Inorganica Chimica Acta, 77 (1983) L89–L93

1,3-Thiazolidine-2-thione: Crystal Structure and Coordination Chemistry

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Received April 30, 1983

Introduction

Compounds, such as thiazolidine-2-thione, (*tzdtH*) which possess a heterocyclic thioamide (HN–C(S)–S–) group are versatile ligands. The *tzdtH* molecule is capable of thiol–thione tautomerism (Fig. 1a and b) and may also be de-protonated to form the thiolato anion (Fig. 1e). Consequently, *tzdtH* has a flexible, pH dependent coordination chemistry (Table I) [1–23]. In neutral and in acid media the imido nitrogen and the exocyclic sulphur (thione) atoms are the major competitive centres for coordination, with the thioethereal sulphur atom relegated to a minor role. In alkaline media it is the S–C–N rather than S–C–S component of the thiolato anion which is involved in monodentate bridging to a variety of metals (Table I).

The molecule has been reported to exist as a H-bonded thioamide complex in the solid [25]. This is supported by the presence of a broad and intense ν(NH) band at 3150 cm^{-1} in the solid state infrared spectrum which is shifted from its usual position in solution of around 3400 cm^{-1} [26]. In this paper we present an X-ray analysis of *tzdtH* and discuss the results in relation to the coordination chemistry of the molecule.

Experimental

Crystallographic data are summarised in Table II. The intensity data were corrected for Lorentz,

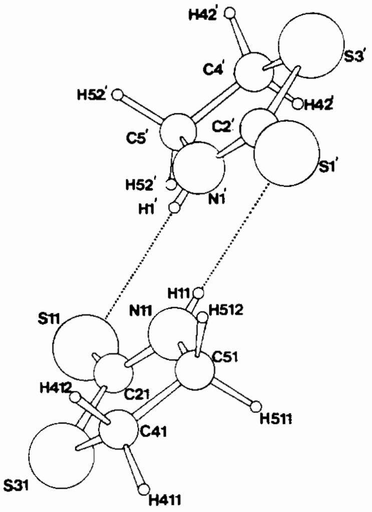

Fig. 2. Perspective diagram of two centro-symmetrically related molecules with atomic labelling and H-bonding.

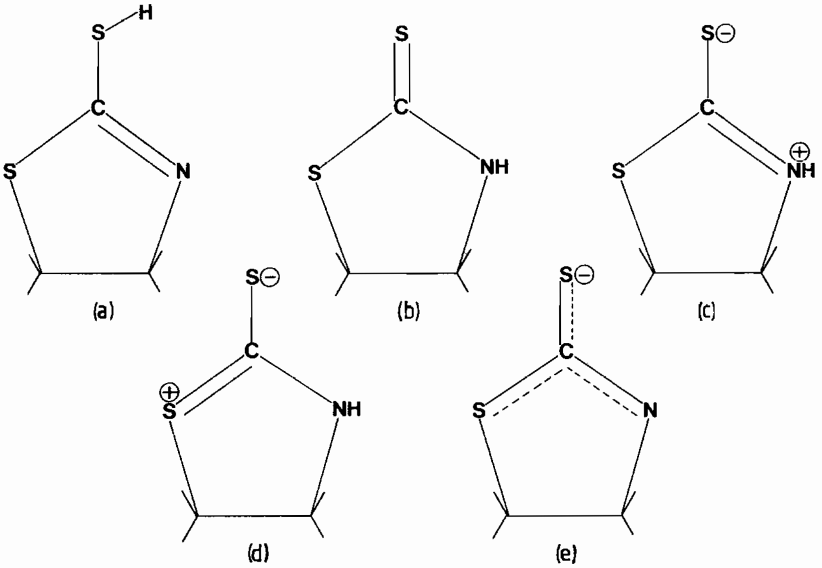

Fig. 1. Major tautomeric and canonical forms of *tzdtH* and *tzdt*.

