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Imidazoline-2-Thione Semihydrate: Crystal Structure, Spectroscopy and Thermal Analysis

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Introduction

Imidazoline-2-thione (*ImtH*) possesses considerable coordination potential. Thiol-thione tautomerism (Fig. 1(a) and (b)) generates a combination of thione and thiol sulphur as well as pyrollic and pyridine nitrogen. De-protonation yields a thiolato anion with both thione sulphur and pyridino nitrogen available for coordination (Fig. 1(e)). Consequently the molecule may be involved in monodentate, chelating bidentate as well as mono or bidentate bridging coordination, each of which may utilise sulphur and, or, nitrogen. Studies with a variety of metals (Table I) [1–8] have shown that monodentate sulphur-donation and chelating bidentate through sulphur and nitrogen, are the most commonly observed coordination modes. The stability of the S,N-chelate appears to be variable; with Pd(II) [4] the complex is stable in solution in the range pH 0–3 whereas with Co(II), and possibly Zn(II) [1], the chelate exists only in the solid and *ImtH* reverts to monodentate sulphur donation in solution. The formation of stable chelates in alkaline media between the imidazole–thiolato anion (Fig. 1(e)) and Fe(III), Cu(II) and Al(III) has been equated with the bacteriostatic activity of the molecule [9]. Of related interest is the fact that silylated *ImtH* produces both mono (N) and di-(N,N′) ribosylated nucleosides [10].

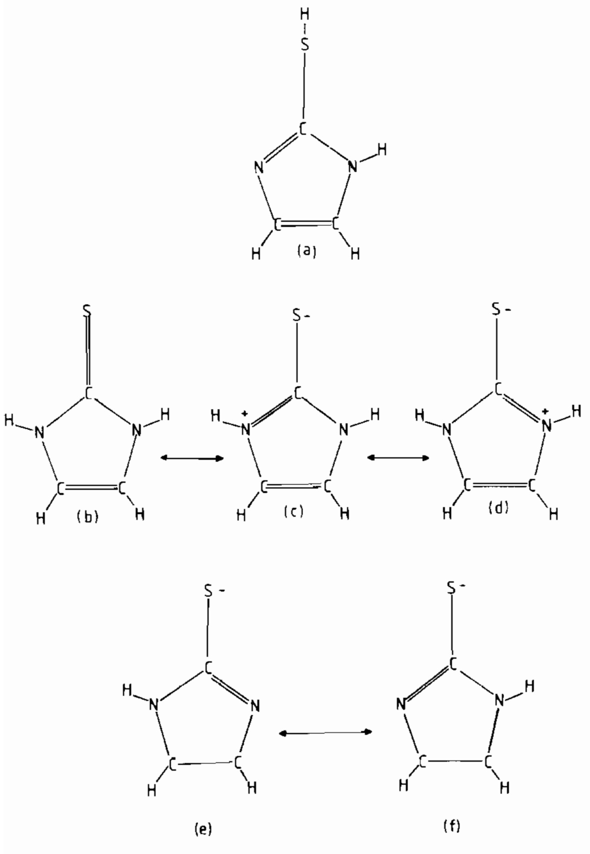

Fig. 1. Major tautomeric and canonical forms for ImtH and $\mathrm{Imt^-}$.

TABLE I. Coordination Characteristics of Imidazoline-2-Thione.

Metal	Stoichiometry	Proposed structure	Donor system and reference	
			Sulphur	Sulphur and nitrogen
Co(II) Zn(II)	$[\mathrm{M(LH)_2X_2}]$ (X = Cl, Br I)	octahedral		*[1]
Co(II) Zn(II)	$[\mathrm{M(LH)_4}]\mathrm{A_2}$ (A = $\mathrm{NO_3}$, $\mathrm{ClO_4}$)	octahedral		*[1]
Ni(II)	$[\mathrm{Ni(LH)_4X_2}]$ (X = Cl, Br, I, NCS, $\mathrm{BF_4}$, $\mathrm{NO_3}$, $\mathrm{ClO_4}$)	tetragonal	*[2]	
Cd(II)	$[\mathrm{M(LH)_2Cl_2}]$	tetrahedral	*[3]	
Pd(II)	$[\mathrm{M(LH)_2Cl_2}]$	square		*[4]
Pt(II)	$[\mathrm{M(LH)_4}]\mathrm{Cl_2}$	square	*[5]	
Mo(O)	$[\mathrm{M(CO)_5LH}]$	octahedral	*[6]	
Cu(I)	$[\mathrm{M(LH)X}]$ (X = Cl, Br, I)	trigonal/ tetrahedral		*[7]
Cu(I)	$[\mathrm{M(LH)_2X}]$ (X = Cl, Br)		*[8]	
Hg(II)	$[\mathrm{M(LH)_2X}]$ (X = Cl, Br)	tetrahedral	*[8]	

