

Sulphur-bonded thalious complexes of thiosemicarbazones

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Abstract. An interesting series of some sulphur-bonded unusual bicoordinated thallium(I) complexes of the type TLL (where L is the anion of a monobasic bidentate thiosemicarbazone) has been obtained by the equimolar reactions of thalious chloride with the sodium salt of the ligands (thiosemicarbazones) derived from the condensation of heterocyclic aldehydes or ketones with thiosemicarbazide. The complexes have been characterized by elemental analyses, conductance measurements, molecular weight determinations and electronic, IR, ^1H and ^{13}C NMR spectral studies.

Keywords. Thallium (I) compounds; thiosemicarbazones, heterocyclic moiety; spectral studies; monobasic bidentate ligand.

1. Introduction

Thiosemicarbazones constitute a class of agents which possess both antineoplastic and antiviral activities (Agrawal and Sartorelli 1975). The first compound to be examined for biological activity, 2-formylpyridine thiosemicarbazone, was shown to possess mild antileukemic activity against L-1210 tumour in mice (Brockman *et al* 1956; Agrawal and Sartorelli 1978). The biological activity of this class of compounds is associated with chelation, and a direct correlation between the antitumour activities and the chelating abilities of several of these compounds has been shown (Michaud and Sartorelli 1968). Similarly, the mode of antiviral action of 1-methylisatin- β -thiosemicarbazone, the first synthetic antiviral drug, is initially thought to be metal chelation (Mikelens *et al* 1976; Stunzi 1981). Although the coordination chemistry of the thiosemicarbazones has been explored as regards the transition metals (Campbell 1975; Padhye and Kauffman 1985), much less attention has been paid to the elements of the main groups (Saxena and Tandon 1986; Saxena and Singh 1992) and particularly the third main group elements. In continuation of our interest in the chemistry of main group metals, it was considered of interest to prepare thallium(I) complexes of the ligands shown in figure 1.

2. Experimental

Chemicals and solvents used were dried and purified by standard methods.

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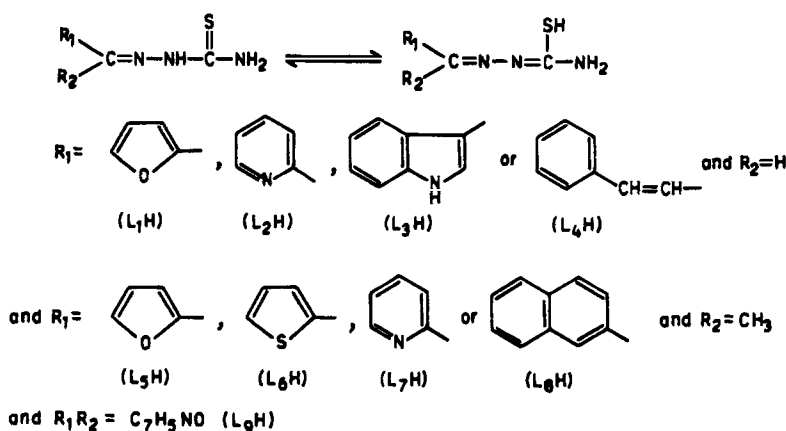


Figure 1. Structures of the ligands used.

2.1 Synthesis of thiosemicarbazones (LH)

Heterocyclic aldehydes (2.13–5.41 g) or ketones (2.05–3.83 g) were mixed with the thiosemicarbazide (1.54–3.73 g) in 1:1 molar ratio in water–ethanolic medium. On refluxing the mixture for about an hour, the crystals of ligands separated out, and were filtered and dried. All the ligands were recrystallized using the same solvent and finally dried under reduced pressure. Details of all these reactions have already been reported in our earlier publications (Singh *et al* 1987; Singh and Singh 1991).

2.2 Synthesis of sodium salt of the ligand (NaL)

This was prepared by reacting the ligand (1.12–1.58 g) with sodium metal (0.13–0.20 g) in 1:1 molar ratio in methanol.