0020-1693/83/$3.00

TABLE I. Coordination Characteristics of Thiazolidine-2-thione.

Metal	Structural Assignment	N(3)–H	Donor System and Reference		
			–S(1)–	C=S(2)	–N(3)–C(2)–S(2)
Ti(IV)	oct.	*[1]			
Mn(II)	oct.	*[2]			
	oct., bridge				*[3]
Cr(III)	oct.	*[4]			
Cr(0)					
Mo(0)	oct.			*[5]	
W(0)					
Fe(II)	tetr.; oct.	*[1, 6]			
Fe(III)	tetr.; oct.	*[6]			
Co(II)	tetr.; oct.	*[7, 10, 11]			
	tetr.			*[8, 9]	
	tetr., bridge				*[3]
Ni(II)	tetr.; oct.	*[10, 11]			
	tetr.			*[9]	
	oct.		*–[9]–*		
	square				*[3]
Ru(III) Os(III) Rh(III) Ir(III)	oct.	*[15]			
Rh(III)	oct.	*[20]			
Rh(I)	oct.	*[20]		*[20]	
Ir(III)	oct.				*[3]
Pd(II) Pt(II)	square	*			*[3, 20]
		*[16, 20]		*[20]	*[3]
	–	*[11, 16]			
Cu(I)	trigonal			*[13]	*[3]
Cu(II)	–			*[8, 23]	*[22]
	–			*[14]	
Ag(I)	linear, bridge				*[3]
Au(II)	square				*[3]
Zn(II)	tetr.	*[10, 17, 18]			
	tetr.			*[8]	
	tetr., bridge				*[3]
Cd(III)	tetr.	*[10, 17, 18]			
	tetr.			*[8]	
	tetr., bridge				*[3]
Hg(II)	tetr.	*[17, 18]			
	tetr., bridge				*[3]
Te(II) and (IV)	oct.	*–[19]–*			
Bi(III)	sq. pyramid	*[21]			
Sn(IV)	oct.	*[1]			

polarisation and absorption effects. The coordinates of all non-H atoms were located by direct methods and were refined with anisotropic temperature factors by full-matrix least-squares analysis. Atomic coordinates for the imido (NH) H-atoms were obtained by difference Fourier methods and those of the methylenic H-atoms were located in ideal positions by the program (C–H = 1.08 Å); these H-atom coordinates were included in the calculations without refinement. Common isotropic temperature factors were applied to the H-atoms and refined to final U values of 0.075(18) Å^2 (imido H-atom) and 0.096(14) Å^2 (methylenic H-atoms). Final positional parameters are in Table III; bond lengths and angles are in Table V. Scattering factors for all atoms were calculated from an analytical approximation [37]. All calculations were performed on the NUMAC IBM 370/168 computer at the University of Newcastle upon Tyne

TABLE II. Crystallographic Data.

Compound	$C_3H_5N_1S_2$
M	119.1
Space group	$P2_1/n$
a (Å)	13.500(1)
b (Å)	5.591(3)
c (Å)	13.823(1)
β (deg)	95.11(4)
Z	8
U (Å^3)	1039.4
D_c (g cm^{-3})	1.52
F(000)	496
μ(CuKα)	77.42 cm^{-1}
Diffractometer	Enraf-Nonius CAD-4
Scanning mode	$\theta/2\theta$
max. 2θ (deg)	58.0
Total data	1777
$F_0 \geqslant 3.0\sigma(F_0)$	1084
R	0.0862
R_w	0.0799
w	$1.0/[(\sigma^2)F_0 + 0.018357(F_0)^2]$

TABLE III. Non H-atoms Final Fractional Coordinates ($\times 10^4$) with E.s.d.'s in Parentheses and B_{eq} Values [36].

