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ORIGINAL PAPER

Reaction of anhydrous zinc chloride with 2,3-thiophenedicarbaldehyde bis(semicarbazone) (2,3BSTCH$_2$) and bis(thiosemicarbazone) (2,3BTSTCH$_2$): Crystal structure of $\{[C_6H_5N_2S]^+[ZnCl_3(C_6H_4N_2S)]^-\}$ complex

[a]Kusaï Alomar, [b]Magali Allain, [a]Pascal Richomme, [a]Gilles Bouet*

[a]*Laboratoire SONAS EA 921, SFR QUASAV 4207, UNAM, Université d'Angers, Faculté de Pharmacie, 16 Bd Daviers, 49045 Angers Cedex 01, France*

[b]*Institut des Sciences et Technologies Moléculaires d'Angers (MOLTECH-Anjou), UMR CNRS 6200, UNAM, Université d'Angers, 2 Bd Lavoisier, 49045 Angers Cedex 01, France*

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The reaction of anhydrous zinc chloride with 2,3-thiophenedicarbaldehyde bis(semicarbazone) or 2,3-bis(thiosemicarbazone) leads to the formation of compound $\{[C_6H_5N_2S]^+[ZnCl_3(C_6H_4N_2S)]^-\}$, where $C_6H_4N_2S$ is thieno[2,3-*d*]pyridazine, via an elimination-cyclisation reaction of the semicarbazone or the thiosemicarbazone moiety. Crystal structures of thieno[2,3-*d*]pyridazine and $\{[C_6H_5N_2S]^+[ZnCl_3(C_6H_4N_2S)]^-\}$ are described.

Keywords: 2,3-thiophenedicarbaldehyde, thiosemicarbazone, semicarbazone, thieno[2,3-*d*]pyridazine, crystal structure, cyclisation

Introduction

Thiosemicarbazone and semicarbazone metal complexes have been extensively studied (Padhyé & Kauffman, 1985; Casas et al., 2000; Lobana et al., 2009). Most papers deal with mono-thiosemicarbazones or semicarbazones. In case of pentagonal heterocycles, like furan or thiophene, these groups are attached to position 2 of the ring. Bis(thiosemicarbazones) or bis(semicarbazones) have not been so extensively described and, in these cases, 2,5-disubstitued compounds are the most studied. As far as it is known, very few reports on complexes with these compounds have been published. Many of them are also relative to their potent biological properties like cytotoxicity (Hall et al., 2000; Beraldo & Gambino, 2004), antifungal (Rodríguez-Argüelles & Cao, 2010) or bactericidal activity.

2-Thiophenecarbaldehyde thiosemicarbazone can form complexes with iron(II) carbonyl (Hong et al., 2004) and a few square pyramidal zinc(II) complexes have also been observed with bis(thiosemicarbazones) as ligands (Rodríguez-Argüelles et al., 1995; Castiñeiras et al., 1999). Various vicinal bis(thiosemicarbazones) can coordinate zinc(II) leading to a binuclear pentacoordinated complex (Anselmo et al., 2012).

Zinc(II) chloride with pyridine and tetramethylstreptamine (Jones et al., 2003), 3,5-dimethylpyrazole derivatives (Jeong et al., 2003) or quinoline (Wang et al., 2001) gives trichlorozincate complexes. A similar behaviour has been observed with quinoline; when the reaction takes place in water, a typical tetrahedral [ZnL$_2$Cl$_2$] complex is obtained but when anhydrous zinc acetate is used (in the presence of MnCl$_2$), a species with quinolinium trichloro(quinoline) zinc(II) occurs (Cui et al., 1998; Wang et al., 2001). On the other hand, 2,3BSTCH$_2$ or 2,3BTSTCH$_2$ in ethanol refluxed for 6 h in acidic medium (H$_2$SO$_4$) pro-

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*Corresponding author, e-mail: gilles.bouet@univ-angers.fr

