

## Normal Vibrations & Donor Characteristics of Thiazoline-2-thione: Complexes with Cu(II), Cd(II), Ni(II) & Hg(II)

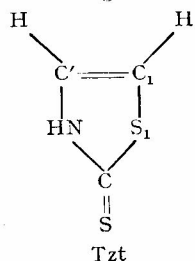
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Received 19 January 1976; accepted 6 March 1976

The complexes of thiazoline-2-thione(Tzt) with Ni(II), Cu(II), Cd(II) and Hg(II) chlorides have been studied. The assignment of infrared bands of the ligand and its metal complexes is made by comparison with related molecules and with the help of normal coordinate treatment of Tzt and N-deuterated Tzt. The ligand is inferred to coordinate through nitrogen in the Cd(II) complex and through the exocyclic thiocarbonyl sulphur in the other three complexes.

A DETAILED IR spectral study of thiazolidine-2-thione (Tzdt) and its metal complexes with various metal chlorides was reported by us earlier<sup>1</sup>. It was found that Tzdt exhibits ambidentate nature, coordinating through nitrogen to Cd(II) and Zn(II), and through the thiocarbonyl sulphur in Co(II), Ni(II) and Hg(II) complexes. A structurally related ligand, but simpler than Tzdt is thiazoline-2-thione (Tzt), whose donor characteristics have not been investigated so far.



It was of interest to study its complexes. The complexes formed by this ligand with Ni(II), Cu(II), Cd(II) and Hg(II) chlorides are reported in this paper. Further, the IR spectra of the ligand and complexes are assigned by comparison with related molecules and also with the aid of normal coordinate treatments of Tzt and N-deuterated Tzt-*d*<sub>1</sub>.

### Materials and Methods

The ligand Tzt was obtained through the courtesy of Prof. M. Chanon and Dr C. Roussel, Laboratoire

associe au CNRS, Marseille, France. The N-deuterated Tzt-*d*<sub>1</sub> was prepared by repeated exchange reaction of Tzt with D<sub>2</sub>O. Other chemicals were of high purity.

*Preparation of the complexes*—The complexes of Cu(II), Cd(II) and Hg(II) chlorides precipitated out when an alcoholic solution of Tzt (0.02M) was added to the corresponding metal chloride solution (0.01M) in ethanol. The precipitate was filtered, washed with ethanol and dried.

The Ni(II) complex was prepared by refluxing a solution of NiCl<sub>2</sub>·6H<sub>2</sub>O (0.01M) in absolute alcohol with Tzt (0.02M) and an excess of ethyl orthoformate for over 8 hr. The precipitated yellow complex was filtered, washed with hot toluene and dried.

*Analysis*—The metals were determined by standard procedures<sup>2</sup> and the C, H and N analyses were performed microanalytically at the Bhabha Atomic Research Centre, Bombay. The analytical data of the complexes are given in Table 1.

*Physical measurements*—The instruments used and the methods adopted have been described earlier<sup>1</sup>.

*Normal coordinate treatment*—We assumed the molecule to be planar with molecular symmetry C<sub>s</sub> and in this model, the 21 fundamental vibrations of Tzt are classified into 15A' + 6A'' modes. The in-plane (A') vibrations are considered for the calculations the out-of-plane (A'') vibrations are assigned empirically by comparison with related molecules.

The secular equations were set up according to the GF matrix method<sup>3</sup>. The internal coordinates

TABLE 1 — ANALYTICAL DATA OF Tzt COMPLEXES

Complex	Colour	Analysis (%)*			
		M	C	H	N
Ni(Tzt) <sub>2</sub> Cl <sub>2</sub>	Yellow	16.28	20.01	1.72	7.88
		(16.15)	(19.80)	(1.65)	(7.70)
Cu(Tzt)Cl <sub>2</sub>	Green	25.11	14.85	1.31	5.46
		(25.27)	(14.32)	(1.19)	(5.50)
Cd(Tzt)Cl <sub>2</sub>	White	37.02	12.21	1.08	4.73
		(37.43)	(11.99)	(0.99)	(4.66)
Hg(Tzt) <sub>2</sub> Cl <sub>2</sub>	White	39.77	14.81	1.23	5.48
		(39.68)	(14.24)	(1.19)	(5.54)

\*Calculated values are given in parentheses.

are shown in Fig. 1 and the internal symmetry coordinates were written down in the same way as for a five-membered ring<sup>4</sup> and are not given here. The structure parameters were taken from the data of related thiazole molecules<sup>5,6</sup>. They are: bond lengths, C-S 1.65, C-S<sub>1</sub>, 1.823, C<sub>1</sub>-S 1.80, C'-N 1.40, C-N 1.50, C-C 1.34, N-H 1.02, C-H 1.08 Å; and bond angles, CNC' 112°, NCS<sub>1</sub>, SCS<sub>1</sub> 109°15', NCC, CCS 115°, HNC 124° and HCN, HCS 122°30'.