2.3 Synthesis of thallium (I) complexes

To a weighed amount of thalious chloride (1.34–2.15 g), the sodium salt of the ligand (1.25–1.75 g) was added in 1:1 molar ratio using methanol as the reaction medium and the mixture refluxed for 10–16 h. The sodium chloride thus precipitated was removed and the compound was dried *in vacuo*. The synthetic and analytical data of the complexes are listed in table 1.

2.4 Analytical methods and physical measurements

Carbon and hydrogen analyses were carried out at the Microanalytical Laboratory of the Department. Nitrogen was determined by Kjeldahl's method. Sulphur was determined as barium sulphate by Messenger's method. Thallium was estimated as thallium chromate (Vogel 1973). Molecular weights were determined by the Gallenkamp ebulliometer. Electronic spectra were recorded on a Hitachi U-2000 Spectrophotometer. IR spectra were recorded on a Perkin-Elmer 577 Grating Spectro-

Table 1. Synthetic and analytical data of thallium (I) complexes.

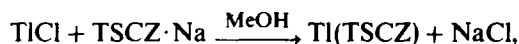
TlCl (g)	Sodium salt of the ligand (g)	Molar ratio	Product, yield (g) and state	M.P. (°C)	Analyses (%)			Molecular weight Found (Calcd.)
					N Found (Calcd.)	S Found (Calcd.)	Tl Found (Calcd.)	
2.15	1.17	1:1	C ₆ H ₆ N ₃ OSTl, (2.66), Brown solid	180d	11.02 (11.28)	8.15 (8.61)	52.16 (54.85)	404.58 (372.57)
1.71	1.44	1:1	C ₇ H ₇ N ₄ STl, (2.35), Dark yellow solid	90d	14.12 (14.60)	7.88 (8.36)	51.74 (53.27)	410.35 (383.60)
1.74	1.74	1:1	C ₁₀ H ₉ N ₄ STl, (2.68), Reddish brown solid	80d	12.75 (13.28)	7.27 (7.60)	45.89 (48.47)	412.37 (421.65)
1.55	1.47	1:1	C ₁₀ H ₁₀ N ₃ STl, (2.43), Yellow solid	205d	9.86 (10.28)	7.49 (7.85)	48.75 (50.01)	422.25 (408.65)
1.79	1.53	1:1	C ₇ H ₈ N ₃ OSTl, (2.37), Black solid	140d	10.46 (10.87)	8.07 (8.29)	50.36 (52.86)	405.55 (386.60)
1.35	1.25	1:1	C ₇ H ₈ N ₃ S ₂ Tl, (1.97), Greenish yellow solid	110d	10.04 (10.43)	15.35 (15.93)	48.84 (50.75)	418.80 (402.66)
1.94	1.75	1:1	C ₈ H ₉ N ₄ STl, (2.64), Orange solid	140d	13.62 (14.09)	7.68 (8.06)	49.48 (51.39)	409.46 (397.66)
1.53	1.69	1:1	C ₁₃ H ₁₂ N ₃ STl, (2.42), Off-white solid	245d	9.00 (9.41)	6.74 (7.18)	44.13 (45.75)	460.63 (446.70)
1.34	1.35	1:1	C ₉ H ₇ N ₄ OSTl, (1.88), Dark yellow solid	150d	12.78 (13.22)	7.17 (7.57)	47.12 (48.24)	438.28 (423.63)

d = decomposed

photometer in the region, $4000\text{--}200\text{ cm}^{-1}$ using KBr optics. Molar conductance measurements were made in anhydrous DMF using a Systronics Conductivity Bridge Model-305. The ^1H and ^{13}C NMR spectra were recorded on a Jeol FX-90Q Spectrometer in $\text{DMSO-}d_6$ and methanol using TMS as the internal standard.