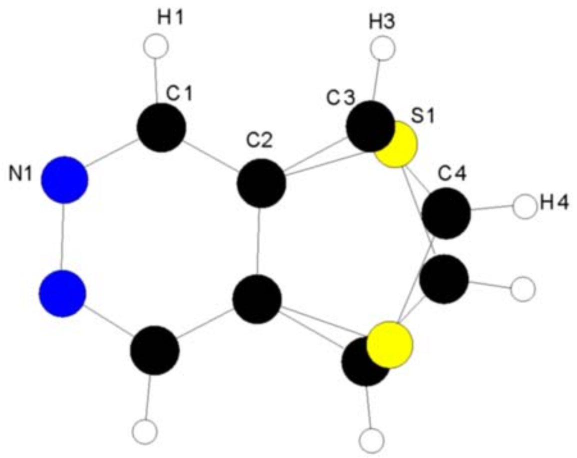

Fig. 1. Structure of thieno[2,3-*d*]pyridazine with atom-numbering.

duced thieno[2,3-*d*]pyridazine as shown in Fig. 1. This molecule was first prepared by Robba et al. (1964) using 2,3-thiophenedicarbaldehyde and hydrazine.

Coordination properties of the ligands, 2,3-thiophenedicarbaldehyde bis(semicarbazone) (2,3BST CH_2) and 2,3-thiophenedicarbaldehyde bis(thiosemicarbazone) (2,3BTSTCH$_2$), towards various transition metals have been previously described (Alomar et al., 2012). On the other hand, 3-thiophenecarbaldehyde thiosemicarbazone (3TTSCH) is able to complex hydrated anhydrous zinc(II) chloride giving [ZnCl$_2$(3TTSCH)$_2$] species with a typical tetrahedral geometry (Alomar et al., 2010) as usually observed with these compounds (Lobana et al., 2009; Dayal et al., 2011; Anselmo et al., 2012). In this paper, the reaction of anhydrous zinc chloride with 2,3BSTCH$_2$ or 2,3BTSTCH$_2$ affording a new complex species, $\{[C_6H_5N_2S]^+[ZnCl_3(C_6H_4N_2S)]^-\}$, where $C_6H_4N_2S$ is thieno[2,3-*d*]pyridazine (Fig. 1), is presented. The heating of 2,3BSTCH$_2$ or 2,3BTSTCH$_2$ in an acidic medium affords thieno[2,3-*d*]pyridazine.

Experimental

Chemicals and methods

All reactants and solvents were of analytical grade. Thiosemicarbazide, semicarbazide hydrochloride, and 3-thiophenecarbaldehyde were purchased from Alfa Aesar (France), and 2,3-thiophenedicarbaldehyde from Sigma–Aldrich Chemie (France). Anhydrous zinc chloride (Prolabo, VWR International) was used as received.

DSC thermograms were recorded in the range of 25–400 ℃ and the heating rate of 10 ℃ min^{-1} on a Mettler DSC 822e unit using the Mettler Toledo STAR^e SW 8.10 System software (Mettler-Toledo, France). All measurements were made in 40 mm^3 sealed Al crucibles. IR spectra (KBr disc technique) were recorded on a Bruker FTIR Vector 22 spectrometer (Bruker Optics, France) in the range of

Table 1. Crystal data and refinement details for thieno[2,3-*d*]pyridazine and zinc(II) complex