	x	y	z	B_{eq}(Å^2)
S(21)	4284(1)	7634(9)	3844(2)	4.64(9)
S(11)	2314(1)	9973(4)	3413(1)	4.56(8)
C(21)	3455(5)	9731(12)	4075(5)	3.3(2)
C(41)	2731(5)	12950(15)	4904(5)	4.5(3)
C(51)	1996(6)	12714(4)	4009(6)	4.7(3)
N(31)	3570(4)	11398(12)	4748(4)	4.1(4)
S(22)	1131(2)	7539(4)	5692(1)	5.22(9)
S(12)	1542(1)	9589(4)	7674(1)	4.70(8)
C(22)	907(5)	9586(12)	6535(5)	3.6(3)
C(42)	936(6)	12327(15)	8025(6)	4.8(4)
C(52)	95(6)	12806(15)	7276(5)	5.1(9)
N(32)	46(5)	11314(12)	11314(12)	4.2(2)

using SHELX [24] and related programs. The infrared spectrum of *tzdtH* was obtained as a CsI pressed disc in the range 4000–200 cm^{-1} on a Perkin-Elmer 577 grating spectrophotometer.

TABLE IV. Equations of Least Squares Planes Referred to Orthogonal Axes with Distances (Å) of Relevant Atoms from the Planes in Square Brackets.

Plane A

S(11), C(21), S(21), N(31).

$0.4550X + 0.6140Y - 0.6449Z - 1.6221 = 0$

[S(11) 0.0015(17); C(21) –0.0055(68); S(21) 0.0019(23); N(31) 0.0021(60); C(41) –0.1277(75); C(57) 0.1846(81)]

Plane B

S(12), C(22), S(22), N(32).

$0.7241X + 0.6026Y - 0.3355Z - 0.5106 = 0$

[S(12) 0.0013(17); C(22) 0.0047(68); S(22) –0.0016(24); N(32) –0.0018(66); C(42) –0.1123(81); C(52) 0.1355(82)]

TABLE V. Bond Lengths (Å) and Angles (°) with Estimated Standard Deviations in Parentheses. Symmetry code: None x, y, z; (i) 1 – x, 2 – y, 1 – z; (ii) –x, 2 – y, 1 – z.

(a) Non H-atom values

Bond (X = 1 or 2)	Molecule 1	Molecule 2
C(2X)–S(2X)	1.671(7)	1.680(7)
C(2X)–S(1X)	1.726(6)	1.724(6)
S(1X)–C(5X)	1.810(8)	1.823(9)
C(5X)–C(4X)	1.520(10)	1.490(11)
C(4X)–N(3X)	1.459(10)	1.464(10)
N(3X)–C(2X)	1.316(9)	1.314(9)
Angle		
S(2X)–C(2X)–S(1X)	122.3(4)	121.9(4)
C(2X)–S(1X)–C(5X)	93.6(3)	92.6(3)
S(1X)–C(5X)–C(4X)	106.2(5)	107.4(6)
C(5X)–C(4X)–N(3X)	106.8(6)	107.5(7)
C(4X)–N(3X)–C(2X)	118.7(5)	118.2(6)
N(3X)–C(2X)–S(1X)	111.3(5)	112.1(5)
N(3X)–C(2X)–S(2X)	126.4(5)	126.0(5)

(b) H-atom values

N(3A)–H(3A)	0.766	N(3B) H(3B)	0.783
		(X = 1)	(X = 2)
C(4X)–N(3X)–H(3X)		121.4(7)	126.0(7)
C(2X)–N(3X)–H(3X)		119.9(7)	113.0(7)

(c) H-bonding values

H(31)······S(21^{i})	2.624	H(32)······S(22^{ii})	2.661
H(31)······S(21^{i})	3.387	N(32)······S(22^{ii})	3.392

Results and Discussion

The asymmetric unit contains two crystallographically independent and essentially non-planar (Table IV) *tzdtH* molecules whose geometries do not differ significantly (Table V). The non-planarity of the molecule is due to the presence of methylenic carbon atoms. Pairs of centro-symmetrically related molecules are H-bonded by means of N–H···S contacts whose overall distances are 3.387 and 3.392 Å (Fig. 2). The corresponding H(3)·····S(2) distances (2.624 and 2.661 Å) are slightly shorter than the sum of the van der Waals radii (2.85 Å) [27]. Similar H-bonding schemes have been reported for other heterocyclic thione molecules [28, 29].

