A NEW CLASS OF COORDINATION COMPOUNDS OF THALLIUM(I) WITH SEMICARBAZONES

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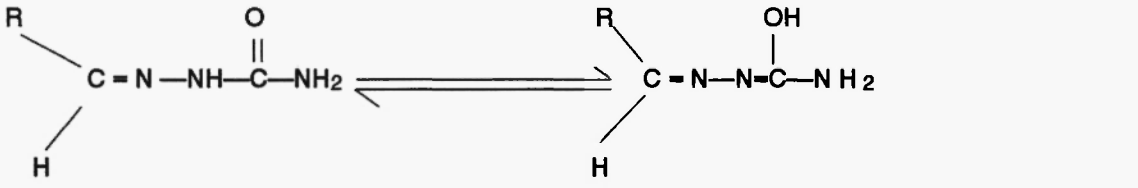
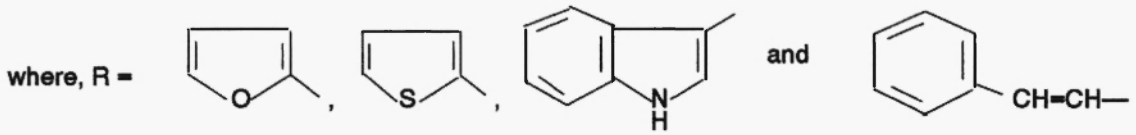
ABSTRACT

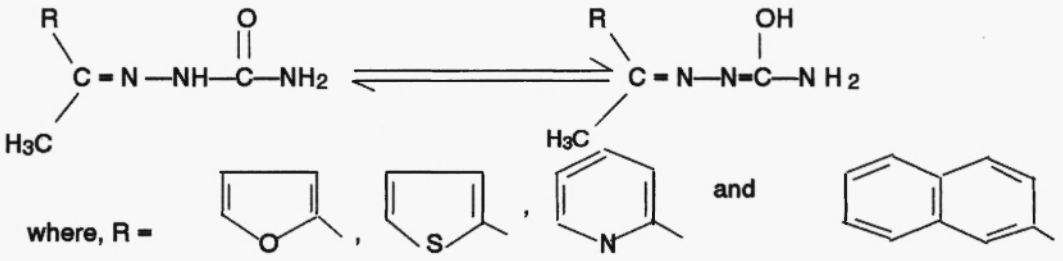
Synthesis and structural features of some thallium (I) complexes of semicarbazones have been described. The newly synthesised complexes Tl(SCZ), where, SCZ^{-1} is the conjugated base of the SCZH molecule, have been characterized by elemental analyses, conductance measurements, molecular weight determinations and electronic, infrared, ^{1}H and ^{13}C nuclear magnetic resonance spectral studies.

INTRODUCTION

Metal complexes of semicarbazones show activity against small- pox, viral diseases and certain kinds of tumours[1-3]. Semicarbazones also constitute an important class of nitrogen donor ligands[4]. Although, a number of references are available on the complexes of these ligands with transition[5-7] and non- transition[8-10] elements, there has been almost no work on the corresponding thallium (I) complexes with these ligands. The IIIrd Main Group elements form tetra-[11], penta-[12] and hexa-[13] coordinated complexes usually, but unusual two coordination state for thallium complexes have been recognised and described in the present paper, which is also evident by the isolation of dithio phosphoric acid[14], dithiophosphinates[15], dithiocarbamates[16] of thallium and $Me_3Si(Me_3CO)(Me_3CNTl)$[17]. It is therefore, considered of interest to synthesize such derivatives by reacting thallous chloride with the following semicarbazones :







EXPERIMENTAL

All the chemicals were distilled and dried by standard methods. The ligands were prepared by the procedures reported elsewhere[18,19] and analyzed before use. The ligands used in the present paper are:

Furfuraldehyde semicarbazone	($C_6H_7N_3O_2$)	(L_1H)
2-Thiophenecarboxaldehyde semicarbazone	($C_6H_7N_3SO$)	(L_2H)
3-Indolecarboxaldehyde semicarbazone	($C_{10}H_{10}N_4O$)	(L_3H)
Cinnamaldehyde semicarbazone	($C_{10}H_{11}N_3O$)	(L_4H)
2-Acetylfuran semicarbazone	($C_7H_9N_3O_2$)	(L_5H)
2-Acetylthiophene semicarbazone	($C_7H_9N_3SO$)	(L_6H)
2-Acetylpyridine semicarbazone	($C_8H_{10}N_4O$)	(L_7H)
2-Acetylnaphthalene semicarbazone	($C_{13}H_{13}N_3O$)	(L_8H)

