

Infrared Spectral Study of Thiazolidine-2-thione & Its Metal Complexes

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Received 14 March 1975; accepted 1 May 1975

The infrared spectral studies of thiazolidine-2-thione (Tzdt) and its complexes with divalent Co, Ni, Cu, Zn, Cd and Hg have been made. The assignment of the infrared frequencies of the ligand is made with the help of normal coordinate treatment of Tzdt and N-deuterated Tzdt. The ligand is inferred to coordinate through nitrogen in Zn and Cd complexes and through the thiocarbonyl sulphur atom in the other four complexes.

COMPOUNDS of the type thiazolidine-2-thione (Tzdt), containing a secondary thioamide group, are of considerable interest as ligands since they are found to provide potential binding sites for metal ions in many physiological systems. A knowledge of the coordinating properties of this ligand will be helpful in understanding the role of metal ions in such systems. Also, Tzdt and its derivatives are important in flotation process and in photographic industry¹.

A few complexes of Tzdt with different metal ions have recently been studied by Rivest and Singh² and by De Filippo *et al.*³⁻⁵. In order to decide the site of coordination, a few infrared bands of the ligand were assigned empirically by these workers. It must be noted that these two groups have come to opposite conclusions regarding the site of coordination in the Co(II) halide complexes^{2,3}. Also Tzdt is said to coordinate in the Hg(II) complex through nitrogen⁴ in spite of the known preference of Hg(II) towards S-donors. Hence, it appeared worthwhile to reexamine the nature of bonding of Tzdt in metal complexes. With this in view, the infrared spectra of metal complexes of Tzdt [of which that of Cu(II) is new] have been reinvestigated. The results of the normal coordinate analysis of Tzdt and N-deuterated Tzdt (Tzdt-*d*₁) are briefly discussed here.

Materials and Methods

The metal chlorides were of AR quality. Ethanolamine (E. Merck) and CS₂ (Purex) were used. D₂O of over 99.4% purity was obtained from Bhabha Atomic Research Centre, Bombay.

Tzdt and tzdt-d₁ — Tzdt was synthesized starting from ethanolamine by Owen's procedure⁶ and recrystallized from water. Tzdt-*d*₁ was prepared by repeated exchange reaction of Tzdt with D₂O.

Metal complexes — The complexes of the type, M(Tzdt)₂Cl₂ (where M = Co, Ni, Zn, Cd and Hg) were prepared as described by De Filippo *et al.*^{3,4}. The compositions of these known complexes were checked by metal analysis (not reported here).

The copper complex, Cu(Tzdt)₂Cl₂, was obtained by mixing ethanol solutions of Tzdt and CuCl₂·2H₂O. It was washed with hot toluene and dried under

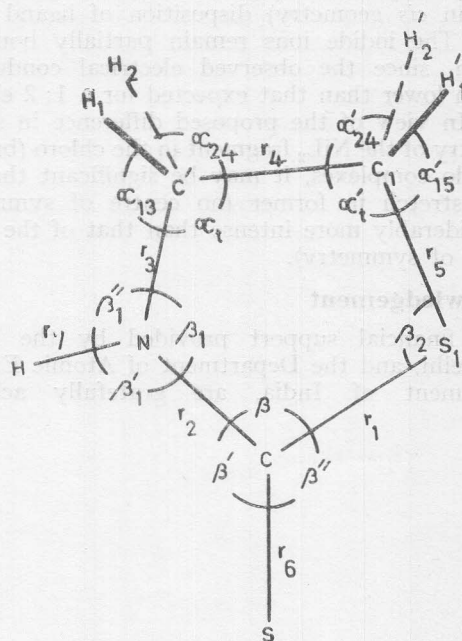


Fig. 1 — Internal coordinates of thiazolidine-2-thione (Tzdt)

vacuum to get a green coloured complex [Found: Cu, 16.98; C, 19.12; H, 2.78; N, 7.49%. Cu(Tzdt)₂Cl₂ requires Cu, 17.06; C, 19.33; H, 2.68; N, 7.52%].

Apparatus — The infrared spectra of the samples were recorded in nujol mull and KBr pellet on Carl-Zeiss UR 10 and Beckman IR 12 spectrophotometers in the range 4000-400 and 650-200 cm⁻¹, respectively.

