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A Study on Some Simple and Mixed Ligand *N,N*-Disubstituted Dithiocarbamates of Thallium(III)

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Neutral tris (*N,N*-disubstituted dithiocarbamato) thallium (III) ((TI(III)) has been prepared from acyclic dimethylamine, diethylamine, dipropylamine, dibutylamine, *N*-methylaniline, dibenzylamine, and from piperidine. Mixed ligand dithiocarbamates were found to form by ligand exchange reactions while mixing the simple, symmetric chelates in nonpolar solvents and got separated on preparative TLC layers of silica gel. These chelates were characterised by elemental analyses, IR, ^{1}H NMR, and electronic spectral studies.

Ligand exchange reaction and the formation of corresponding mixed ligand complexes have been reported by some authors for neutral *N,N*-disubstituted dithiocarbamates of some transition elements.[1–4] HPLC[1] and ^{1}H NMR[5] studies have shown that the rate of ligand exchange among the bis-chelates with square planar structure (with vacant axial positions) is faster than in tris-chelates with octahedral structure. The ligand exchange among neutral non-transition metal dithiocarbamates has so far not been studied in detail except the report of Stary and Ruzicka[6] about the formation of dithiocarbamate–dithizone mixed ligand complexes in solution for some Group V-a metalloids. It is also found that works dealing with tris(*N,N*-disubstituted dithiocarbamato)thallium(III) complexes are rare[7] than those of thallium(I) dithiocarbamates. Though Usatenko and Kucenko[8] speak of the relative instability of thallium(III) dithiocarbamates, solvent extraction studies[9] provide them with greater extraction and formation constants. Literature survey revealed that dimethyl and diethyl dithiocarbamates[10–13] of thallium(III) alone have been studied in some detail.

This work reports the preparation and characterisation of some simple symmetric tris (dithiocarbamate)s of thallium(III) from dipropylamine, dibutylamine, dibenzylamine, *N*-methylaniline, and piperidine. This also reports the formation of mixed ligand dithiocarbamates of thallium(III) from symmetric chelates in nonpolar solvents, their separation on preparative TLC layers and characterization.

Experimental

Sodium salts of the *N,N*-disubstituted dithiocarbamic acids were prepared from dimethylamine, diethylamine (BDH samples), dipropylamine (Fluka AG), dibutylamine (Merck-Schuchardt), *N*-methylaniline (BDH), dibenzylamine (KL), and from piperidine (Riedel) following the standard procedure.[7] At 0—5°C, amine, carbon disulfide (both in dioxane) and sodium hydroxide in minimum quantity of water were mixed in equimolar proportions with constant mechanical stirring. The sodium salts formed as white solids were separated by filtration and recrystallized from 2-propanol. Good yields were obtained in dioxane medium than in acetone (reported recently[14]) while this work was in progress).

Thallium(III) tris (dithiocarbamate)s were prepared by mixing the metal ion (Tl(III) prepared from Tl(I) as reported[15]) and sodium salt of the ligand in aqueous solutions in 1:3 molar ratio. The yellowish orange solids precipitated were repeatedly washed with water, dried and recrystallized from chloroform.

Preparation of Mixed Ligand Complexes

20 mM (1M=1 mol dm^{-3}) of a thallium(III) dithiocarbamate (which is to be present in greater proportions) in 40 ml benzene was mixed with 10 mM (in 20 ml benzene) of another thallium(III) dithiocarbamate with different *N*-alkyl substituents and stirred well magnetically for 30 min at room temperature (29 °C). Mixed ligand chelates were formed in solution by the ligand exchange reaction among the symmetric chelates, and the following equilibrium was established.

$$2\mathrm{Tl(S_2CNR_2)_3} + \mathrm{Tl(S_2CNR_2')_3} \rightleftharpoons 3\mathrm{Tl(S_2CNR_2)_2(S_2CNR_2')}.$$

The resulting solution was concentrated under low pressure (0.1 Torr, 1 Torr≈133.322 Pa), spotted on preparative TLC plates (50 to 60 μl of solution per spot) and developed with xylene as the mobile phase. After development, the TLC layers corresponding to the mixed ligand complexes were scrapped off, extracted with minimum quantity of xylene or CCl_4 under inert atmosphere and the solvent was removed in a vacuum evaporator to get the shiny orange crystals of mixed ligand complexes.