Monodentate sulphur donation has been established by an X-ray analysis of Cd$(ImtH)_2\mathrm{Cl_2}$ [3] but no structural details of the heterocycle were included in that report. ^{13}C NMR studies, in deuteriated dimethyl sulphoxide, have produced high field chemical shifts, (δ) of the order, 3–5 ppm (Cd(II)) and 10 ppm (Hg(II)), to the C(2) atom (160.37 ppm) of *ImtH* on coordination; these are also indicative of sulphur donation [8].

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We now report the crystal structure of *ImtH*. The results are compared with those of related molecules and discussed in relation to the coordination chemistry of the molecule.

Experimental

Crystallographic data are summarised in Table II. The coordinates of all non-H atoms were obtained by direct methods and refined with anisotropic temperature factors by full-matrix least-squares analysis. H-atom coordinates were obtained by difference Fourier methods and were included in the calculations without further refinement. Common isotropic temperature factors were applied to groups of H-atoms and refined to final U-values of 0.077(7) Å^2 (imido-H-atoms), 0.055(5) Å^2 (ethylenic H-atoms), 0.091(14) Å^2 (water H-atom). Final positional parameters are in Table III; bond lengths and angles are in Table IV. Scattering factors were obtained from an analytical approximation [11].

TABLE II. Crystallographic Data.

Compound	$C_3H_4N_2S \cdot 1/2H_2O$
Mr	109.1
Space group	*C2/c*
a (Å)	13.21(2)
b (Å)	5.105(1)
c (Å)	15.298(2)
β (deg)	105.61(5)
Z	8
U (Å)^3	994.0
*D*c (g cm^{-3})	1.46
Dm (g cm^{-3})	1.45(1)
F(000)	446
Radiation, Å	0.71073
μ(MoKα) cm^{-1}	4.45
Diffractometer	Enraf-Nonius CAD-4
Scanning mode	$\theta/2\theta$
Total data	789
$F_o > 2\sigma(F\text{o})$	658
R	0.029
Rw	0.031
w	$1.7455/[\sigma(F_o)^2 + 0.000184(F_o)^2]$

All calculations were performed on the NUMAC IBM 370/168 computer at the University of Newcastle upon Tyne using SHELX [11] and related programs.

Thermogravimetric (TG) and Differential Thermal Analysis Curves (DTA) were obtained from Stanton Redcroft TG 750, DTA 673/4 and DuPont 900 instruments in either air or nitrogen.

Infrared spectra were obtained as CsI pressed discs in the range 4000–200 cm^{-1} on a Perkin-Elmer 577 grating spectrophotometer which was calibrated with polystyrene discs to an accuracy of ±3 cm^{-1}.

TABLE III. Non H-atoms Fractional Coordinates (X10^4) with e.s.d.s in Parentheses and B$_{eq}$ Values [21].

	x	y	z	B$_{eq}$ (Å^2)
S(2)	4255(0)	2631(1)	855(0)	2.95(1)
C(21)	5567(2)	3182(5)	1081(2)	2.4(1)
N(1)	6120(2)	5061(4)	1621(1)	2.7(1)
N(3)	6276(2)	1841(4)	772(1)	2.7(1)
C(4)	7265(2)	2889(5)	1106(2)	3.0(1)
C(5)	7164(2)	4910(6)	1634(2)	3.2(1)
O(1)	5000(0)	8564(5)	2500(0)	3.2(1)

Results and Discussion

A low temperature (51–133 °C) mass loss (9.0%) on the TG curve (Fig. 2) is consistent with the presence of the stoichiometric equivalent of one-half of a water molecule per formula unit (theor. 9.0%). A corresponding low temperature endotherm (Tp = 87 °C) on the DTA curve produced a dehydration enthalpy of 84.1 (±10) kJ mol^{-1}. Little indication of the presence of water is indicated in the infrared spectrum of the compound apart from an increased broadening in the range 3500–3100 cm^{-1} relative to the spectrum of the anhydrous material. The thioamide IV band in the semihydrate however consists of four components (870, 830, 790 and 730 cm^{-1}) compared with the two (780 and 735 cm^{-1}) normally observed in the anhydrous compound. The remaining thioamide (I–III) bands are essentially the same in both hydrated and anhydrous compounds (1470, 1225 and 1070 cm^{-1}). The presence of these thioamide bands as well as low frequency (C–S) activity at 670, 520 and 340 cm^{-1} strongly suggest that the thione form (Fig. 1(b)) is the dominant tautomer in the solid [13].