Normal coordinate treatment — Tzdt belongs to the point group C_s and has 27 normal modes (17A' + 10A''). The A' modes were only considered for the coordinate treatment and the vibrations of present interest belong to this species. The internal coordinates of Tzdt are defined in Fig. 1 and the internal symmetry coordinates were constructed by standard procedure⁷ and are not given here. The structural parameters for Tzdt were taken from similar molecules^{8,9} and these are: bond lengths, C-S 0.1650, C-S₁ 0.1696, C₁-S₁ 0.180, C-C 0.150, C'-N 0.134, C-N 0.1376,

TABLE 1 — FORCE CONSTANTS (mdyn/Å) OF Tzdt

Stretching*		Bending		Repulsion	
KCS	3.40	HNCS	0.29	FSCS ₁	0.35
KCS ₁	2.45	HNCS ₁	0.53	FNCS ₁	0.60
KC ₁ S ₁	1.65	HSCS	0.13	FNCS	0.95
KCN	5.50	Hcsc	0.25	FSCC	0.50
KC'N	5.10	HSCC	0.10	FCNC'	0.25
KCC	2.70	HNCC	0.12	FCSC	0.15
KNH	5.02	HCNC'	0.28	FNCC	0.45
KC'H	4.25	HHCH	0.13	FCC,H	0.30
KC ₁ H	4.12	HHC'C	0.16	FCC'H	0.30
KCH ₂	0.136	HHC'H	0.46	FC'NH	0.42
¹ HCC,HCC	0.057	HHC ₁ H	0.40	FCNH	0.42
¹ HCH,HCC	0.057	HHC ₁ C	0.15	FNCH	0.40
		HHC ₁ S	0.23	FSCH	0.18
		HHNC	0.22	FHCH	0.20
		HHNC'	0.17		

*K denotes intramolecular tension in mdyn/Å; l' and l' are non-UB constants in mdyn/Å.

N-H 0.102, C-H 0.108 nm; and bond angles, NCS₁ 114°, NCS 132°, CSC 90°, CNC' 117° 04', HNC 125° 52', and the angles at the CH₂ carbons 109° 28'.

The Urey-Bradley (UB) force constants were initially transferred from *n*-propylmercaptan¹⁰ for the thiol part (—CH₂—CH₂—S—) and from *N*-methylthioacetamide^{11,12} (NMTA) for the thioamide grouping. The initial force constants required only slight modifications to obtain a desired agreement between the observed and calculated frequencies indicating good transferability of these force constants. However, two non-UB force constants for the interaction between the angles within the CH₂ groups, i.e. HCC, HCC(1) and HCH, HCC(1') were necessary to adjust the calculated bending and wagging frequencies of the CH₂ groups to the observed ones. These non-UB constants have the same values as those used for *n*-propylmercaptan¹⁰. The final set of force constants is given in Table 1.

Results and Discussion

The calculated and observed frequencies of Tzdt and Tzdt-*d*₁ along with their assignments are given in Table 2. The assignment of NH, CN and CS frequencies which are of particular interest is briefly discussed below. The earlier empirical assignment² of a few infrared bands of Tzdt needs revision in the light of the present work (vide infra).

NH vibrations — The νNH of the ligand occurs at 3420 cm⁻¹ in CHCl₃ and at 3160 cm⁻¹ in the solid, lowered mainly due to hydrogen bonding.

A band at 1260 cm⁻¹ is chiefly due to NH in-plane bending. This assignment is supported by the shift of this band to 860 cm⁻¹ on deuteration. Earlier investigators^{2,4} had attributed the 1520 cm⁻¹ to NH bending. Interestingly NH bending in Tzdt occurs at a lower frequency than that in secondary thioamides^{11,12}, where it is found near 1550 cm⁻¹.

A strong band at 705 cm⁻¹ is assigned to NH out-of-plane bending. This band is absent in the spectrum of Tzdt-*d*₁, which exhibits a new band at 492 cm⁻¹, assignable to ND out-of-plane bending.