Molecular weights were determined cryoscopically in benzene. Elemental analyses (C and H) were performed with a Perkin-Elmer (model 240 B) analyzer. Nitrogen was estimarted by micro Kjeldahl method and sulfur by gravimetry as $BaSO_4$. Electronic spectra were obtained with a Beckmann (Model 25)-UV-visible spectrophotometer in CCl_4. IR spectra were recorded with a Perkin-Elmer (model 199) spectrometer scanning the region 4000 to 200 cm^{-1} in KBr pellets. ^{1}H NMR spectra were recorded on a Varian 60 MHz instrument in CCl_4 ($CDCl_3$ in some cases) with TMS as the internal standard. Photodensitometric studies were made with Carl Zeiss, Jena (GDR) instrument and the spot areas were measured with an Angler Planimeter. Silica gel supplied by BDH were employed for preparing thin layers. All chemicals employed in this study were of analytical grade.

TABLE 1. ANALYTICAL DATA OF SOME SIMPLE AND MIXED LIGAND DITHIOCARBAMATES OF THALLIUM(III)

Complex	Found (Calcd) (%) C	H	N	S	Mol wt	Mp-m/°C	Absorbance in 10^3 cm^{-1} in the visible region (log ε)
A	34.26 (34.39)	5.71 (5.79)	5.78 (5.73)	26.36 (26.23)	758 (733.3)	164	23.5 (3.36)
B	39.52 (39.67)	6.65 (6.66)	5.22 (5.14)	23.62 (23.53)	887 (817.5)	150	23.5 (3.41)
C	52.88 (52.90)	4.11 (4.14)	4.04 (4.11)	18.88 (18.82)	1044 (1021.6)	147	23.2 (3.43)
D	38.35 (38.37)	3.18 (3.22)	5.62 (5.59)	25.68 (25.61)	793 (751.2)	170 (decomp)	23.9 (3.32)
E	31.52 (31.55)	4.35 (4.41)	6.10 (6.13)	28.0 (28.10)	708 (685.2)	180 (decomp)	23.5 (3.30)
F	45.52 (45.58)	3.90 (3.94)	4.89 (4.83)	22.20 (22.13)	883 (869.4)	170 (decomp)	23.4 (3.38)
G	30.04 (30.15)	5.02 (5.06)	6.28 (6.21)	28.5 (28.4)	698 (677.2)	186	23.6 (3.31)
H	32.24 (32.36)	5.29 (5.43)	6.03 (5.96)	27.32 (27.27)	756 (705.3)	182 (decomp)	23.5 (3.32)
I	38.81 (38.83)	4.38 (4.43)	5.47 (5.43)	24.93 (24.87)	787 (773.3)	175 (decomp)	23.4 (3.31)

A: $Tl(S_2CN(n\text{-}C_3H_7)_2)_3$, B: $Tl(S_2CN(n\text{-}C_4H_9)_2)_3$, C: $Tl(S_2CN(CH_2C_6H_5)_2)_3$, D :$Tl(S_2CN(CH_3\ C_6H_5)_2)_3$, E: $Tl(S_2CN(C_5H_{10}))_3$, F: $Tl(S_2CN(CH_3)_2)\cdot(S_2CN(CH_2C_6H_5)_2)_2$, G: $Tl(S_2CN(C_2H_5)_2)_2\cdot(S_2CN(n\text{-}C_3H_7)_2)$, H: $Tl(S_2CN(C_2H_5)_2)_2\cdot(S_2CN(n\text{-}C_4H_9)_2)$, I: $Tl(S_2CN(C_2H_5)_2)_2\cdot(S_2CN(CH_2C_6H_5)_2)$.

