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ZINC HALIDE COMPLEXES OF THIONICOTINAMIDE; CRYSTAL STRUCTURE OF DICHLORIDO BIS(THIONICOTINAMIDE-κ*N*)ZINC(II)

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Zinc halide complexes of thionicotinamide (TNA) having the general formula $[Zn(TNA)_2X_2]$ ($X = Cl^-$, Br^-, I^-) are prepared and characterized by thermal analysis, IR and NMR spectroscopy. The crystal structure of one of them, dichloridobis(thionicotinamide-κ*N*)zinc(II), $[Zn(TNA)_2Cl_2]$ (**1**), is determined using X-ray crystallography. In **1**, the zinc atom is coordinated by two thionicotinamide ligands through nitrogen atoms and two chloride ions in a distorted tetrahedral coordination environment. The molecular structure of the complex is stabilized through intermolecular hydrogen bonding.

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The Zn^{+2} ion is known to have a high affinity towards nitrogen and sulfur donor ligands, as demonstrated by a considerable body of knowledge on Zn(N,S-ligands) complexes [1—10]. Heterocyclic thiones possessing a combination of soft sulfur and hard nitrogen donor atoms are among the ligand systems used to mimic bio-relevant metal-sulfur interactions [11—17]. Thionicotinamide in the form of Thio—NAD(H) or Thio—NADP(H) is involved in the activity of various enzymes such as dehydrogenases [18]. Several structural reports on zinc(II) complexes with thiones are available in the literature, which demonstrate that thiones coordinate with zinc(II) through a sulfur atom in a tetrahedral environment [19—29]. We have previously examined the coordination behavior of thione ligands towards d^{10} metals with the aim of gaining more information about the structural, spectral, and biological properties of the resulting complexes [29—33]. Herein, we report the synthesis and spectral studies of three zinc(II) complexes of thionicotinamide (TNA) and the crystal structure of one of them, $[Zn(TNA)_2Cl_2]$. The title complex $[Zn(TNA)_2Cl_2]$ (**1**) presents a unique example of zinc(II)-thione complexes where zinc is coordinated to the thione ligand through the nitrogen atom instead of the sulfur atom.

Experimental. Chemicals. $ZnCl_2$, $ZnBr_2$, and ZnI_2 were obtained from Merck Chemical Co. Germany. Thionicotinamide (TNA) was obtained from Acros Organics, USA.

Preparation of complexes. The complexes were prepared by adding 2 equivalents (0.28 g) of thionicotinamide in 15 ml methanol to 1 mmol. ZnX_2 (0.14 g, 0.23 g, and 0.32 g for $X = Cl^-$, Br^-, and I^-

respectively) dissolved in 10 ml methanol. Mixing resulted in the yellow color solutions which were stirred for 30 min. The solutions were filtered. and on slow evaporation of the filtrates yellow products were obtained. The crystals of **1** were isolated by adding 10 ml of acetonitrile to 5 ml of the above solution and then it was slowly evaporated. Yield = 40—50 %.

Spectroscopic measurements. The solid state IR spectra of TNA and the zinc(II) complexes were recorded on a Perkin—Elmer Spectrum One IR spectrophotometer using KBr pellets over the range 4000—450 cm^{-1}. The ^{1}H and ^{13}C NMR spectra of the ligand and complexes in DMSO-d_6 were obtained on a Bruker Avance 300 MHz NMR spectrometer operating at frequencies of 300.00 MHz and 75.47 MHz, respectively at 298 K. The spectral conditions were: 32 K data points, 1.822 s acquisition time, 2.00 s pulse delay, and 6.00 μs pulse width. The ^{1}H and ^{13}C chemical shifts were measured relative to TMS.

Structure determination. Single crystal data collection for complex **1** was performed on a Bruker SMART APEX-II CCD diffractometer using graphite monochromated MoK_α radiation (λ = 0.71073 Å) at 296 K [34]. The structure was solved by direct methods using the SHELXS-97 program [35]. The refinement and all further calculations were carried out using SHELX-2014 [36]. PLATON was used for absorption correction and molecular graphics [37]. Crystal data and details of the data collection are summarized in Table 1.