3. Results and discussion

The formation of thallium (I) complexes by the equimolar reaction of thallos chloride and the monosodium salt of the ligands can be depicted by the following equation:



(where $\text{TSCZ} \cdot \text{Na}$ represents the sodium salt of thiosemicarbazones).

The resulting coloured complexes are soluble in most of the common organic solvents and their molar conductance values ($8\text{--}14\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$) in DMF showed that they are nonelectrolytes. All the complexes are monomeric as revealed by their molecular weights. The monomeric nature of the complexes indicates the bicoordinated state for the central thallium atom which has been confirmed with the help of spectral studies also.

3.1 Electronic spectra

The electronic spectra of the ligands and their thallium complexes have been recorded in dry methanol. The maxima at 265 ± 10 and 315 ± 5 nm in the case of the ligands are due to $\pi - \pi^*$ electronic transitions. These bands are almost unchanged in the spectra of thallium derivatives. The spectra of the ligands show a broad band at 340 ± 10 nm (Singh *et al* 1988) due to $n - \pi^*$ transitions within the $>\text{C}=\text{N}$ chromophore which shows a bathochromic shift of $20\text{--}25$ nm (Pellerito *et al* 1972) due to the donation of a lone pair of electrons to the metal atom and hence the coordination of azomethine nitrogen to the metal atom (table 2).

3.2 IR spectra

Thiosemicarbazones exist in the thioketo form in the solid state as evidenced from the IR spectral data. The ligands do not show any band of νSH vibrations at $\sim 2570\text{ cm}^{-1}$. In solution, however, thiosemicarbazones can exist in the thioketo (A) and thioenol (B) forms.



The IR spectra of the free ligands display two sharp bands around 3450 and 3350 cm^{-1} assignable to $\nu\text{ asym}$ and $\nu\text{ sym}$ NH_2 , respectively, which remain unaltered in the thallium complexes. A medium intensity band appearing in the region $3120\text{--}3220\text{ cm}^{-1}$, which may be assigned to νNH vibrations, disappears in the metal

Table 2. Electronic spectra (nm) of ligands and their corresponding thallium (I) complexes.

Compound	λ_{\max}		
L ₁ H	264	315	340
Tl(L ₁)	267	316	362
L ₂ H	275	322	342
Tl(L ₂)	270	320	366
L ₄ H	265	310	350
Tl(L ₄)	260	315	372
L ₆ H	262	314	332
Tl(L ₆)	265	317	353
L ₇ H	255	322	345
Tl(L ₇)	260	325	368

Table 3. IR spectral data (ν , cm^{-1}) of ligands and their corresponding thallium (I) complexes.

Compound	NH	>C=N	>C=S	Tl-S	Tl←N
L ₁ H	3120–3180	1580	1040	810	—
Tl(L ₁)	—	1620	—	780	260
L ₂ H	3120–3160	1590	1030	820	—
Tl(L ₂)	—	1620	—	790	270
L ₃ H	3120–3200	1590	1030	815	—
Tl(L ₃)	—	1610	—	790	275
L ₄ H	3140–3180	1590	1035	825	—
Tl(L ₄)	—	1620	—	795	270
L ₅ H	3140–3180	1580	1045	810	—
Tl(L ₅)	—	1615	—	775	265
L ₆ H	3120–3200	1590	1040	830	—
Tl(L ₆)	—	1620	—	810	275
L ₇ H	3120–3180	1585	1040	825	—
Tl(L ₇)	—	1615	—	780	260
L ₈ H	3120–3200	1580	1035	815	—
Tl(L ₈)	—	1610	—	780	260
L ₉ H	3140–3200	1590	1040	830	—
Tl(L ₉)	—	1620	—	785	280