We used a Urey-Bradley force field and the force constants were transferred for the HN-C(S)-S-group from our earlier results of Tzt<sup>1</sup> and those for -HC=CH-group from imidazole<sup>7</sup>. An interaction constant,  $f(C=C, C'C_1H)$ , was however found necessary. Some of the force constants were iterated within the small ranges found in related molecules to obtain better frequency fits both for Tzt and Tzt-d<sub>1</sub>. The Urey-Bradley force constants were found to be satisfactorily transferable. The final

force constants are shown in Table 2. The calculated frequencies for Tzt and Tzt-d<sub>1</sub> are listed in Table 3 together with the observed frequencies and assignments from the potential energy distributions (PED).

## Results and Discussion

Most of the bands of Tzt arise from mixed vibrations as in secondary thioamides<sup>8,9</sup> and many ring compounds<sup>7,10</sup>. For the assignment of Tzt (Tables 3 and 4), the comparison with structurally closely related thiazole<sup>10</sup> is extremely satisfactory. For

Stretching		Bending		Repulsion	
KCS	3.65	HNCS	0.27	FNCS	1.10
KCS <sub>1</sub>	2.65	HSCS	0.20	FSCS	0.40
KC <sub>1</sub> S <sub>1</sub>	3.05	HNCS <sub>1</sub>	0.35	FNCS <sub>1</sub>	0.60
KCN	4.65	HCSC	0.32	FCS <sub>1</sub> C	0.55
KC'N	5.35	HCCS	0.30	FCCS <sub>1</sub>	0.44
KCC	4.45	HNCC	0.35	FNCC	0.60
KNH	4.70	HCNC	0.25	FCNC	0.42
KC'H	4.45	HHCN	0.17	FHCN	0.35
KC <sub>1</sub> H	4.25	HHC'C <sub>1</sub>	0.26	FHC'C <sub>1</sub>	0.32
f <sub>CC,C'C<sub>1</sub>H</sub>	0.25	HHC <sub>1</sub> C'	0.22	FHC <sub>1</sub> C'	0.32
(mdyn/rad.)					
		HHC <sub>1</sub> S	0.14	FHC <sub>1</sub> S	0.15
		HHNC	0.29	FHNC	0.50
		HHNC'	0.22	FHNC'	0.40

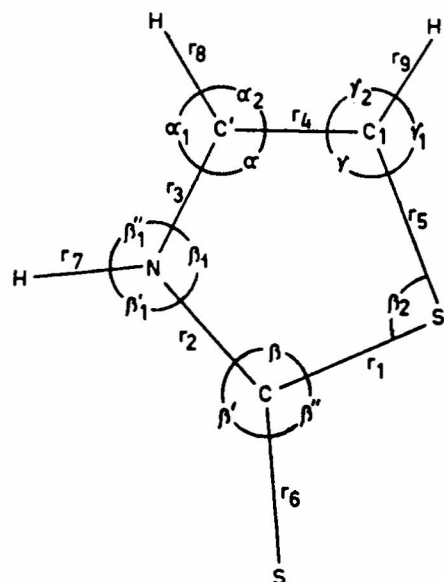


Fig. 1 — Molecular structure and internal coordinates of thiazoline-2-thione (Tzt)