Results and discussion. Spectroscopic studies. The $[Zn(TNA)_2X_2]$ complexes were prepared by the reaction of zinc halides with thionicotinamide in a 1:2 molar ratio. In the IR spectra of complexes, the characteristic bands were observed in three frequency regions: ν(C=S) at 699 cm^{-1}, ν(C—N) at

Table 1

Crystal data and refinement details for compound **1**

Formula	$C_{12}H_{12}N_4S_2ZnCl_2$
Formula weight	412.65
Crystal system	Triclinic
Space group	*P*-1
a, *b*, *c*, Å	8.4653(3), 9.5066(3), 11.7320(4)
α, β, γ, deg.	76.7360(10), 88.734(2), 69.6280(10)
V, Å^3	859.75(5)
Z	2
ρ_{calc}, g/cm^3	1.594
μ(MoK_α), mm^{-1}	1.753
F(000)	416
Crystal size, mm	0.40×0.26×0.24
Temperature, K	296(2)
λMoK_α, Å	0.71073
2θ range, deg.	1.787—27.000
h, *k*, *l* limits	–10:10, –11:12, –14:14
Reflections collected / uniq.	13196 / 3716 [*R*(int) = 0.0215]
Reflections observed [$I > 2\sigma(I)$]	3358
T_{min}, T_{max}	0.506, 0.650
Data / restraints / parameters	3716 / 0 / 190
R_1, wR_2, S [$I > 2\sigma(I)$]	0.0292, 0.0768, 1.087
Largest diff. peak, hole, e/Å^3	0.468, –0.481

$w = [\sigma^2(F_0^2) + (0.0312P)^2 + 0.7344P]^{-1}$ where $P = (F_0^2 + 2F_c^2)/3$.

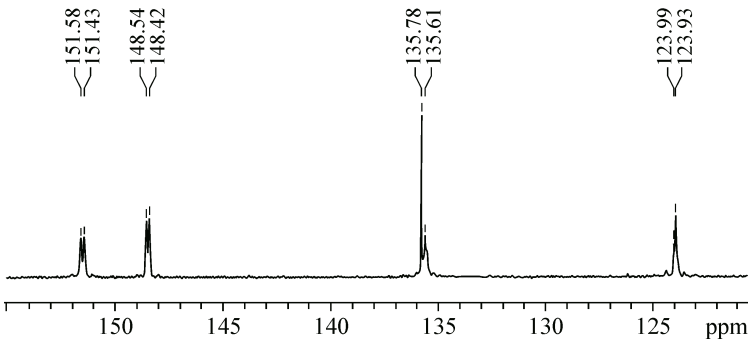

Fig. 1. ^{13}C NMR spectrum of $[Zn(TNA)_2I_2]$ showing two sets of resonances

T a b l e 2

^{13}C *chemical shifts of thionicotinamide and its zinc*(II) *complexes in* DMSO-d_6

Species	C-2	C-3	C-4	C-5	C-6	C-7
Tna	151.59	135.31	134.87	123.06	147.61	197.92
$[Zn(TNA)_2Cl_2]$	151.36	136.16	135.60	123.50	147.75	197.60
$[Zn(TNA)_2Br_2]$	151.50	135.85	135.65	123.80	150.21	197.76
$[Zn(TNA)_2I_2]$*	151.43	135.78	135.61	123.93	148.42	197.63
	151.58			123.99	148.54	

* Two sets of resonances were observed in the ^{13}C NMR spectrum of $[Zn(TNA)_2I_2]$.

1480 cm^{-1}, and ν(N—H) at 3315 cm^{-1} and 3155 cm^{-1}. For free TNA these bands are observed at 698 cm^{-1}, 1468 cm^{-1}, and 3300 cm^{-1} and 3180 cm^{-1} respectively.

In the ^{1}H NMR spectra of the complexes, the signals for N—H and aromatic protons of TNA appeared almost at the same positions as they were observed in the free ligand (NH_2 at 9.77 ppm, 10.12 ppm, and aromatic protons at 7.50—9.05 ppm). Similarly, no significant shifts were observed in the ^{13}C NMR spectrum, except for the C-6 resonance. The ^{13}C chemical shifts are presented in Table 2. A small change in C-6 shows that the ring nitrogen atom can be involved in coordination. One interesting feature was observed in the spectrum of the iodide complex, namely, two sets of resonances were detected in its ^{13}C spectrum as shown in Fig. 1. This observation suggests that the complex undergoes dissociation in solution to give some other species.

X-Ray structure description. The perspective view of complex **1** along with the atomic numbering scheme is given in Fig. 2, and selected bond lengths and bond angles are summarized in Table 3. The title complex consists of independent monomeric molecules in each of which the Zn(II) ion is bound to two nitrogen atoms of TNA and two chlorine atoms adopting a tetrahedral geometry. The N—Zn—N, N—Zn—Cl, and Cl—Zn—Cl angles lie in the range of 103—117°, which are within the experimental error. Thionicotinamide functions as a nitrogen donor ligand and is coordinated in a monodentate terminal mode. The Zn—N (2.043(2) Å) and Zn—Cl (2.2135(7) Å & 2.2333(6) Å) bond lengths are similar to the values in the reported structures [26, 27, 29, 38—40]. The structure is closely related to that of $[Zn(Nicotinamide)_2Cl_2$ [38].