Results and Discussion

Dithiocarbamates of thallium(III) ion derived from dipropylamine, dibutylamine, *N*-methylaniline, dibenzylamine, and piperidine are reported for the first time. The results of the elemental analyses presented in Table 1 are in accordance with their tris-chelate chemical compositions. In solid state, these chelates are stable indefinitely, if stored in dark. However in solutions of nonpolar solvents like benzene, chloroform, *etc.*, they decompose after a week. Molecular weight determination showed the presence of monomeric species in solution. Conductivity measurements in nitrobenzene showed their neutral, nonionic character.

On mixing the individual symmetric dithiocarbamates in nonpolar solvents, the unsymmetric mixed ligand complexes are formed and equilibrium is established.

$$2TlL_3 + TlL_3' \rightleftharpoons 3TlL_2L'$$

Photodensitometric studies at 420 nm of the resolved spots on thin layers (spotting known quantities of the stirred mixture)corresponded to about 60 to 65% conversion of symmetric chelates into ternary unsymmetric chelates. The log K values for the formation of these mixed ligand complexes (K=equilibrium constant=$([TlL_2L']^3/[TlL_3]^2[TlL_3'])$ arrived at from the equilibrium concentrations are around 1.36 to 1.45. (compound F=1.36, G=1.44, H=1.41, and I=1.38). The greater log K values observed relative to the statistical value of 0.83 show the stabilization of mixed ligand complexes by solvation or entropy effects. The total area of the spots of symmetric and unsymmetric chelates on the chromatogram is almost equal with the sum of the areas of two spots of the symmetric chelates, spotted separately. The mixed ligand chelates of Tl(III) are found not so labile as other transition metal chelates reported earlier[1–3,16] facilitating their separation on preparative TLC layers. However, the pale yellow streaks observed, with active, nonpolar solvents like chloroform, dichloro methane, *etc.*, as mobile phases indicate their partial disintegration into symmetric complexes. It is also found that with increase in

TABLE 2. THE hR_f VALUES OF SOME SIMPLE AND MIXED LIGAND DITHIOCARBAMATES OF THALLIUM(III)

Complex	Eluent $CHCl_3 : C\text{-}C_6H_{12}$ (1 : 1)	$CHCl_3 : CCl_4$ (1 : 1)	Xylene
I. Symmetric Simple Complexes			
$Tl(Me_2dtc)_3$	13.8	18.6	17.1
$Tl(Et_2dtc)_3$	29.7	40.6	33.3
$Tl(Pr_2dtc)_3$	57.7	67.4	56.6
$Tl(Bu_2dtc)_3$	82.5	95.9	91.4
$Tl((Pip)(dtc))_3$	28.8	35.4	23.8
$Tl(Bz_2dtc)_3$	67.4	81.6	80.0
II. Unsymmetric Mixed Ligand Complexes			
$Tl(Me_2dtc)_2Pr_2dtc$	28.2	44.8	37.8
$Tl(Me_2dtc)_2Bu_2dtc$	42.7	55.2	47.9
$Tl(Me_2dtc)(Bz_2dtc)_2$	30.3	54.1	49.5
$Tl(Et_2dtc)_2Pr_2dtc$	40.0	57.6	46.7
$Tl(Et_2dtc)_2Bu_2dtc$	51.4	67.0	60.8
$Tl(Et_2dtc)_2Bz_2dtc$	38.8	63.0	53.7
$Tl((Pip)(dtc))_2Pr_2dtc$	41.0	53.1	50.2
$Tl((Pip)(dtc))_2Bu_2dtc$	51.2	67.0	60.0
$Tl((Pip)(dtc))_2Bz_2dtc$	48.0	59.2	55.2

Layer thickness 0.25 mm. Activated at 100 °C for half an hour. Ascending development in closed chambers preequilibrated with eluent vapours for 1 h. Mobile phase movement upto 11 cm from the spotted region. $C\text{-}C_6H_{12}$=Cyclohexane solvent phase polarity, the disintegration is accelerated, *i. e.*, in the order.

xylene < toluene < benzene < chloroform
< dichloromethane.... .