The C(2)–S(2) distances and the presence of the labile proton at the N(3) position confirm the existence of the thione tautomer (Fig. 2b) in both independent molecules. The solid state infrared spectrum of *tzdtH* also shows four 'thioamide' bands at 1515, 1300, 1050 and 600, 650 cm^{-1} which are typical of many heterocyclic thiones [30].

Angles within *tzdtH* reflect the differing hybridisation states of the atoms. Those at C(4) and C(5) are close to the tetrahedral value while those at C(2) and N(3) are essentially trigonal. The angle at S(1) is typical of thiazoles in that such angles are invariably slightly greater than 90° [28, 29].

In spite of the fact that *tzdtH* is a formally saturated molecule the 'thioamide' portion, [–S(1)–C(2)–[S(2)]–N(3)–], shows extensive π-character. The exocyclic C(2)–S(2) bond and the endocyclic C(2)–S(1) bonds have respectively 56% and 37% SCF-π-character [31], while the C(2)–N(3) bonds have about 50% π-character [32]. In direct contrast to this the bond lengths within the [–S(1)–C(5)–C(4)–N(3)–] portion of the molecule are essentially σ in character and are consistent with those of a saturated, thiazolidine, molecule [33].

The bond lengths in *tzdtH* may be rationalised by means of a combination of the canonical forms (b)–(d) (Fig. 1).

There is evidence (Table 1) that *tzdtH* uses all of its potential donor sites, to some extent, in coordinating to metals. The principle donor in neutral media appears to be the imido, (N(3)–H(3)) group. This is rather surprising in view of the trigonal nature of the N(3) atom and the fact that it is involved in π-bonding within the thioamide section of the molecule. Consequently in order for the imido group to coordinate a change in the hybridisation state of the N(3) atom would normally be necessary as well as delocalisation of two p_z-electrons. An alternative proposal for the attachment of the N(3) atom to Pt(II), Pd(II), Rh(I) and Rh(III), in acid media, involves attachment of the labile 'thioamide' proton at the S(2) atom of the molecule in the complexes. This has been established by ^{1}H nuclear magnetic resonance [20].

The thione sulphur, S(2), atom has good coordination potential but involvement of this atom in the coordination of *tzdtH* is somewhat less extensive than that of the imido group (Table I). However, the coordination geometry of S(2)-bonded *tzdtH* has been established by X-ray studies [34, 35]. Apart from the fact that the geometry of *tzdtH* appears to be essentially unchanged upon coordination the X-ray results show that Pd(*tzdtH*)$_4$Cl$_2$, which is described in the literature as containing N-bonded *tzdtH* [16], actually contains S-bonded molecules [35].

The relative lack of coordinating ability of the endocyclic S(1) atom is not unexpected in view of the presence of the more electronegative endocyclic N(3) atom in the molecule. Similarly, it is the [–S(2)–C(2)–N(3)–] portion rather than the [–S(2)–C(2)–N(3)–] portion of the thiolato anion which is involved in bridging metals as a result of interactions in alkaline media [3].

Acknowledgement

We are grateful to S.E.R.C. and to Dr. M. B. Hursthouse of Queen Mary College, University of London, for the provision of X-ray intensity data.