Parameter	Value^a	
	Thieno[2,3-*d*]pyridazine	$\{[C_6H_5N_2S]^+[ZnCl_3(C_6H_4N_2S)]^-\}$
Empirical formula	$C_6H_4N_2S$	$C_{12}H_{19}Cl_3N_4S_2Zn$
Formula mass	136.17	445.07
Wavelength (Å)	0.71073	0.71073
Crystal system	Tetragonal	Triclinic
Space group	$P4_32_12$	P1
a (Å)	5.5831(6)	6.8890(6)
b (Å)	5.5831(3)	7.5484(8)
c (Å)	19.510(3)	7.9999(8)
α (°)	90	84.612(6)
β (°)	90	80.567(8)
γ (°)	90	82.147(9)
Volume, V (Å^3)	608.15(12)	405.44(7)
Formula per unit cell, Z	4	1
Density, D_{calc} (g cm^{-3})	1.487	1.823
Crystal size (mm)	0.39 × 0.28 × 0.11	0.37 × 0.37 × 0.10
Absorption coefficient, μ (mm^{-1})	0.423	2.264
θ range for data collection (°)	4.81 to 30.02	3.82 to 30.08
Index ranges	$-7 \leq h \leq 7$	$-9 \leq h \leq 9$
	$-7 \leq k \leq 5$	$-10\ h \leq k \leq 10$
	$-27 \leq l \leq 27$	$-11 \leq l \leq 11$
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0308$, $wR_2 = 0.0628$	$R_1 = 0.0293$, $wR_2 = 0.0738$

a) Standard deviations in parentheses.