Tzt-d <sub>1</sub>			Tzt			Assignment†‡ (PED %)§
Obs.	Calc.	Δ*(%)	Obs.	Calc.	Δ*(%)	
2250	2253	0.1	3080	3080	0.6	νNH(100)
			3120			
2983	2983	0.0	2980	2983	0.1	ν <sub>a</sub> CH(52), ν <sub>s</sub> CH(47)
2885	2882	0.1	2885	2882	0.1	ν <sub>s</sub> CH(52), ν <sub>a</sub> CH(47)
940	941	0.1	1555	1547	0.5	δNH(45), νC'N(28), νCN(14)
1480	1502	1.5	1465	1456	0.6	δC'H(31), δNH(22), νCC(22)
1385	1390	0.4	1340	1329	0.8	νCN(57), νC=S(15), δNH(12)
1250	1241	0.7	1245	1229	1.3	δC <sub>1</sub> H(39), νCC(35), νC <sub>1</sub> S <sub>1</sub> (11)
1175	1189	1.2	1145	1132	1.0	δC'H(56), νC'N(22)
1100	1107	0.6	1070	1085	1.4	δC <sub>1</sub> H(29), νC=S(17), νC'N(14)
1070	1079	0.8	1050	1053	0.3	δring(23), νCC(18), νCS <sub>1</sub> (18)
850	851	0.1	850	853	0.4	δring(41), νC <sub>1</sub> S <sub>1</sub> (38)
690	664	3.8	690	683	1.0	νCS <sub>1</sub> (46), νC=S(15), δring(17)
642	646	0.6	650	646	0.5	δring(48), νC <sub>1</sub> S <sub>1</sub> (14)
465	467	0.4	465	470	1.1	δring(55), νC=S(30)
312	318	1.9	320	320	0.6	δC=S(75), νCS <sub>1</sub> (13)

\*Δ(%) = (|ν<sub>obs</sub> - ν<sub>calc</sub>| × 100) / ν<sub>obs</sub> where ν denotes frequency.

†ν = stretching, δ = bending, s = symmetric and a = antisymmetric.

‡The assignment given here is for Tzt and approximately corresponds as shown with that for Tzt-d<sub>1</sub>.

§PED less than 10% is omitted.

TABLE 4 — INFRARED FREQUENCIES\* (cm<sup>-1</sup>) OF Tzt AND ITS COMPLEXES AND THEIR ASSIGNMENT

Tzt	Ni(Tzt) <sub>2</sub> Cl <sub>2</sub>	Cu(Tzt)Cl <sub>2</sub>	Hg(Tzt) <sub>2</sub> Cl <sub>2</sub>	Cd(Tzt)Cl <sub>2</sub>	Cd(Tzt-d <sub>1</sub> )Cl <sub>2</sub>	Main assignment†
1555 s	1556 s	1555 s 1510 ms 1498 mw	1567 s	1565 s	931 mw	δNH(D), νCN
1465 s	1462 vs 1445 s	1465 m	1470 s	1460 s	1465 vs	δCH, νCC
1390 w	1388 w	1386 w	1385 w	1382 w	1338 w	Combnd band
1340 vs	1350 sh 1340 s	1358 m 1310 ms	1363 s	1345 ms	1390 ms	νCN
1278 vw	1305 vw	—	1305 vw	1305 vw	1319 mw	Combnd band
1245 vs	1258 m 1235 mw	1266 mw	1275 m	1252 m	1250 w	νCC, δCH
1144 s	1145 m 1130 s	1155 s 1138 sh	1140 s	1132 s	1130 mw	δCH
1070 vs	1070 vs	1098 m 1088 m	1070 vs	1070 vs	1100 sh 1088 vs	δCH, ring str.
1050 vs	1053 vs	1052 s	1050 vs	1060 vs 1050 vs	1062 s 1050 vs	Ring str.
850 vs	860 s	880 m 862 m	870 vs	855 s 862 m	868 s 852 s	δring, νCS
800 vs	790 m	785 m	818 m	695 vs	505 ms	πNH(D)
732 vs	732 vs	745 vs	740 m	740 m	740 sh	πCH
710 vs	717 vs	730 sh	730 s	715 s	732 m	πCH
690 vs	—	—	—	—	699 vs	νCS
650 s	650 w	655 mw	655 vw	655 sh	650 vw	δring, νCS
580 m	582 vw	630 ms 614 ms	585 mw	—	597 vs	πring
491 s	492 ms	517 w 495 m	495 ms	490 ms	490 s	πring
465 s	463 mb	445 m	445 ms	461 ms	458 ms	δring
322 s	340 w	343 s	340 vs	322 s	ni‡	δC=S
305 s	300 w	300 s	—	295 w	ni‡	πring
—	265 wb 230 w	290 sh 275 mw	220 vs	265 mw	ni‡	νM-Cl

\*NH and CH stretching frequencies are not tabulated.

†π=out-of-plane bending; ν, δ same as in Table 3.

‡ni=not investigated.

brevity, we shall now discuss only some of the major assignments of Tzt, which could be useful in the study of its complexes.