The packing of the complex is stabilized by the intermolecular H-bonding interactions between the sulfur or chlorine atoms and the NH_2 or pyridine ring hydrogen atoms. The C=S moiety is directed away from the coordination sphere and is not involved in the intramolecular H-bonding as it is observed for C=O in $[Zn(Nicotinamide)_2Cl_2$ [38]. The H-bonding parameters are listed in Table 4. A view of the crystal packing in **1** showing hydrogen bonds is given Fig. 3. As expected based on the polarity, the N—H…Cl bond is stronger than the C—H…Cl bond.

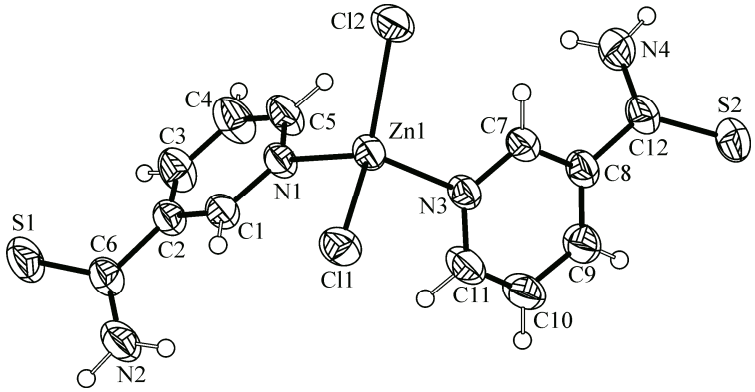

Fig. 2. Molecular structure of **1**; thermal ellipsoids are drawn at a 50 % probability level

T a b l e 3

Selected geometric parameters for **1**

Bond lengths (Å)				Bond angles (deg.)			
Zn1—N1	2.043(2)	C1—N1	1.337(3)	N1—Zn1—N3	103.01(8)	Cl1—Zn1—Cl2	117.13(3)
Zn1—N3	2.041(2)	C6—N2	1.316(4)	N1—Zn1—Cl1	107.14(6)	C1—N1—Zn1	121.64(16)
Zn1—Cl1	2.2333(6)	C6—S1	1.658(3)	N1—Zn1—Cl2	111.46(6)	C5—N1—Zn1	119.67(17)
Zn1—Cl2	2.2135(7)			N3—Zn1—Cl1	108.61(6)	C1—N1—C5	118.6(2)
				N3—Zn1—Cl2	108.54(6)		

T a b l e 4

Hydrogen bonds in complex **1** (Å, deg.)

Donor—H···Acceptor	D—H	H···A	D···A	∠D—H···A
N2—H2A…Cl1	0.8	2.53	3.326(3)	155.3
N2—H2B…S2	0.86	2.62	3.450(2)	162.1
N4—H4A…Cl2	0.86	2.45	3.304(3)	170.1
N4—H4B…S1	0.86	2.58	3.428(3)	167.8
C1—H1…Cl1	0.93	2.95	3.546(2)	123.3
C5—H5…Cl2	0.93	2.73	3.652(3)	173.0
C11—H11…Cl1	0.93	2.80	3.721(3)	172.7

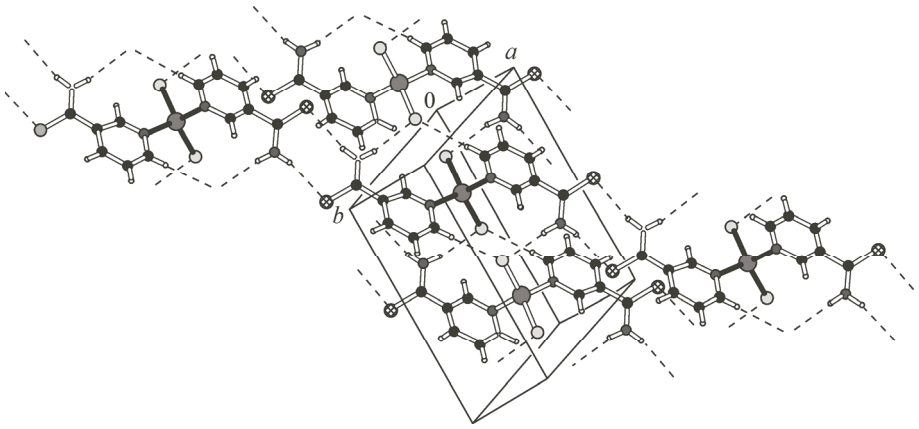

Fig. 3. Crystal packing diagram of **1** showing hydrogen bonding interactions

The present study shows an important finding that thionicotinamide coordinates with zinc(II) through the nitrogen atom unlike other thiones that bind through the sulfur atom [19—29].

Supplementary material. The crystallographic data of **1** (CCDC No. 1452918) can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

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