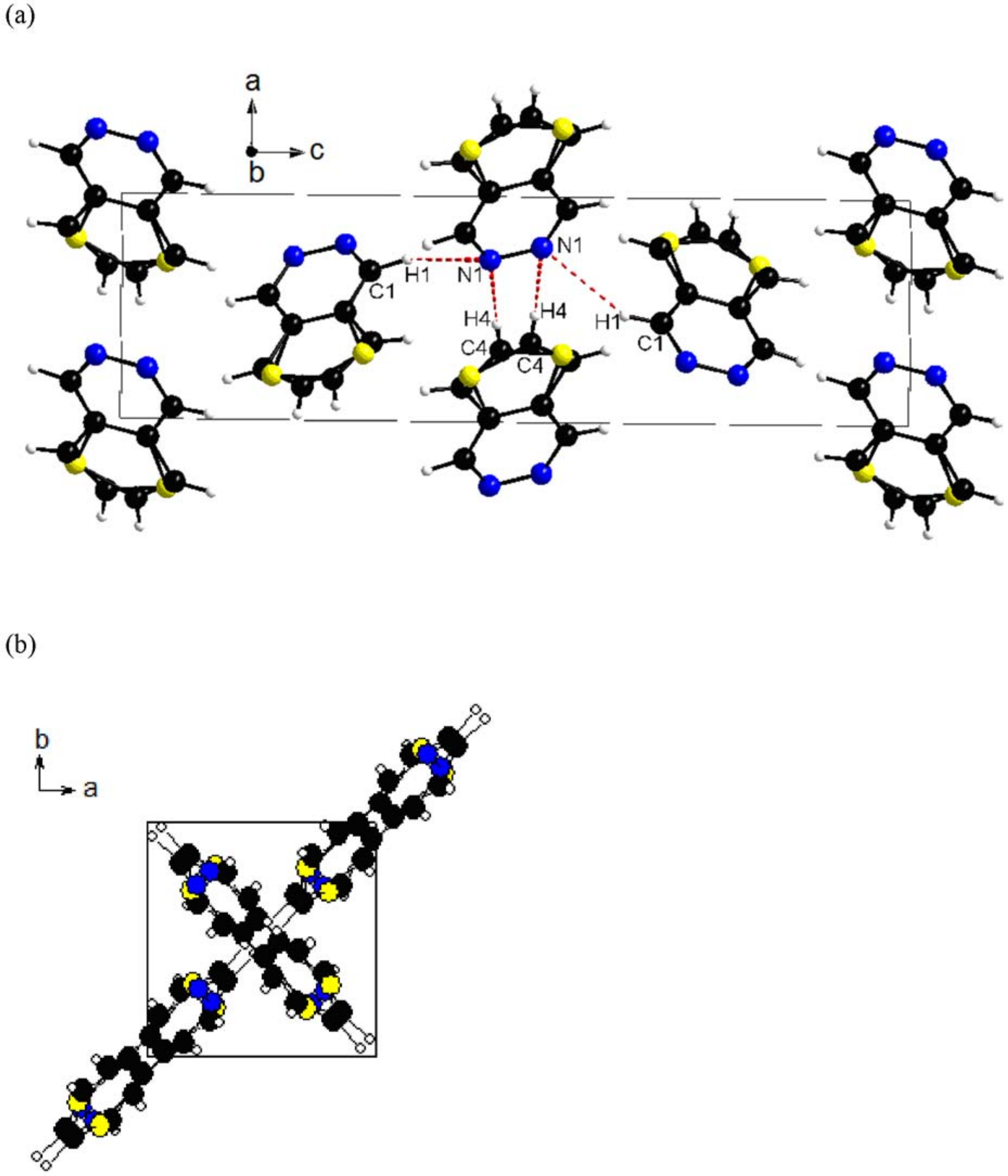

Fig. 2. Hydrogen bonding (a) and planes (b) in a thieno[2,3-*d*]pyridazine crystal; black circle – carbon; blue circle – nitrogen; yellow circle – sulfur; white circle – hydrogen.

400–4000 cm^{-1}. ^{1}H NMR (270 MHz) spectra were recorded on a Jeol GSX WB spectrometer (Jeol, France) in DMSO-d_6 using TMS as the internal reference.

X-ray single-crystal diffraction data were collected at 293 K on a Bruker-Nonius Kappa CCD diffractometer (Bruker, The Netherlands) equipped with a graphite monochromator using Mo K_α radiation (λ = 0.71073 Å) (MOLTECH-Anjou, France). The structures were solved by direct methods and refined on F^2 by the full-matrix least-squares method with anisotropic approximation for all non-hydrogen atoms using the SHELX97 package (Sheldrick, 1997). The H atoms were included in the calculation without refinement. Crystals of $\{[C_6H_5N_2S]^+[ZnCl_3(C_6H_4N_2S)^-]\}$ are triclinic while those of thieno[2,3-*d*]pyridazine are tetragonal with space groups P1 and $P4_32_12$, respectively. The crystal and instrumental parameters used in the unit-cell determination and data collection are summarised in Table 1.

Preparation and reactions of 2,3BSTCH$_2$ and 2,3BTSTCH$_2$ ligands

The ligands were prepared by heating stoichiometric amounts of thiosemicarbazide or semicarbazidium chloride with 2,3-thiophenedicarbaldehyde in EtOH under reflux as previously described (Alomar et al., 2012). The ligands were recrystallised from an EtOH/H$_2$O ($\varphi_\mathrm{r} = 3 : 1$) mixture.

Reaction of ligands with anhydrous zinc chloride was performed as follows: the mixture of equimolar amounts of ligand and ZnCl$_2$ in EtOH was heated under reflux for 3 h and then cooled to ambient temperature. The precipitated complex was filtered and recrystallised from EtOH to yield 66 % of the product.

For acidic medium cyclisation, 2,3BSTCH$_2$ or 2,3BTSTCH$_2$ were dissolved in EtOH with three drops of concentrated sulfuric acid and heated under reflux for 6 h. The solvent was evaporated under reduced pressure, thieno[2,3-*d*]pyridazine was filtered and recrystallised from EtOH to yield 71 % or 78 % of the product, respectively. Spectral data and melting points were found to be in good agreement with those previously described (Robba et al., 1964).

Results and discussion

Crystal structure of thieno[2,3-d]pyridazine

Suitable thieno[2,3-*d*]pyridazine single crystals were obtained by recrystallisation from ethanol. The main crystallographic data parameters are given in Table 1. The structure (Fig. 1) showed two possible configurations for the heterocycle since the thiophene ring is disordered with the occupancy rate of 50 % of each position. In the system, there is half a molecule, while the second part is defined by a symmetry transformation (Table 2). The bond lengths are an intermediate between single and double bonds and consequently, the whole molecule is aromatic.