Synthesis of Thallium (I) Complexes

For the synthesis of these complexes, thallous chloride (0.66- 1.91 g) was mixed with equimolar amount of the sodium salt of the ligand (0.62-1.51 g) which was prepared by treating the ligand (0.56-1.33 g) with sodium metal (0.06-0.18 g) in dry methanol (40 ml). The methanolic mixture was refluxed for about 18 hours. Sodium chloride, precipitated as a white solid, was removed and the complexes were dried under vacuum. Their physical properties and analytical data are given in Table I.

Analytical Methods and Physical Measurements

Carbon and hydrogen analyses were carried out at the Microanalytical Laboratory of the Department. Nitrogen was determined by the Kjeldahl's method[20]. Sulfur was determined as barium sulphate by Messenger's method[21]. Thallium was estimated as thallium chromate[22]. Molecular weights were determined in THF by the Ebullioscopic method. Electronic spectra were recorded on Hitachi U-2000 Spectrophotometer. IR spectra were recorded as KBr pellets on a Perkin-Elmer 577 Grating Spectrophotometer. The ^1H and ^{13}C NMR spectra were recorded on a Jeol FX-90 Q Spectrometer in $CDCl_3$ and methanol using TMS as the internal standard.

RESULTS AND DISCUSSION

The reactions of thallous chloride with the monosodium salt of semicarbazones (Na.SCZ) in 1:1 molar ratio in anhydrous methanol proceed smoothly with the elimination of sodium chloride. These reactions can be represented by the following equation :

$$TlCl + Na.SCZ \xrightarrow{\text{Methanol}} Tl(SCZ) + NaCl$$

Table I - Analyses and Physical Properties of Thallium (I) Complexes

Compound and Empirical formula	Colour	M.P. (°C)	Yield (%)	Analyses (%) C Found (Calcd.)	H Found (Calcd.)	N Found (Calcd.)	Tl Found (Calcd.)	Mol. Wt. Found (Calcd.)
$Tl(L_1)$	Light brown	110d	80	19.98	1.64	11.06	56.78	370.80
$C_8H_6N_3O_2Tl$				(20.21)	(1.69)	(11.78)	(57.32)	(356.50)
$Tl(L_2)$	Light brown	152d	86	18.98	1.58	10.86	54.02	385.15
$C_8H_6N_3SOTl$				(19.34)	(1.62)	(11.27)	(54.85)	(372.56)
$Tl(L_3)$	Dark brown	92d	75	29.25	2.19	13.33	49.94	421.73
$C_{10}H_9N_4OTl$				(29.61)	(2.23)	(13.81)	(50.39)	(405.57)
$Tl(L_4)$	Yellow	183d	90	30.16	2.51	10.32	51.62	412.75
$C_{10}H_{10}N_3OTl$				(30.59)	(2.56)	(10.70)	(52.05)	(392.58)
$Tl(L_5)$	Yellow	105d	88	22.35	2.12	10.98	54.58	396.60
$C_7H_8N_3O_2Tl$				(22.69)	(2.17)	(11.34)	(55.15)	(370.53)
$Tl(L_6)$	Yellow	175d	85	21.47	2.04	10.48	52.25	404.35
$C_7H_8N_3SOTl$				(21.74)	(2.08)	(10.86)	(52.86)	(386.59)
$Tl(L_7)$	Yellow	125d	82	24.85	2.33	14.11	52.92	411.23
$C_8H_9N_4OTl$				(25.18)	(2.37)	(14.68)	(53.56)	(381.55)
$Tl(L_8)$	Light yellow	240d	95	35.87	2.75	9.97	48.06	453.18
$C_{13}H_{12}N_3OTl$				(36.25)	(2.80)	(9.75)	(47.45)	(430.63)

d = decomposed

The resulting coloured solid complexes are soluble in most of the common organic solvents and their molar conductance values (10-14 ohm^{-1} cm^2 mol^{-1}) in DMF show them to be non-electrolytes (non-electrolytes generally have less than 20 ohm^{-1} cm^2 mol^{-1} molar conductance values). All the complexes were found to be monomeric as revealed by their molecular weights.