Location of the hydrogen atoms attached to N(1) and N(3) confirms the thione character of *ImtH*. The molecule is essentially planar with a maximum displacement of −0.011 Å for the sulphur atom from the mean plane of the molecule. Bond angles with *ImtH* are similar to those reported for other imidazole-thiones (Table IV(a)) with the largest internal angle in all cases occurring at the nitrogen atoms. Furthermore, N-methyl substitution appears to have no recognisable effect on the relevant internal angle.

Bond lengths within *ImtH* are similar to those reported for related molecules (Table IV). The average C–N distances involving the C(2) atom (1.345 Å) are significantly shorter than those which involve the ethylenic carbon (C(4) and C(5)) atoms (1.377 av. Å). This suggests a greater concentration of π-electron density in the 'thioamide' than in the 'ethylenic' portion of the molecule. The C(2)–S(2)

TABLE IV.

(a) Bond Lengths (Å) and Angles (°) in *ImtH* and Related Molecules (e.s.d.'s in parentheses).

	ImtH	*MImtH*[a]	*DmImtH*	*BzImtH*	*ImdtH*
C(2)–S(2)	1.698(2)	1.685(2)	1.696(5)	1.671(8)	1.708(8)
N(1)–C(2)	1.346(3)	1.351(4)	1.349(6)	1.362(6)	1.322(8)
C(2)–N(3)	1.344(3)	1.345(4)	1.349(6)	1.362(6)	1.322(8)
N(3)–C(4)	1.377(3)	1.387(4)	1.392(4)	1.383(8)	1.471(8)
C(4)–C(5)	1.339(3)	1.333(5)	1.325(5)	1.400(7)	1.536(8)
C(5)–N(1)	1.376(3)	1.374(4)	1.392(4)	1.383(8)	1.471(8)
N(1)–C(2)–N(3)	105.3(2)	105.6(2)	106.4(4)	106.5(3)	110.2(14)
C(2)–N(3)–C(4)	110.7(2)	110.4(3)	109.2(3)	110.4(4)	112.6(10)
N(3)–C(4)–C(5)	106.5(2)	106.2(2)	107.5(3)	106.4(4)	102.4(10)
C(4)–C(5)–N(1)	107.2(2)	108.0(3)	107.5(3)	106.4(4)	102.4(10)
C(5)–N(1)–C(2)	110.2(2)	109.8(2)	109.2(3)	110.4(4)	112.6(10)
S(2)–C(2)–N(1)	126.8(2)	127.3(2)	126.7(4)	126.8(3)	124.8(10)
S(2)–C(2)–N(3)	127.9(2)	127.1(2)	126.7(4)	126.8(3)	124.8(10)

(b) Hydrogen Bonded Distances and Angles. Symmetry code; none, x, y, z; (′) x, 1 + y, z.

Bond				
D–H···A	D···A	D–H	H···A	D–H···A
N(1)–H(1)···O(1)	2.876	1.005	1.881	170
O(1)–H(6)>···S(2′)	3.208	0.777	2.473	158.3

[a]Methylimidazoline-2-thione [17], dimethylimidazoline-2-thione [18], benzimidazoline-2-thione [19], imidazolidine-2-thione [20]