Cohesion in the lattice was obtained via hydrogen bonds: though they are not very strong, they can stabilise the crystal as already observed for similar compounds (Alshahateet et al., 2004). These hydrogen bonds (Fig. 2a) occur first with C1—H1· · ·N1 with dH1· · ·N1 = 2.64 Å with a 147.11° bond angle and second through C4—H4· · ·N1 with dH1· · ·N1 = 2.31 Å and the bond angle of 177.97°. Each molecule is planar and they are located in orthogonal planes in the lattice as shown in Fig. 2b.

Table 2. Selected bond lengths and bond angles for thieno[2,3-*d*]pyridazine

Bond	Bond length^a/Å	Bond	Bond angle^a/°
C1—N1	1.3142(17)	N1—C1—C2	123.13(11)
C1—C2	1.3886(19)	C1—C2—C2^i	117.14(7)
C1—H1	0.987(14)	C2—S1—C4	94.60(16)
C2—C2^i	1.390(2)		
C2—C3	1.502(10)		
C2—S1	1.692(2)		
C3—C4	1.384(10)		
C3—H3	0.94(3)		
C4—S1^i	1.718(4)		
C4—H4	0.96(4)		
N1—N1^i	1.354(2)		
S1—C4^i	1.718(4)		

a) Standard deviations in parentheses. Symmetry transformations to generate equivalent atoms: (*i*) y, x, $-z + 1$.

Crystal structure of trichlorozincate(II) complex

The reaction of equimolar amounts of 2,3BSTCH$_2$ or 2,3BTSTCH$_2$ with anhydrous zinc chloride in ethanol afforded the same complex molecule: $\{[C_6H_5N_2S]^+[ZnCl_3(C_6H_4N_2S)]^-\}$, where C$_6H_4N_2$S is thieno[2,3-*d*]pyridazine.

The main crystallographic data parameters are given in Table 1. The structure of this complex is formed by two ions. Cation $[C_6H_5N_2S]^+$ is a protonated thieno[2,3-*d*]pyridazine. The anion is a coordination compound with one thieno[2,3-*d*]pyridazine molecule acting as a neutral ligand and $ZnCl_3^-$ as an inorganic moiety. A comparable behaviour was observed in case of the 6-methyl-2-pyridine carboxylic acid (Pons et al., 2006). The ORTEP and molecule views of the zinc(II) complex with atom-numbering are shown in Fig. 3.

The crystal (triclinic system, space group P1) of this species contains one molecule per unit cell. In the $[C_6H_5N_2S]^+$ cation, proton H4 is linked to the N4 nitrogen atom. The bond lengths and bond angles (Table 3) are typical of a fully delocalised aromatic molecule. For the $[ZnCl_3(C_6H_4N_2S)]^-$ anion, a slightly distorted tetrahedral geometry around the Zn(II) ion was observed with Zn—Cl bond lengths in the range of 2.240–2.252 Å. Due to the repulsion of chlorides negative charges, the bond angles Cl1—Zn1—Cl2 and Cl2—Zn1—Cl3 are 113.07(5)° and 114.81(5)°, respectively. These bond lengths and bond angles have already been observed in similar complexes (Wang et al., 2001; Kefi et al., 2005).

Neutral thieno[2,3-*d*]pyridazine is coordinated to the zinc(II) ion through the N1 atom, by a shorter bond length (2.045(2) Å) than those of the Zn—Cl bonds in this compound as it has already been described for similar bonds in quinolinium complexes (Wang et al., 2001) or for 2-aminomethylpyridinium (Kefi et al., 2005). In both ions, organic moieties of this complex are planar (deviation is less than 0.01 Å).