Spectral Studies

The electronic spectra of the ligands and their thallium complexes have been recorded in anhydrous methanol. The maxima at ~260 and ~315 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 ligands show a broad band at ~350 nm due to n - π^* transitions within

the C= N chromophore[8]. In the spectra of complexes, this band shows a bathochromic shift[23] due to the polarization in the C= N bond caused by the metal ligand electron interaction during the chelation.

In the IR spectra of the ligands, a broad band in the region 3100- 3160 cm^{-1} due to ν NH vibrations, disappears in the spectra of the complexes suggesting the loss of a proton on the α - nitrogen on complexation with the metal ion. Sharp and strong bands in all the ligands in the region 1590-1615 cm^{-1} can be assigned to the stretching mode of the C= N group. In the case of metal complexes, however, two bands are observed at 1620+ 15 cm^{-1} and 1590+ 10 cm^{-1} suggesting the presence of two dissimilar C=N groups[24]. The shifting of band towards higher frequency side indicated the coordination of the azomethine nitrogen to the metal atom[25], whereas the lower frequency band is due to the uncoordinated azomethine group[24].

The complexes exhibit two bands at ~440 cm^{-1} and ~425cm^{-1} which may be attributed to the different vibrational modes of Tl-O[26] and Tl←N[27], respectively (Table II). In the case of semicarbazones, the bands observed at ~3440 and ~3320 cm^{-1} are due to asymmetric and symmetric modes of NH_2 group. These bands are observed at almost the same positions in the spectra of metal complexes, suggesting the non-involvement of this amino group in chelation[28].

The bonding pattern discussed above gets further support by the proton magnetic resonance spectral studies of the ligands and their corresponding thallium complexes. The broad signals due to NH / OH protons at δ 10.68 (L_1H), 10.88 (L_2H), 11.52 (L_3H), 11.86 (L_4H), 10.90 (L_5H), 10.68 (L_6H), 10.83 (L_7H) and 10.65 ppm (L_8H) in the ligands disappear in the case of thallium complexes indicating the coordination of oxygen to thallium. The azomethine proton signals (- CH=N) appearing at δ 7.94-8.16 ppm and methyl proton signals (H_3C- C= N) appearing at δ 1.72-2.32 ppm in the ligands undergo deshielding in the corresponding thallium complexes, confirming the coordination of the azomethine nitrogen to the thallium atom (Table III).

Table II — IR Spectral Data (ν, cm^{-1}) of Semicarbazones and their Corresponding Thallium (I) Complexes

Compound	NH	C=N	Tl-O	Tl<—N
L_1H	3100-3160bw	1590s	-	-
$Tl(L_1)$	-	1625bm	440bm	420s
L_2H	3100-3150bw	1600s	-	-
$Tl(L_2)$	-	1630bw	445m	430s
L_3H	3100-3140bm	1610s	-	-
$Tl(L_8)$	-	1635bm	450bw	425s
L_4H	3120-3160bm	1595s	-	-
$Tl(L_4)$	-	1620bm	440m	420m
L_5H	3100-3140bw	1610s	-	-
$Tl(L_5)$	-	1630bw	450w	420s
L_8H	3100-3140bs	1615s	-	-
$Tl(L_8)$	-	1635bm	445m	430m
L_7H	3100-3150bm	1615m	-	-
$Tl(L_7)$	-	1625bm	450bw	430m
L_8H	3120-3160bm	1610m	-	-
$Tl(L_8)$	-	1635bw	445bm	425s

bm = broad medium, bs=broad sharp, bw=broad weak, m = medium, s = sharp and w = weak.

^{13}C NMR spectral studies (Table IV) show the reasonable shifting of the amido and azomethine carbons in the metal complexes, further supporting the coordination of oxygen and nitrogen to the central metal atom.

On the basis of the above discussions, a bicoordinated structure (Foot note of Table IV) has been proposed for the resulting complexes.