complexes, indicating the possible deprotonation on the α -nitrogen after complexation with the metal ion. The band at $\sim 1035 \text{ cm}^{-1}$ for the free ligand due to $\nu\text{C}=\text{S}$ vibrations also disappears in the metal complexes indicating the coordination of the ligand through the sulphur atom, while the second $\nu\text{C}=\text{S}$ band, which lies at $\sim 820 \text{ cm}^{-1}$ for the free ligand shifts to lower wavenumbers upon complexation further indicating the coordination of the ligand through the sulphur atom (Kato *et al* 1974). The band at $1590 \pm 10 \text{ cm}^{-1}$ of the free ligand due to $\nu\text{C}=\text{N}$ shifts to higher wavenumbers ($20\text{--}40 \text{ cm}^{-1}$) in the metal complexes suggesting the coordination of azomethine nitrogen to the central metal atom (Samuel *et al* 1970). The complexes exhibit two new bands at $\sim 270 \text{ cm}^{-1}$ and $\sim 425 \text{ cm}^{-1}$ which may be assigned to the different

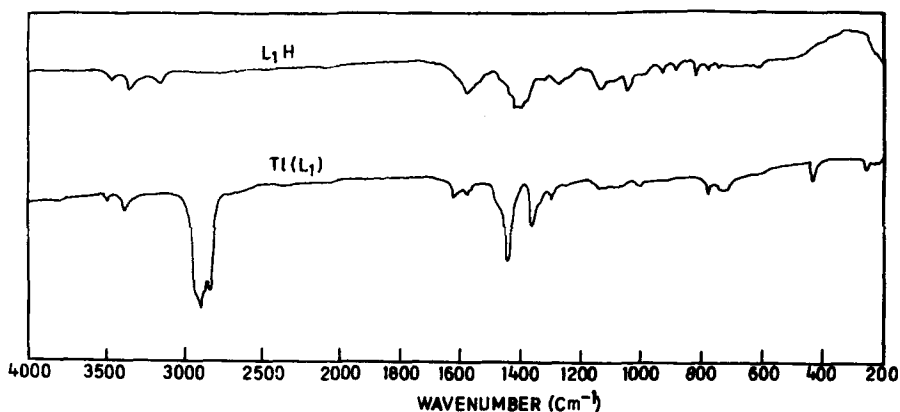


Figure 2. IR spectra of L_1H and its complex $Tl(C_1)$.

Table 4. 1H NMR spectral data (δ , ppm) of ligands and their corresponding thallium (I) derivatives.

Compound	NH (bs)	Aromatic (m)	$>CH=N$ (s)	$\begin{array}{c} -C=N \\ \\ CH_3 \end{array}$ (s)	NH_2 (bs)
L_3H	11.78	7.60–6.60	8.32	—	2.40
$Tl(L_3)$	—	7.72–6.68	8.60	—	2.33
L_4H	11.76	8.00–7.32	8.15	—	2.96
$Tl(L_4)$	—	8.16–7.44	8.36	—	2.94
L_6H	10.68	8.68–7.16	—	1.68	2.81
$Tl(L_6)$	—	8.40–7.04	—	2.08	2.88

bs = broad singlet, m = multiplet and s = singlet

vibrational modes of $Tl-S$ and $Tl \leftarrow N$ (Macias *et al* 1989), respectively (table 3). This discussion has been supported by including the IR spectra of one ligand (L_1H) and its complex [$Tl(L_1)$] (figure 2).

3.3 Proton magnetic resonance spectra

The 1H NMR spectra of L_3H , L_4H and L_6H and their thallium complexes have been recorded in $DMSO-d_6$ (table 4). The signals at δ 11.78 (L_3H), 11.76 (L_4H) and 10.68 (L_6H) ppm in the case of the ligands are due to NH protons which disappear in the spectra of thallium (I) complexes indicating the deprotonation of the functional groups during the complexation with the thallium atom.