In the crystal, the molecules lie in parallel planes with the chloride ions located outside of these planes (Fig. 4a). In a plane, two hydrogen bonds were ob-

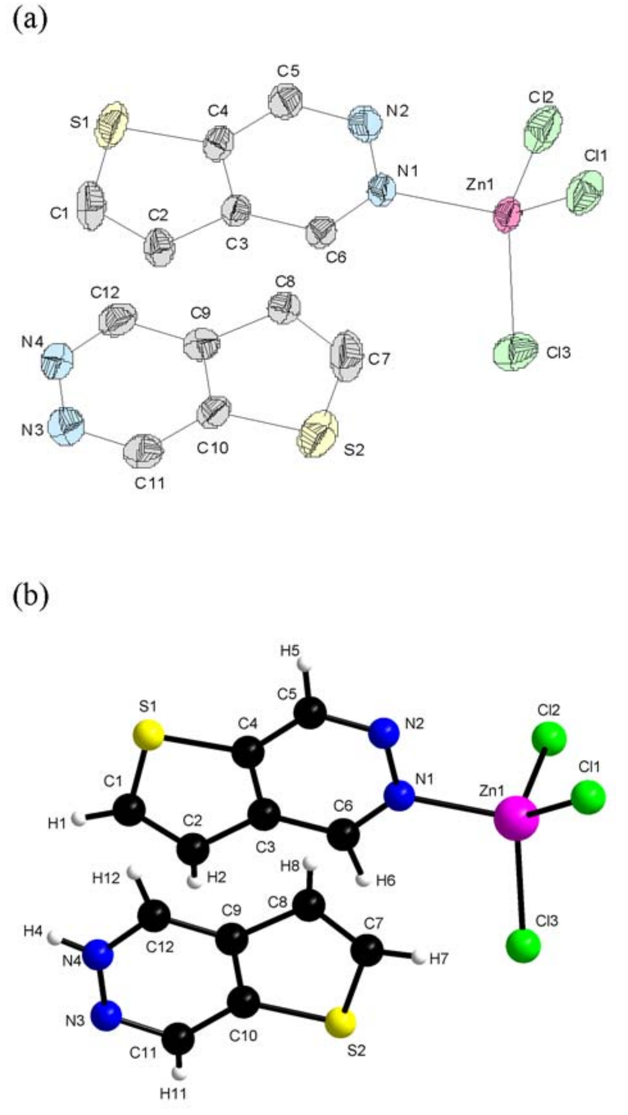

Fig. 3. ORTEP (displacement ellipsoids at 50 % probability level) (a) and molecule (b) views with atom-numbering of the zinc(II) complex.

served between C2—H2 · · ·N2 (2.89 Å, 133.66°) and C8—H8 · · ·N3 (2.70 Å, 138.26°). Each of these bonds connects identical moieties: the first for the anion and the second for the cation (Fig. 4b). In addition, π–π interactions between the aromatic cycles in two different planes occur as already observed in similar structures (Alshahateet et al., 2004; Mishra et al., 2010).

Spectroscopic and thermal analyses

IR spectrum of the complex exhibited bands at 3182 cm^{-1} and 426 cm^{-1} corresponding to the ν(N—H) and ν(Zn—N) vibrations, respectively (Ferraro, 1971). The bands at 1548 cm^{-1}, 1447 cm^{-1}, 1128 cm^{-1} and 983 cm^{-1} are due to the pyridazine vibrations (Vázquez et al., 1998). In addition, the thiophene ring-breathing band was observed at 786 cm^{-1}.

Table 3. Selected bond lengths and bond angles for $\{[C_6H_5N_2S]^+[ZnCl_3(C_6H_4N_2S)]^-\}$