Table III - ^{1}H NMR Spectral Data (δ , ppm) of Semicarbazones and their Corresponding Thallium (I) Complexes

Compound	-NH (bs)	Aromatic (m)	- NH_2 (bs)	Azomethine (s)	-CH_3 (s)
L_1H	10.68 (1H)	7.69-6.32 (3H)	2.55 (2H)	7.94(1H)	-
$Tl(L_1)$	-	7.94-6.44 (3H)	2.62 (2H)	8.00 (1H)	-
L_2H	10.88 (1H)	6.89-6.42 (3H)	2.52 (2H)	7.96(1H)	-
$Tl(L_2)$	-	7.04-6.58 (3H)	2.57 (2H)	8.12 (1H)	-
L_3H	11.52 (1H)	7.76-6.32 (6H)	2.56 (2H)	8.16(1H)	-
$Tl(L_3)$	-	7.92-6.40 (6H)	2.64 (2H)	8.48 (1H)	-
L_4H	11.86 (1H)	8.08-7.45 (5H)	2.48 (2H)	8.16(1H)	-
$Tl(L_4)$	-	8.16-7.52 (5H)	2.52 (2H)	8.40 (1H)	-
L_5H	10.90 (1H)	7.68-6.64 (3H)	2.32 (2H)	-	1.72(3H)
$Tl(L_5)$	-	7.76-6.80 (3H)	2.36 (2H)	-	1.84 (3H)
L_8H	10.68 (1H)	7.84-7.20 (3H)	2.84 (2H)	-	2.32(3H)
$Tl(L_6)$	-	7.96-7.36 (3H)	2.96 (2H)	-	2.48 (3H)
L_7H	10.83 (1H)	7.93-7.34 (4H)	2.12 (2H)	-	1.80(3H)
$Tl(L_7)$	-	8.00-7.36 (4H)	2.16 (2H)	-	1.92 (3H)
L_8H	10.65 (1H)	8.64-7.56 (8H)	2.88 (2H)	-	1.88(3H)
$Tl(L_8)$	-	8.68-7.64 (8H)	3.00 (2H)	-	2.09 (3H)

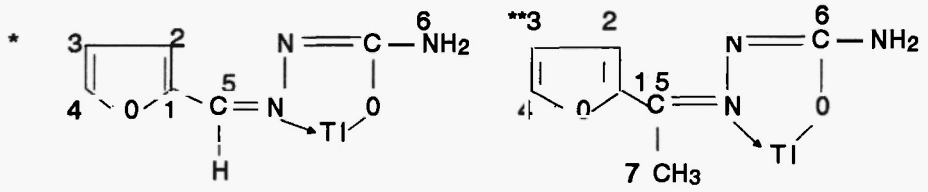
bs = broad singlet, m = multiplet and s = singlet

Table IV - ^{13}C NMR Spectral Data (δ, ppm) and C-H coupling constants (Hz) of the Ligands and their Thallium (I) Complexes

Compund	Carbons
L_1H	179.64 (C-6), 169.53 (ds, $^1J_{CH}$ = 177.00, C-5), 151.21 (st, $^2J_{CH}$ = 3.25, C-1), 145.14 (dd, $^1J_{CH}$ = 163.58, $^2J_{CH}$=5.79, C-4), 133.01 (dd, $^1J_{CH}$ = 163.57, $^2J_{CH}$ = 7.32, C-2), 114.79 (dt, $^1J_{CH}$ = 173.34, $^2J_{CH}$ = 12.81, C-3)
$Tl(L_1)$*	170.14 (C-6), 160.30 (ds, $^1J_{CH}$ = 170.14, C-5), 151.29 (st, $^2J_{CH}$ = 5.18, C-1), 144.52 (dd, $^1J_{CH}$ = 162.26, $^2J_{CH}$=6.12, C-4),132.60 (dd, $^1J_{CH}$ = 165.04, $^2J_{CH}$ = 6.97, C-2), 112.34 (dt, $^1J_{CH}$ = 170.24, $^2J_{CH}$ = 14.00, C-3)
L_5H	177.35 (C-6), 160.07 (sq, $^2J_{CH}$ = 3.90, C-5), 153.02 (sd, $^2J_{CH}$ = 3.41, C-1), 144.19 (dd, $^1J_{CH}$ = 164.80, $^2J_{CH}$=6.10, C-4), 139.80 (dd, $^1J_{CH}$ = 163.57, $^2J_{CH}$ = 7.32, C-2), 112.17 (dt, $^1J_{CH}$ = 172.12, $^2J_{CH}$ = 11.60, C-3), 12.33 (qs, $^1J_{CH}$ = 118.86, C-7).
$Tl(L_5)$**	173.01 (C-6), 157.61 (sq, $^2J_{CH}$ = 5.79, C-5), 153.13 (sd, $^2J_{CH}$ = 5.12, C-1), 143.14 (dd, $^1J_{CH}$ = 163.57, $^2J_{CH}$=6.71, C-4), 139.64 (dd, $^1J_{CH}$ = 164.79, $^2J_{CH}$ = 7.02, C-2), 112.12 (dt, $^1J_{CH}$ = 169.19, $^2J_{CH}$ = 12.73, C-3), 12.33 (qs, $^1J_{CH}$ = 114.62, C-7).