References

1 P. P. Singh, O. P. Agrawala and A. K. Gupta, *Inorg. Chim. Acta, 18,* 19 (1976).
2 C. Preti and G. Tosi, *Aust. J. Chem., 29,* 543 (1976).
3 C. Preti and G. Tosi, *Can. J. Chem., 54,* 1558 (1976).
4 C. Preti and G. Tosi, *Can. J. Chem., 52,* 2845 (1974).
5 D. DeFilippo, F. Devillanova, C. Preti, E. F. Trogu and P. Viglino, *Inorg. Chim. Acta, 6,* 23 (1972).
6 C. Fregni, C. Preti, G. Tosi and G. Verani, *J. Inorg. Nucl. Chem., 37,* 1837 (1975).
7 P. P. Singh and R. Rivest, *Can. J. Chem., 46,* 2361 (1968).
8 K. Geetharani and D. N. Sathyanarayana, *Ind. J. Chem., 14A,* 170 (1976).
9 D. DeFilippo and C. Preti, *J. Chem. Soc. A,* 1904 (1970).
10 C. Preti and G. Tosi, *J. Chem. Soc. Dalton,* 685 (1976).
11 C. Preti and G. Tosi, *Can. J. Chem., 53,* 177 (1975).
12 P. P. Singh, O. P. Agrawal and M. K. Singh, *Ind. J. Chem., 15A,* 45 (1977).
13 F. A. Devillanova, F. Isaia and G. Verani, *J. Inorg. Nucl. Chem., 43,* 2749 (1981).
14 A. Parentich, L. H. Little and R. H. Ottewill, *J. Inorg. Nucl. Chem., 35,* 2271 (1973).
15 C. Preti and G. Tosi, *Trans. Met. Chem., 3,* 17 (1978).
16 D. DeFilippo, F. Devillanova, E. F. Trogu, G. Verani, C. Preti and P. Viglino, *Can. J. Chem., 51,* 1172 (1973).
17 D. DeFilippo, F. Devillanova, C. Preti and G. Verani, *J. Chem. Soc. A,* 1465 (1971).
18 G. Colombini and C. Preti, *J. Inorg. Nucl. Chem., 37,* 1159 (1975).
19 E. R. Clarke and M. A. Al-Turaihi, *J. Inorg. Nucl. Chem., 38,* 1441 (1976).
20 J. Dehand and J. Jordanov, *Inorg. Chim. Acta, 17,* 37 (1976).
21 C. Preti and G. Tosi, *J. Mol. Struct., 50,* 7 (1978).
22 W. D. Basson and A. L. du Preez, *J. Chem. Soc. Dalton,* 1708 (1974).
23 A. C. Fabretti, M. Ferrari, G. C. Franchini, C. Preti, L. Tossi and G. Tosi, *Trans. Met. Chem., 7* 279 (1982).
24 G. M. Sheldrick, 'Programs for Crystal Structure Analysis', University of Cambridge, England (1976).
25 M. St. C. Flett, *J. Chem. Soc.,* 347 (1953).
26 L. H. Little and R. H. Ottewill, *Can. J. Chem., 40,* 2110 (1962).
27 L. Pauling, 'The Nature of the Chemical Bond', 3rd Cornell University Press, Ithaca, N.Y. (1960).
28 G. R. Form, E. S. Raper and T. C. Downie, *Acta Cryst., B32,* 345 (1976).
29 J. P. Chesick and J. Donohue, *Acta Cryst., B27,* 1441 (1971).
30 B. Singh and K. P. Thakur, *J. Inorg. Nucl. Chem., 36,* 1735 (1974).

31 N. Trinajstic, *Tetrahedron Letts.*, 1529 (1968).
32 P. J. Wheatley, *Acta Cryst.*, *8*, 224 (1955).
33 R. F. Bryan, P. Hartley, S. Peckler, E. Fujita, V. Nagao and K. Seno, *Acta Cryst.*, *B36*, 1709 (1980).
34 M. Cannas, G. Carta, G. Marongiu and E. F. Trogu, *Acta Cryst.*, *B30*, 2252 (1974).
35 M. Kubiak and T. Glowiak, *Acta Cryst.*, *B38*, 2031 (1982).
36 B. T. M. Willis and A. W. Pryor, 'Thermal Vibrations in Crystallography' University of Cambridge Press, Cambridge (1975).
37 'International Tables for X-ray Crystallography', Vol. 4, The Kynoch Press, Birmingham (1974).