Bond	Bond length^a/Å	Bond	Bond angle^a/°
C5—N2	1.315(4)	N2—C5—C4	122.2(3)
C6—N1	1.318(4)	N1—C6—C3	121.5(3)
C11—N3	1.305(5)	N3—C11—C10	122.2(4)
C12—N4	1.320(5)	N4—C12—C9	118.2(3)
N1—N2	1.362(4)	C6—N1—N2	122.1(3)
N1—Zn1	2.045(2)	C6—N1—Zn1	123.5(2)
N3—N4	1.325(5)	N2—N1—Zn1	114.2(2)
Cl1—Zn1	2.2460(9)	C5—N2—N1	118.4(3)
Cl2—Zn1	2.2524(10)	C11—N3—N4	116.5(3)
Cl3—Zn1	2.2400(10)	N3—N4—C12	127.1(3)
C1—S1	1.700(5)	N1—Zn1—Cl3	105.23(9)
C4—S1	1.721(3)	N1—Zn1—Cl1	113.45(9)
C7—S2	1.683(5)	N1—Zn1—Cl2	102.57(9)
C10—S2	1.699(3)	Cl1—Zn1—Cl3	107.54(5)
–	–	Cl2—Zn1—Cl3	114.81(5)
–	–	Cl2—Zn1—Cl1	113.07(5)

a) Standard deviations in parentheses.

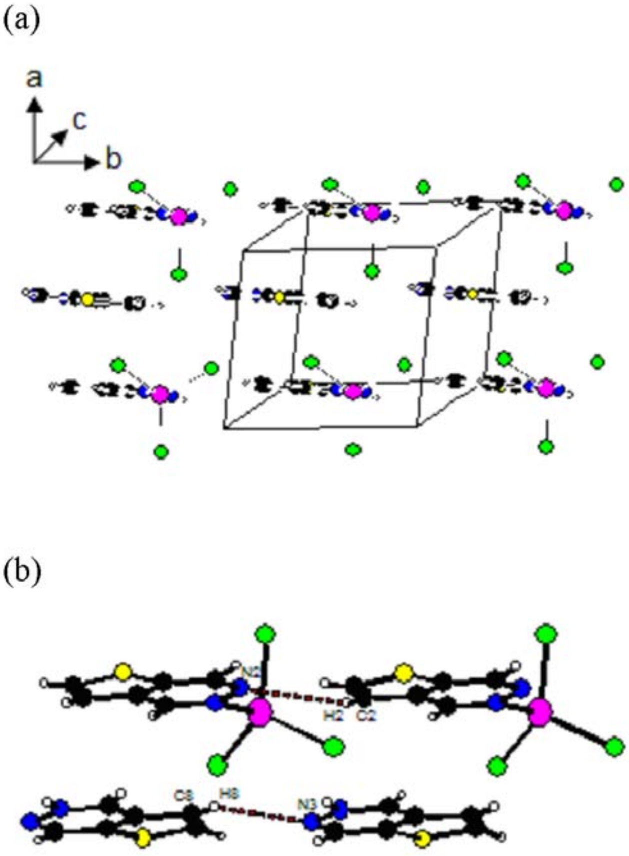

Fig. 4. Molecules in unit cell (a) and hydrogen bonds (b) in $\{[C_6H_5N_2S]^+[ZnCl_3(C_6H_4N_2S)]^-\}$; black circle – carbon; blue circle – nitrogen; yellow circle – sulfur; white circle – hydrogen; pink circle – zinc; green circle – chlorine.

The thieno[2,3-*d*]pyridazine was first obtained by a reaction of equimolar amounts of hydrazine and

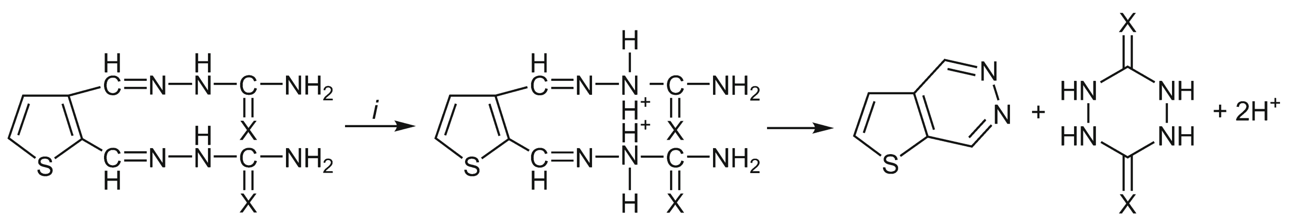

Fig. 5. Reaction pathway for thieno[2,3-*d*]pyridazine and by-product formation. Reaction conditions: *i*) acidic medium; X = O or S.