The ligands show a complex multiplet in the region δ 8.68–6.60 ppm for the aromatic protons which remains at almost the same position in the spectra of the thallium complexes, indicating their noninvolvement in coordination. The proton signals for the azomethine protons at δ 8.32 (L_3H) and 8.15 ppm (L_4H) and methyl protons at δ 1.68 ppm (L_6H) in the ligands shift appearing downfield at δ 8.68, 8.36 and 2.08 ppm, respectively, in the spectra of the corresponding thallium complexes. This shifting is

due to the deshielding of the protonic environment on donating the lone pair of electrons by the azomethine nitrogen to the central thallium atom and which clearly shows the coordinate bond formation by the azomethinenitrogen with the thallium atom. The proton signals for NH_2 protons remains at almost the same position indicating their noninvolvement in coordination. The ^1H NMR spectra of one ligand

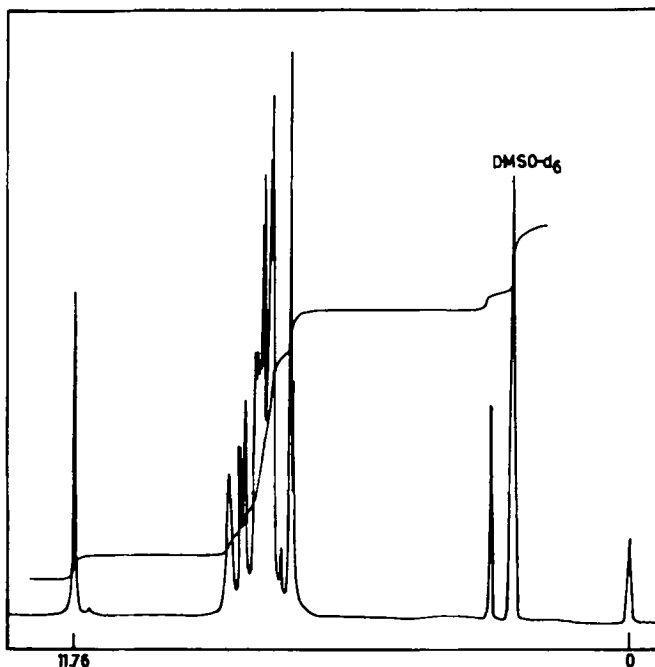


Figure 3. ^1H NMR spectra of L_4H .

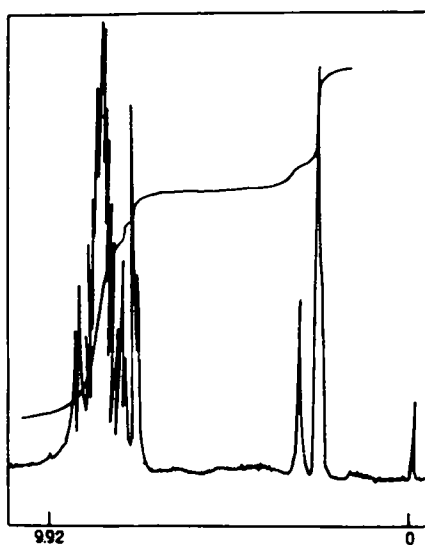


Figure 4. ^1H NMR spectra of $\text{Tl}(\text{L}_4)$.

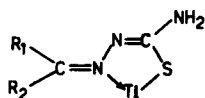


Figure 5. General structure of the complexes.

(L_4H) and its thallium complex $[Tl(L_4)]$ have been shown in figures 3 and 4, respectively.

3.4 ^{13}C NMR spectra

^{13}C NMR spectra of the ligand L_7H and its thallium (I) complex, $Tl(L_7)$ were also recorded. The main features of the spectra are the shifting of the amido carbon from δ 179.19 to 172.65 ppm and of the azomethine carbon from δ 156.20 to 151.24 ppm in the metal complex, which further support the coordination of sulphur and nitrogen to the central metal atom.

On the basis of the above discussions, a bicoordinated structure has been proposed for the resulting complexes as shown in (figure 5).

Acknowledgement

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