The formation of diagonally arranged spots on two dimensional TLC plates, as reported earlier,[1] with moderately polar mobile phases containing $CHCl_3$ or CH_2Cl_2 also support their instability in polar solvents. Since Moriyasu and Hashimoto[2] showed that ligand exchange is dependent only on statistical factor, the nonpolar solvent molecules surrounding the neutral mixed ligand chelate molecules in solution may be presumed to prevent their collision among themselves, which lead to their disintegration. The hR_f values reported in Table 2 show that these mixed ligand chelates are intermediate in their migratory behaviour with respect to their parent chelates.

Electronic Spectra. All simple and mixed ligand dithiocarbamates show strong absorptions in the UV region around $38.5\times10^3\,cm^{-1}$ due to π–π^* transition.[17] Absorption maxima in the visible region around $23.5\times10^3\,cm^{-1}$ (log ε 3.3 to 3.4) for simple chelates (n–π^* transition) are considerably broadened for mixed ligand chelates (from 23.7 to 23.4×10^3 cm^{-1}, Figs. 1 and 2 and Table 1).

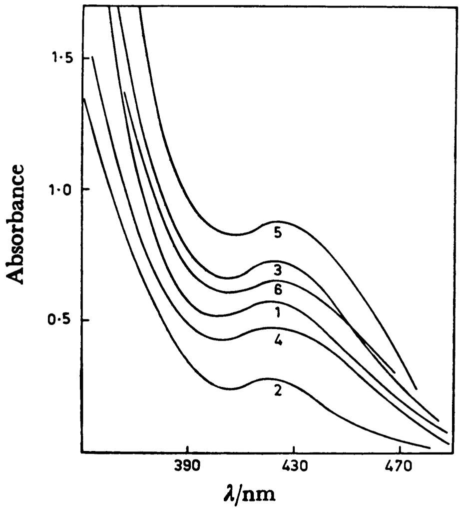

Fig. 1. Absorption spectra of symmetric simple dithiocarbamates of Thallium(III) in CCl_4.
1: $Tl(Me_2\,dtc)_3=2.5\times10^{-4}$ M, 2: $Tl(Et_2\,dtc)_3=1.4\times10^{-4}$ M, 3: $Tl(Pr_2\,dtc)_3=3.0\times10^{-4}$ M, 4: $Tl(Bu_2dtc)_3=1.8\times10^{-4}$ M, 5: $Tl(Bz_2\,dtc)_3=3.3\times10^{-4}$ M, 6: $Tl((Pip)(dtc))_3=3.3\times10^{-4}$ M.

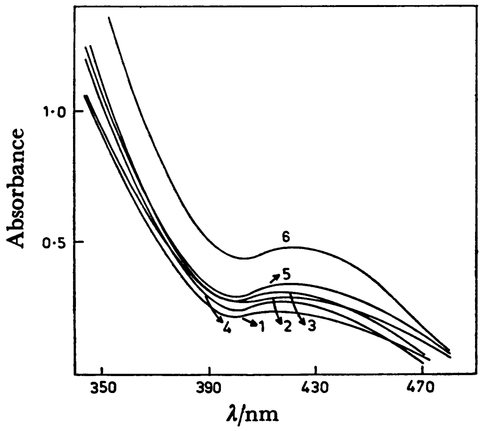

Fig. 2. Absorption spectra of some unsymmetric mixed ligand dithiocarbamates of Thallium (III) in CCl_4.
1: $Tl((Pip)(dtc))_2(Pr_2\,dtc)=1.2\times10^{-4}$ M, 2: $Tl((Pip)(dtc))_2(Bz_2dtc)=1.4\times10^{-4}$ M, 3: $Tl(Me_2\,dtc)_2(Pr_2\,dtc)=1.4\times10^{-4}$ M, 4: $Tl(Me_2\,dtc)_2(Bu_2\,dtc)=1.2\times10^{-4}$ M, 5: $Tl(Me_2\,dtc)(Bz_2\,dtc)_2=1.4\times10^{-4}$ M, 6: $Tl(Et_2\,dtc)_2(Pr_2\,dtc)=2.3\times10^{-4}$ M.