2,3-thiophenedicarbaldehyde in refluxing methanol (Robba et al., 1964). In the ^{1}H NMR spectrum in DMSO-d_6, four peaks were recorded at δ: 7.86 (1H, H8), 8.50 (1H, H7), 9.84 (1H, H12) (Rozin et al., 2015) and 10.06 (1H, H11) (for proton numbering see Fig. 3). These values are comparable with those obtained in $CDCl_3$ (Kessler & Wegner, 2012). The signal of the H4 proton is not present because there is an easy and fast exchange with solvent deuterium atoms.

The thermogram did not show any endotherms relative to the melting of the complex. On the opposite, a feeble exotherm at 244 °C is followed by a massive exotherm at 330 °C. Shapes of these two peaks are representative of a crystallisation phenomenon rather than the decomposition reaction.

Cyclisation and $ZnCl_2$ role

The reaction pathway for bis(semicarbazone) or bis(thiosemicarbazone) protonation in an acidic medium resulting in the formation of thieno[2,3-*d*]pyridazine as the main product and *p*-urazine or dithio-*p*-urazine as the by-product (Lutz, 1964) is shownn in Fig. 5.

When using hydrated zinc chloride, complexation occurs via a ligand substitution reaction involving water molecules providing a typical tetrahedral complex (Alomar et al., 2010). The molecule of the thiophenic ligand can only coordinate one zinc chloride as observed with hydrated zinc chloride and $2{,}3BTSTCH_2$ (Alomar, 2012).

The reaction of anhydrous zinc chloride and bis(semicarbazone) or bis(thiosemicarbazone) was accomplished using the 1 : 1 ligand to metal ratio. One ligand molecule ($2{,}3BSTCH_2$ or $2{,}3BTSTCH_2$) can only coordinate one Zn^{2+} ion and the bonding of a Zn(II) ion to $2{,}3BSTCH_2$ or $2{,}3BTSTCH_2$ induces electron delocalisation along with the molecule obtained as an intermediate product. It has to be emphasised that Zn^{2+} ions act as a Lewis acid in order to transform the semicarbazone or thiosemicarbazone into thieno[2,3-*d*]pyridazine. The mechanism is comparable with the pathway proposed above in an acidic medium. However, as *p*-urazine or dithio-*p*-urazine are able to complex Zn(II) ions (Campi et al., 1963; Singh & Mishra, 1981) as well as thieno[2,3-*d*]pyridazine, there is a competition between these two substances resulting in the trichlorozincate(II) complex.

Conclusions

2,3-Thiophenedicarbaldehyde bis(semicarbazone) and 2,3-thiophenedicarbaldehyde bis(thiosemicarbazone) can be transformed into thieno[2,3-*d*]pyridazine in an acidic medium. When reacted with anhydrous zinc chloride, these two molecules produced a new complex species, $\{[C_6H_5N_2S]^+[ZnCl_3(C_6H_4N_2S)]^-\}$, where $C_6H_4N_2S$ is thieno[2,3-*d*]pyridazine. The crystal structures of thieno[2,3-*d*]pyridazine and the $\{[C_6H_5N_2S]^+[ZnCl_3(C_6H_4N_2S)]^-\}$ complex are described.

Supplementary data

Crystallographic data for $\{[C_6H_5N_2S]^+[ZnCl_3(C_6H_4N_2S)]^-\}$ complex and thieno[2,3-*d*]pyridazine reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 922483 and 922484. Copies of the information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1IEZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk) or via http://www.ccdc.cam.ac.uk/data_request/cif.

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