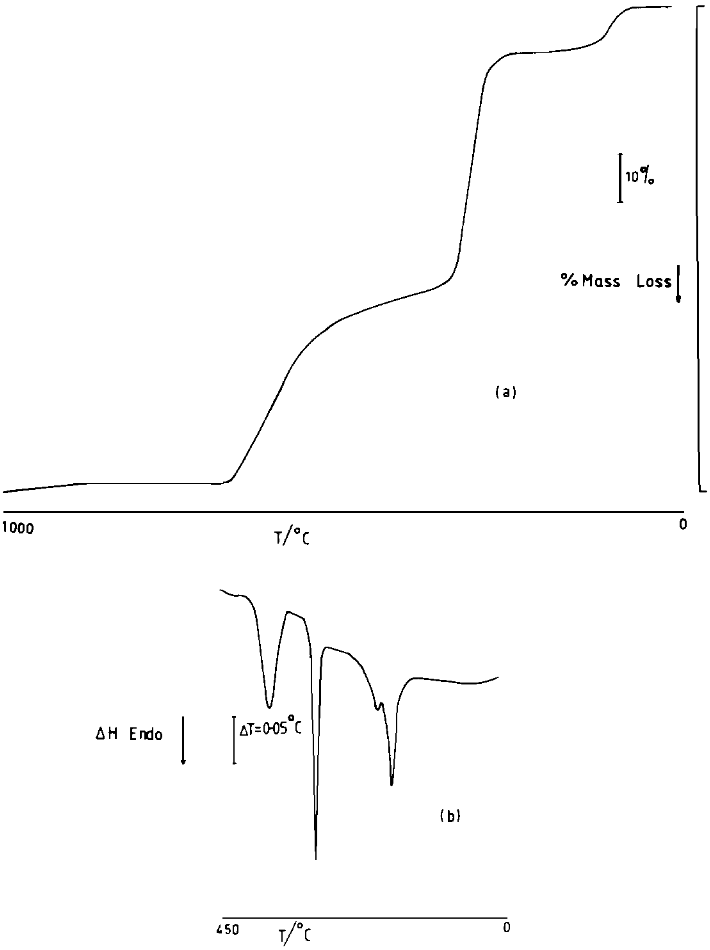

Fig. 2. Thermal analysis curves (a) TG, (b) DTA.

distance (1.698(2) Å) is interesting in that it is significantly longer than that recently reported for (1.685(2) Å) (Table IV). The proportions of π-SCF character in the C–S bond of *ImtH* (47%) [22] suggests that 1(c and d) (Fig. 1) are major contributing canonical forms.

Water molecules occupy two-fold rotation axes and link pairs of molecules by means of hydrogen bonds (Table IV(b); Fig. 3). The angle (H(6)–O(1)–H(6′)) increases to 125.2(3)° in order to accommodate these hydrogen bonds, which, on the basis of separation distances and angles at the respective hydrogen atoms, appear to be relatively strong, particularly those which involve the imido (N(1)–H(1)) group. This hydrogen bonding scheme probably accounts for the magnitude of the dehydration enthalpy, lengthening of the C(2)–S(2) bond as well as perturbation of the thioamide IV band. An additional band appears at 2650 cm^{-1} in the spectrum of the semi hydrate which we assign to ν(SH). This also results from the proximity of water molecules and thione sulphur atoms, and the resultant hydrogen bonding scheme.

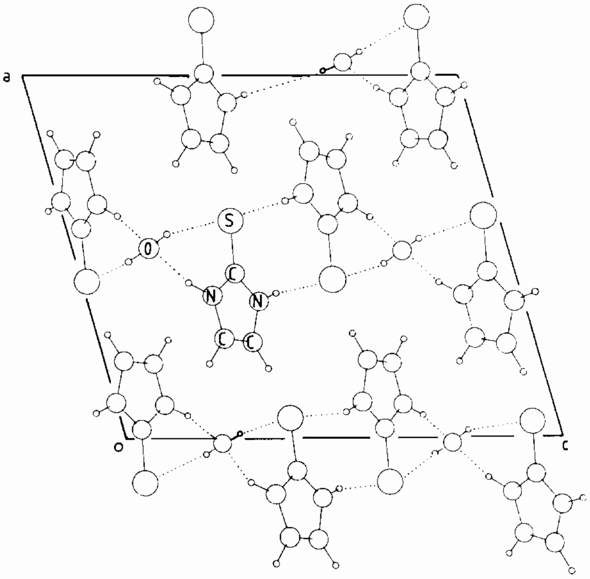

Fig. 3. Unit cell contents viewed down *b*.

Coordination of imidazole–thione molecules, by means of their thione sulphur atoms, is known to affect the vibrational character of thioamide IV bands and to lengthen relevant C–S bonds [14–17]. It is apparent that similar effects occur in hydrated *ImtH* due to the juxtaposition of heterocyclic molecules and water molecules.

The fact that the thione sulphur atom is the major donor in the complexes of *ImtH* (Table I) is entirely consistent with its structure. Chelation in acid or neutral media is probably facilitated by the fact that M–S–C angles in related thione donor complexes range from 101 to 111° [14, 15] and generate M·····N(H) distances in the region of 3.0 Å [16]. In view of the large pKa value (10.78) [9] deprotonation of *ImtH* (Fig. 1(e), (f)) is probably only achieved at relatively high pH, with subsequent chelation or bridging by the thiolate anion.

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