	0·081 (4)	0·253 (3)	2·4 (6)*
H(C6)2	0·685 (3)	0·334 (5)	0·273 (4)	4·5 (8)*

* B_{iso}.

Table 2. *Bond distances* (Å) *and angles* (°) *(e.s.d.'s are given in parentheses)*

S(1)—C(2)	1·795 (3)	C(2)—H(C2)1	0·88 (3)
S(1)—C(6)	1·795 (3)	C(2)—H(C2)2	1·05 (3)
C(2)—C(3)	1·505 (3)	N(4)—H(N4)	0·73 (2)
C(3)—O(3)	1·237 (3)	C(5)—H(C5)1	1·04 (3)
C(3)—N(4)	1·322 (3)	C(5)—H(C5)2	1·01 (4)
N(4)—C(5)	1·452 (3)	C(6)—H(C6)1	1·06 (3)
C(5)—C(6)	1·490 (3)	C(6)—H(C6)2	0·97 (3)

C(2)—S(1)—C(6)	93·7 (1)	C(5)—N(4)—H(N4)	117· (2)
S(1)—C(2)—C(3)	114·5 (2)	N(4)—C(5)—H(C5)1	113· (1)
C(2)—C(3)—O(3)	118·4 (3)	N(4)—C(5)—H(C5)2	109· (2)
C(2)—C(3)—N(4)	119·1 (2)	C(6)—C(5)—H(C5)1	109· (1)
O(3)—C(3)—N(4)	122·4 (2)	C(6)—C(5)—H(C5)2	109· (2)
C(3)—N(4)—C(5)	129·7 (2)	S(1)—C(6)—H(C6)1	109· (1)
N(4)—C(5)—C(6)	114·0 (2)	S(1)—C(6)—H(C6)2	103· (1)
S(1)—C(6)—C(5)	111·6 (2)	C(5)—C(6)—H(C6)1	108· (1)
S(1)—C(2)—H(C2)1	106· (1)	C(5)—C(6)—H(C6)2	105· (2)
S(1)—C(2)—H(C2)2	111· (1)	H(C2)1—C(2)—H(C2)2	108· (2)
C(3)—C(2)—H(C2)1	111· (1)	H(C5)1—C(5)—H(C5)2	102· (3)
C(3)—C(2)—H(C2)2	107· (1)	H(C6)1—C(6)—H(C6)2	119· (3)
C(3)—N(4)—H(N4)	112· (2)		

the two S atoms are related by a center of symmetry with $\theta_i = \theta_j$ [$= 66°$; θ_i and θ_j are spherical polar coordinates specifying the direction of the vector $S_i \cdots S_j$ with respect to the planes Y_i—S_i—Z_i and Y_j—S_j—Z_j (Guru Row & Parthasarathy, 1981)].

Our analysis of coordination geometry around S, Se has shown that of the two lone pairs available for coordination around S and Se, a $p\pi$ type and an sp^2 hybrid type orbital (Boyd, 1978), metal ions choose the $p\pi$ type orbital exclusively for coordination (Rosenfield *et al.*, 1977; Guru Row & Parthasarathy, 1981; Ramasubbu & Parthasarathy, 1987). This electronic preference may be due to the achievement of better overlap between the two interacting orbitals. However, for a particular S- or Se-containing heterocycle, both electronic and steric factors may be important for determining the geometry of monocoordinated metal complexes. For example, by considering the interaction between the axial substituent and the β methylene groups of the ring, Lambert, Mixan & Johnson (1973) have shown that the axial isomer predominates at Se whereas both axial and equatorial isomers occur at S in similar compounds. Several monocoordinated complexes with such bonding have been reported in many crystal structures (Barnes, Hunter & Lown, 1977; Fowler & Griffiths, 1978).

Our analysis of the interaction of S or Se with metal ions in these and other complexes shows that irrespective of axial or equatorial coordination, the metal ions tend to approach S or Se nearly perpendicular to the sulfide or selenide plane with $\theta \simeq 20°$ (Rosenfield *et al.*, 1977; Ramasubbu & Parthasarathy, 1987). Since the pz orbital is symmetrical with respect to the sulfide or selenide plane, approaches from above and from below the plane are possible; one may be characterized as being 'axial' and the other 'equatorial'. However, it is clear that the electrophiles do not approach S or Se in the plane seeking the other lone pair (sp^2 type) at $\theta = 90°$ and $\varphi = 180°$ since this lone pair is not a HOMO (Rosenfield *et al.*, 1977).

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Structure of a Triclinic Modification of 4,4,4′,4′,6,6,6′,6′,8,8,8′,8′-Dodecachloro-2,2′-dimethylbi(cyclotetraphosphazene)

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Abstract. $C_2H_6Cl_{12}N_8P_8$, $M_r = 815{\cdot}35$, triclinic, $P\bar{1}$, $a = 8{\cdot}436$ (1), $b = 10{\cdot}005$ (1), $c = 17{\cdot}153$ (2) Å, $\alpha = 86{\cdot}19$ (1), $\beta = 80{\cdot}26$ (1), $\gamma = 108{\cdot}83$ (1)°, $V = 1339{\cdot}1$ (3) Å^3, $Z = 2$, $D_x = 2{\cdot}022$ g cm^{-3}, λ(Mo $K\alpha$) $= 0{\cdot}71073$ Å, $\mu = 17{\cdot}4$ cm^{-1}, $F(000) = 796$, $T = 110$ K, $R = 0{\cdot}044$ for 4553 observed reflections with

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