 TABLE 2 — INFRARED FREQUENCIES (cm⁻¹) OF Tzdt AND Tzdt-*d*₁ AND THEIR ASSIGNMENTS

Tzdt- <i>d</i> ₁		Tzdt		Assignment* (PED, %)
Obs.	Calc.	Obs.	Calc.	
2350	2312	3160	3160	νNH (100)
3010	—	3005	—	νCH ₂ (A'')
2935	2937	2935	2937	ν'CH ₂ (55), νCH ₂ (45)
2870	2856	2870	2856	νCH ₂ (55), ν'CH ₂ (45)
1528	1525	1520	1533	δC'H ₂ (41), νC'N (21), νCN (16)
1450	1459	1468	1466	δC'H ₂ (43), νCN (24)
1440	1441	1442	1444	δC ₁ H ₂ (80)
—	—	1385	—	overtone or combination band
1370	1349	1350	1357	ωC ₁ H ₂ (41), νC'N (18), νCN (10)
1310	1308	1302	1311	ωC ₁ H ₂ (61), νCC (18)
860	850	1260	1267	δNH (51), νCN (28)
1210	—	1212	—	tCH ₂ (A'')
1170	—	1168	—	tCH ₂ (A'')
1120	1149	1095	1094	ωC'H ₂ (42), νC'N (16), δNH (15)
1055	1071	1060	1071	νC=S (39), δ ring (26), νCS ₁ (16)
1026	—	1040	—	rCH ₂ (A'')
995	98P	930	930	νCC (74)
855	—	855	—	rCH ₂ (A'')
492	—	705	—	πNH (A')
655	644	655	671	νC ₁ S ₁ (39), δ ring (30), νCS ₁ (21)
645	—	—	—	—
588	608	620	621	νCS ₁ (31), νC ₁ S ₁ (21), δ ring (20), νC=S (15)
563	—	585	—	πSK (A'')
543	530	545	533	δ ring (48), νC ₁ S ₁ (34)
432	430	435	432	δ ring (63), νC=S (25)
289	290	292	292	δC=S (75), νCS ₁ (11)

*The assignment given is for Tzdt and it corresponds approximately to Tzdt-*d*₁.

This assignment is reasonable from the expected frequency change upon replacement of H by D.

CN stretching modes — The CN stretching vibrations overlap with CH₂ bending or wagging modes and occur in the region 1520-1090 cm⁻¹ (Table 2).

C = S vibrations — The exocyclic C = S stretching vibration is delocalized in a number of frequencies in Tzdt and a very strong band at 1060 cm⁻¹ (with a shoulder at 1040 cm⁻¹) has substantial contribution from νC = S mode. It corresponds approximately to the 1040 cm⁻¹ band of Ni(II) ethylxanthate¹³, and the 990 cm⁻¹ band of Ni(II) ethylthioxanthate¹⁴ and the 1062 cm⁻¹ band of ethylene trithiocarbonate¹⁵. This is in contrast to some primary and secondary thioamides^{11,12,16}, which have localized C = S stretching mode, near 700 cm⁻¹.

An intense band at 292 cm⁻¹ is due to a nearly pure C = S bending.

Out-of-plane vibrations — Tzdt has 10A'' vibrations. An empirical assignment of these vibrations is made by comparison with those of *n*-propylmercaptan¹⁰, ethylene trithiocarbonate¹⁵ and other related molecules¹⁷. This is included in Table 2.

A few infrared frequencies of Tzdt and its complexes along with their assignments are presented in Table 3.

TABLE 3 — CHARACTERISTIC INFRARED BANDS (cm^{-1}) OF TZDT COMPLEXES AND THEIR ASSIGNMENT

Tzdt	Co(Tzdt) ₂ Cl ₂	Ni(Tzdt) ₂ Cl ₂	Cu(Tzdt) ₂ Cl ₂	Hg(Tzdt) ₂ Cl ₂	Zn(Tzdt) ₂ Cl ₂	Cd(Tzdt) ₂ Cl ₂	Main assignment
3160 w, b	3170 ms	3160 w	3100 w, b	3110 m	32255 ms	3270 ms	ν NH
1520 vs	1540 vs	1565 m 1529 vs	1540 vs, b	1565 s	1530 vs	1530 vs	δ CH ₂ , ν CN
705 s	718 m	720 s 700 vw	738 vs	740 s 695 m	644 m	612 vs	π NH(A')
—	400 m	400 w 355 mw	398 m 372 sh	340 mb		320 m	ν MS(ν MN)
—	Not investigated	330 m 260 sh	332 vw 262 m 242 m	315 sh 235 s 212 s	332 s 312 s	240 m 220 s	ν MCl

In the complexes of Co(II), Ni(II), Hg(II) and Cu(II), the NH stretching mode occurs at 3170, 3160, 3110 and 3100 cm^{-1} respectively, whereas in Cd(II) and Zn(II) complexes, it is observed at 3270 and 3255 cm^{-1} respectively, in contrast to the ligand NH band at 3160 cm^{-1} . In the former compounds, the coordination is inferred to be through the exocyclic thiocarbonyl sulphur atom, while in the latter, it is via the nitrogen of the secondary thioamide group. The increase (85-100 cm^{-1}) in NH stretching frequency on coordination of nitrogen to a metal ion may be expected due to the increase in the positive character of N atom which increases the NH stretching force constant. The inference regarding the site of coordination from NH stretching frequency is supported by other evidences cited below.