**NH modes** — The NH stretching mode of Tzt is easily assigned and it occurs as a doublet at 3080, 3120 cm<sup>-1</sup> in the solid state. The NH in-plane bending band at 1555 cm<sup>-1</sup> is coupled with CN stretching and occurs in the same region as in secondary thioamides, but is about 100 cm<sup>-1</sup> lower than in N-alkyl dithiocarbamates<sup>11</sup>. On deuteration this band vanishes and the ND bending mode is observed near 940 cm<sup>-1</sup>.

**CN stretching** — The CN, C'N stretching vibrations are mixed with other vibrations, mainly NH and CH bending modes. The bands at 1340 and 1555 cm<sup>-1</sup> have major contributions from CN stretching modes. In Tzdt, the bands at 1520, 1302 and 1260 cm<sup>-1</sup> have large contributions from CN stretching mode<sup>1</sup>. The CN stretching mode in secondary thioamides is fairly localized and is found near 1440 cm<sup>-1</sup>.

**CS modes** — The exocyclic C=S stretching vibration is highly delocalized and the bands at 1340, 1070 and 690 cm<sup>-1</sup> have smaller contributions from this mode, and the 465 cm<sup>-1</sup> band arising mainly from ring deformation has 30% C=S stretching. This situation is similar to that in Tzdt. The endocyclic C-S stretching bands near 850, 690 and 650 cm<sup>-1</sup> are comparable with those of simple and

n-alkyl dithiocarbamates<sup>11</sup> which have (asymmetric and symmetric) C-S frequencies near 820 and 620 cm<sup>-1</sup>. A band at 320 cm<sup>-1</sup> may be attributed to the exocyclic C=S bending corresponding to the 290 cm<sup>-1</sup> band of Tzdt.

**Out-of-plane vibrations** — A very strong band at 800 cm<sup>-1</sup> is assigned to the NH out-of-plane bending. This band disappears on deuteration and the ND bending mode in Tzt-d<sub>1</sub> is observed at 548 cm<sup>-1</sup> as is to be expected. This frequency is about 100 cm<sup>-1</sup> higher than in Tzdt<sup>1</sup> and secondary thioamides<sup>8,9</sup>, but is nearly 100 cm<sup>-1</sup> lower than in N-alkyl dithiocarbamates<sup>11</sup>. The remaining CH and ring bending modes are easily assigned by comparison with thiazole<sup>10</sup> (see Table 4).

**Complex of Tzt** — The Ni(II) complex decomposes on exposure to moisture, while the other complexes are stable. The molar conductances of these complexes in nitrobenzene (10<sup>-3</sup>M) were nearly zero (Λ<sub>M</sub> ~1 to 10) showing the coordination of chloride ions to the metal.

**Infrared spectra of the complexes** — The infrared frequencies of the ligand and its complexes together with their main assignments are presented in Table 4. On comparing the spectrum of the ligand with the spectra of the complexes, no striking changes are observed in the C-N and C-S stretching regions. However, the bands due to the NH group are shifted considerably in the complexes.

The NH stretching band is generally observed as a doublet in the complexes as in the ligand. In the Cd(II) complex the NH stretching frequency is observed at a considerably higher frequency, at  $3220\text{ cm}^{-1}$  whereas in the other complexes, it is found almost in the same region,  $3090\text{--}3160\text{ cm}^{-1}$  as in the ligand. This is similar to that of Tzdt<sup>1</sup>, where the NH stretching band of the ligand is shifted to higher frequencies in Cd(II) and Zn(II) complexes, indicated to have N-coordinated Tzdt. The NH stretching band of Tzdt is not much affected in the complexes of Ni(II), Cu(II), etc. containing S-bonded Tzdt. The increase in NH stretching frequency of Tzt in the N-bonded complexes is attributed to an increase in the positive character of the ring nitrogen on bonding to a metal ion. The results seem to indicate the Tzt is bonded through nitrogen in the Cd(II) complex, and through the exocyclic sulphur in other complexes. This inference is supported by the different behaviour of NH out-of-plane bending in the Cd(II) complex in contrast to the other complexes. The NH out-of-plane bending of Tzt at  $800\text{ cm}^{-1}$  is found in Ni(II), Cu(II) and Hg(II) complexes almost unaffected but with slightly reduced intensity. On the other hand, the Cd(II) complex has no band in this region but exhibits a very strong band at  $695\text{ cm}^{-1}$  (absent in the other complexes). Similar substantial downward shifts ( $60\text{--}80\text{ cm}^{-1}$ ) of the ligand NH out-of-plane bending are noted in the N-coordinated Cd(II) and Zn(II) complexes of Tzdt, while the S-bonded complexes show no or negligible shift<sup>1</sup>. That the NH out-of-plane bending band shifts to lower frequencies in the Cd(II) complex is further confirmed by preparing the Tzt-d complex of CdCl<sub>2</sub> (using the procedure given for Tzt complex), presumed to be CdCl<sub>2</sub>·Tzt-d<sup>1</sup> and studying its IR data (Table 4). The  $548\text{ cm}^{-1}$  band due to ND out-of-plane bending of Tzt-d<sub>1</sub> is shifted to a lower frequency ( $505\text{ cm}^{-1}$ ) in the complex. Thus the NH out-of-plane bending band seems to be sensitive to the type of bending.