TABLE 3. ^{1}H NMR SPECTRAL DATA OF SOME SIMPLE AND MIXED LIGAND COMPLEXES OF THALLIUM(III) (IN CCl_4+TMS)

Complexe	A	B	C	D
$Tl(Me_2dtc)_3$	6.88(18 s)	—	—	—
$Tl(Et_2dtc)_3$	5.93(12 q)	8.47(18 t)	—	—
$Tl(Pr_2dtc)_3$	6.39(12 t)	8.14(12 m)	9.07(18 t)	—
$Tl(Bu_2dtc)_3$	6.46(12 t)	8.81(12 m)	8.92(12 m)	9.13(18 t)
$Tl(Bz_2dtc)_3$	4.74(12 s)	2.44(30 s-ϕ)	—	—
$Tl(Bu_2dtc)_2(Me_2dtc)$				
Me_2dtc	6.61(6 s)	—	—	—
	6.44(6 s)	—	—	—
Bz_2dtc	4.87(4 s)	2.74(20 s-ϕ)	—	—
	5.07(4 s)	—	—	—
$Tl(Et_2dtc)_2(Pr_2dtc)$				
Et_2dtc	5.87(8 s)	8.41(12 t)	—	—
Pr_2dtc	6.14(4 t)	8.00(4 m)	8.82(6 t)	—
$Tl(Et_2dtc)_2(Bu_2dtc)$				
Et_2dtc	6.28(8 q)	8.54(12 t)	—	—
Bu_2dtc	6.34(4 t)	8.67(4 m)	8.81(4m)	9.09(6 t)
$Tl(Et_2dtc)_2(Bz_2dtc)$				
Et_2dtc	6.22(8 q)	8.61(12 t)	—	—
Bz_2dtc	5.11(2 s)	2.83(10 s-ϕ)	—	—
	4.91(2 s)	—	—	—

s = singlet; t = triplet; q = quartet; m = multiplet.

Infrared Spectra. The characteristic absorption due to 'thioureide' bond (N=C) is observed in the region 1470 to 1490 cm^{-1}. The mixed ligand complexes show uniformly greater ν(C=N) infrared absorption frequencies corresponding to the increased flow of electron from N-atom to donor centres resulting in stronger M–S bond and more stable chelates. However, in general, for mixed ligand complexes, the dithiocarbamate group present in greater proportions determines their IR spectral characteristics. For simple chelates, the ν(C=N) frequencies are in the order diethyl->dipropyl->dibutyl->pentamethylene->dibenzyldithiocarbamates with respect to *N*-substituents.

The inductive effect of benzyl groups and the rigid heterocyclic ring structure of piperidino group[18] restrict the easy drift of electrons from N to C-atom resulting in decreased C=N bond order in their chelates. Though basic character increases from dimethylamine to dibutylamine, the increasing *N*-alkyl chain length (by mass effect) prevent[19] the electron flow from N to C-atom *via* hyperconjugation. The ν(C=S) frequencies are observed as single and strong peaks in the region 980 to 1005 cm^{-1} indicating the bidentate nature of dithiocarbamate moieties.[20] The increased ν(C=N bond order generally resulted in decreased ν(C=S) frequencies.

^{1}H NMR Spectra. Table 3 shows the ^{1}H NMR spectral data of some simple and mixed ligand dithiocarbamates of thallium(III). The α-proton signals are shifted significantly to new energy regions (mostly in downfield direction) in mixed ligand complexes in addition to the observation of new peaks for some mixed ligand chelates. The splitting of α-proton signals of methyl and benzyl groups in Tl (die. dtc)$_2$ (dibenz. dtc) (Table 3) and Tl (dime. dtc) (dibez. dtc)$_2$ observed may be due to complex stereochemical positioning of the two benzyl and methyl groups. In moderately polar $CDCl_3$+TMS solvent, the ^{1}H NMR signals of the mixed ligand chelates gradually get shifted to the regions as in parent chelates indicating their disintegration as discussed earlier. This observation as against that of Duffy[16] for iron(III) dithiocarbamates show the greater stability of thallium(III) mixed ligand chelates and also the importance of ^{1}H NMR spectra in the study of ligand exchange reactions as observed earlier.[4]

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