dd = doublet doublet, ds=doublet singlet, dt=doublet triplet,

qs= quatret singlet, sd= singlet doublet, sq= singlet quatret and st= singlet triplet.



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REFERENCES

1. N. Orlova, V.A. Aksensova, V.A. Sclidovkin, N.S. Bagdanvova and G.N. Perksin, Russ. Pharm. Toxicol., (1968), 348.

2. D.J. Baver, L.S. Vincent, C.H. Kempe and A.W. Downie, Lancet., **20** (1963), 494.

3. H.G. Petering, H.H. Buskik and G.E. Underwood, Cancer Res., 64 (1964), 367.

4. P.L. Maurya, B.Y. Agrawala and A.K. Dey, J. Indian Chem. Soc., **57** (1960), 275.

5. S. Chandra, Synth. React. Inorg. Met. - Org. Chem., 13 (1983), 89.

6. Neeta Kanoongo, R.V. Singh and J.P. Tandon, Synth. React. Inorg. Met-Org. Chem., **17** (1987), 837.

7. A. Garg and J.P.Tandon, Synth. React. Inorg. Met.-Org. Chem., **18** (1988), 705.

8. Kiran Singh, R.V. Singh and J.P. Tandon, Polyhedron, **7** (1988), 151.

9. Kiran Singh, R.V. Singh and J.P. Tandon, J. Prakt. Chem., **330** (1988), 621.

10. V.P. Singh and R.V. Singh, Nat. Acad. Sci. Lett., **12** (1989), 311.

11. Mithlesh Agrawal, J.P. Tandon and R.C. Mehrotra, J. Indian Chem. Soc., 56 (1979), 758.

12. J. Lewinski and S. Pasynkiewicz, Inorg. Chim. Acta, **130** (1987), 23.

13. D.F. Evans and D.A. Jakubovic, Polyhedron, **7** (1988), 2723.

14. F. Bonati and G. Minghetti, Istituto di Chimica Generale, (1968), 161.

15. F. Bonati, S. Cenini and R. Ugo, J. Organomet. Chem., 9 (1967), 395.

16. S. Akerstroem, Arkiv for Kemi, **24** (1965), 495.

17. M. Veith and R. Rosler, J. Organomet. Chem., 229 (1982), 131.

18. Neeta Kanoongo, R.V. Singh and J.P. Tandon, Trans. Met. Chem., 13 (1988), 343.

19. Chitra Saxena and R.V. Singh, Synth. React. Inorg. Met.- Org. Chem., **22** (1992), 1061.

20. A.I. Vogel, "A Text Book of Quantitative Inorganic Analysis", ELBS and Longman, (1978), 312.

21. R.V. Singh and J.P. Tandon, Synth. React. Inorg. Met.-Org. Chem., 11 (1981), 109.

22. A.I. Vogel, "A Text Book of Quantitative Inorganic Analysis", ELBS and Longman, (1973), 482.

23. M. Agrawal, J.P. Tandon and R.C. Mehrotra, Indian J. Chem., **18A** (1979), 151.

24. A. Macias, M.C. Rodriguez-Arguelles, M.I. Suarez, A. Sanchez, J.S. Casas and J. Sordo, J. Chem. Soc. Dalton Trans., (1989), 1787.

25. N.C. Bhardwaj and R.V. Singh, Proc. Indian Acad. Sci., 1993, in press.

26. A.G. Lee, J. Chem. Soc., **(A)** (1970), 467.

27. M.C. Castano, A. Sanchez, J.S. Casas, J. Sordo, J.L. Brianso, J.F. Piniella, X. Solans, G. Germain, T. Debaerdemaeker and J. Glaser, Organometallics, **7** (1988), 1897.

28. M.N. Mookerjee, R.V. Singh and J.P. Tandon, Synth. React. Inorg. Met. - Org. Chem., **15** (1985), 13.

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