The C=S bending of Tzt at  $322\text{ cm}^{-1}$  is unaffected in the Cd(II) complex, whereas in the other complexes it is shifted to near  $340\text{ cm}^{-1}$  as expected when bonding of Tzt is through the exocyclic sulphur.

We exclude the bonding of Tzt through ring sulphur since the exocyclic thiocarbonyl sulphur is likely to be the donor as in secondary thioamides and more negative charge residing on this atom by resonance. The possibility of Tzt coordinating as a chelate through both the sulphur atoms seems unlikely since in such a case substantial changes in the IR bands below  $600\text{ cm}^{-1}$  on chelation due to ring deformation modes are expected. Furthermore, the electronic spectral band positions of the Ni(II) complex (given later) closely resemble those of benzothiazole<sup>12</sup>, ethylenethiourea<sup>13</sup> and Tzdt<sup>14</sup> complexes of the type NiCl<sub>2</sub>·2L containing S-bonded ligands and bridging Cl<sup>-</sup> groups. The M-Cl bands appear to support the presence of bridging chloride groups.

**Metal-chloride and metal-ligand vibrations** — In the Ni(II) complex, there are two weak bands at  $265$  and  $230\text{ cm}^{-1}$ , which could be attributed to M-Cl stretching. This is in agreement<sup>15</sup> with that expected for polymeric octahedral complexes of com-

position NiL<sub>2</sub>Cl<sub>2</sub>, where L = pyridine, toluidines, etc. A medium weak band at  $265\text{ cm}^{-1}$  in Cd(Tzt)Cl<sub>2</sub>, and at  $275\text{ cm}^{-1}$  in Cu(Tzt)Cl<sub>2</sub> for bridging M-Cl stretching are compatible with the values reported in polymeric complexes of the type LMCl<sub>2</sub> containing bridging chloride groups<sup>15</sup>. Hg(Tzt)<sub>2</sub>Cl<sub>2</sub> shows an intense absorption at  $220\text{ cm}^{-1}$  which could be assigned to M-Cl stretching vibration<sup>15,16</sup>. This complex is likely to have a tetrahedral geometry and the other M-Cl stretching mode expected for tetrahedral complexes of composition L<sub>2</sub>MCl<sub>2</sub> may be below  $200\text{ cm}^{-1}$ .

Metal-nitrogen stretching for the Cd(II) complex is expected around  $320\text{ cm}^{-1}$ , and the metal-sulphur frequencies for the other complexes, around  $320\text{--}360\text{ cm}^{-1}$ . But no new bands are found in this region, presumably these bands may be too weak, overlapping with the ligand bands.

**Electronic spectra** — The solid state spectra of Cu(II) and Ni(II) complexes were taken in the visible region. Cu(Tzt)Cl<sub>2</sub> shows a weak absorption at  $700\text{ nm}$  indicating square planar or octahedral geometry for this complex. A polymeric Cu(II) complex with bridging chloride ions is likely. The visible spectrum of the nickel(II) complex shows a fairly strong absorption at  $448\text{ nm}$ , as a shoulder to an intense charge-transfer band, a weak broad band at  $770\text{ nm}$  and a still weaker band at  $1250\text{ nm}$  typical of nickel(II) ion in an octahedral geometry. The band positions closely agree with those in octahedral NiCl<sub>2</sub>·2L complexes, where L = Tzdt<sup>14</sup>, ethylene thiourea<sup>13</sup> and benzothiazole<sup>12</sup>.

#### Acknowledgement

The award of a Science Talent Search Fellowship to K.G.R. by the National Council of Educational Research and Training, New Delhi, is gratefully acknowledged.

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