The band due to NH out-of-plane bending at 705 cm^{-1} shifts to higher frequencies, to 718, 720, 738 and 740 cm^{-1} , in Co(II), Ni(II), Cu(II) and Hg(II) complexes respectively. In the complexes of Zn(II) and Cd(II), there is no band in the region 700-800 cm^{-1} , but a new fairly intense band is observed at 644 cm^{-1} in the Zn(II) complex and at 612 cm^{-1} in the Cd(II) complex, which could be assigned to NH out-of-plane bending. The magnitude of the shift of the NH out-of-plane bending to lower frequencies is of the same order as that of NH stretching frequency to higher frequencies. The NH out-of-plane bending appears to be sensitive to the nature of coordination.

The CN stretching modes contribute considerably to the bands at 1520, 1468 and 1350 cm^{-1} . However, only the 1520 cm^{-1} band shifts to higher frequencies in Co(II), Ni(II), Cu(II) and Hg(II) complexes by 20-45 cm^{-1} whereas in Zn(II) and Cd(II) complexes, the shift is negligible ($\sim 10 \text{ cm}^{-1}$) (Table 3). This band has been assigned to NH in-plane bending by Rivest and Singh². But the coordinate treatment shows it to be due to CH₂ bending coupled with CN stretching. This is supported by the fact that there is a band at 1528 cm^{-1} in Tzdt-*d*₁ with an assignment analogous to that in Tzdt. Further, in N-methylthiazolidine-2-thione a similar band is observed¹⁸ at 1528 cm^{-1} .

The in-plane NH bending at 1260 cm^{-1} is unaffected in the complexes. This may be attributed to the nature of this mixed vibration. Similarly, since the exocyclic C = S stretching is delocalized

over a number of frequencies, the shift in band positions in complexes is not considerable.

Rivest and Singh² in their study of Co(II) complexes have compared the NH stretching frequency of the ligand in CHCl₃ with that of the complexes in solid state and suggested that a large negative shift in the NH stretching frequency of the ligand showed nitrogen coordination. On the same basis, Filippo *et al.*⁴ indicated bonding through nitrogen in the complexes of Zn(II), Cd(II) and Hg(II) halides. However, for comparison, it would be appropriate if the spectra of both the ligand and its complexes were measured in the same phase, since effects other than that due to coordination could nearly cancel out.

It may be noted that the NH frequency has not been employed when the ligand coordinates through sulphur, as in Ni(II) and Co(II) complexes³. As could be observed from our data (Table 3), both for S- and N-bonded Tzdt, there is a large negative shift in the NH frequency if the band in solid complexes is compared with that of Tzdt in solution.

Also, in the S-coordinated Tzdt complexes of metal carbonyls⁵ where the spectra of both Tzdt and the complexes were measured in CHCl₃, no shift in the NH stretching frequency was observed, which is consistent with the present work. These data explain the incorrect inferences drawn by earlier workers^{2,4} regarding the coordination site in Co(II) and Hg(II) complexes.

As indicated previously, Rivest and Singh² have empirically assigned some of the frequencies of Tzdt. Their assignments of the 1520 cm^{-1} to NH bending, 1302 cm^{-1} to CS stretching coupled with NCS bending, 1005 cm^{-1} to a mixed CN and CS stretching vibration; 705 cm^{-1} to ring C-S stretching and the 585 cm^{-1} band as due to NCS bending are different from the present assignments. The assignment of the 1060, 655, 435 and 290 cm^{-1} bands are somewhat similar to the present assignments. The infrared assignments of Filippo *et al.*³⁻⁵ are based on those of Rivest and Singh².

Metal-chloride and metal-ligand vibrations are assigned in comparison with those in related molecules^{19,20} and are given in Table 3.

In the Zn(II) complex no band could be assigned to MN stretching, possibly it is overlapping with the intense absorption due to M-Cl modes.

Acknowledgement

The authors thank Prof. P. T. Manoharan, Department of Chemistry, Indian Institute of Technology, Madras, for the spectra on Beckman IR 12. 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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