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II. CHEMISTRY

Coordination Compoudns

STUDIES ON MIXED LIGAND COMPLEXES OF THALLIUM(I) HALIDES : INTERACTION OF THALLIUM(I) MONO- AND DIPHENYL THIOUREA HALIDES WITH 2, 2'-DIPYRIDYL AND 1, 10-PHENANTHROLINE

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Complexes of Thallium(I) halides with phenyl thiourea and diphenyl thiourea and their adducts with dipyridyl and o-phenanthroline have been synthesised and characterised with elemental analyses, m.p., molar conductance and infrared spectra. Thallium(I) forms mono or bicoordinate complexes (Pfeiffer & Werdelmann, 1950) with thioureas and still is capable of coordinating with strong coordinating agents to achieve higher coordination number.

Keywords : Thallium Halides; Complexation; Substituted Thioureas; Heterocyclic Amines.

INTRODUCTION

THE chemistry of Tl(I) has some resemblance with Ag(I) and Cu(I) as far as the behaviour of halides is concerned. Like Cu(I) and Ag(I), Tl(I) ion forms mono or bicoordinate complexes as reported by Pfeiffer and Werdelmann (1950) and Psheritsyn and Prokofena (1959) and still has ample room to accommodate some strong coordinating agent in order to achieve its coordination maximum.

EXPERIMENTAL

Reagents:

Monophenylthiourea (PTU), Diphenylthiourea (DPTU) and thallous chloride were all B. D. H. products. 1, 10-phenanthroline and 2, 2'-dipyridyl were Analar reagents.

Preparation of the Complexes:

To a 50 ml well stirred suspension of thallium(I) halide (2×10^{-1}M) in ethanol, 50 ml alcoholic solution of PTU/DPTU ($1\times10^{-1}M$) was added with constant shaking. The resulting mixture was warmed over a water bath for 5–10 minutes followed by intermittent stirring for about half an hour. The mixture was then centrifuged. The clear solution was separated for crystallization whereas the residue consisting mainly of Tl(I) halide was rejected. The solution was concentrated and left for crystallization. Crystals of the complex appeared after about 6 hours.

For the preparation of mixed ligand complexes, equimolar ethanolic solutions of Tl(I) halide-substituted thiourea complex and the heterocyclic amine were mixed

TABLE I

Chemical analyses and some characterizing data of thallium(I) complexes

	Compounds	Metal (%)	Carbon (%)	Hydrogen (%)	Nitrogen (%)	M.Pt. °C	Λ M Ohm^{-1} cm^2 mole^{-1}
1.	Pentakis (PTU) Tl(I) chloride $C_{35}H_{40}ClN_{10}S_5Tl$	20.45 (20.11)	41.06 (41.34)	3.96 (3.93)	13.98 (13.78)	152	32.5
2.	Chloropentakis (PTU) mono (dipy) thallium (I) $C_{45}H_{48}ClN_{12}S_5Tl$	18.44 (17.43)	46.28 (46.07)	4.12 (4.09)	13.84 (13.33)	124	12.8
3.	Chloropentakis (PTU) mono (o-phen) Thallium (I) $C_{47}H_{48}ClN_{12}S_5Tl$	17.14 (17.08)	46.64 (46.15)	4.24 (4.01)	14.48 (14.04)	132	8.4
4.	Pentakis (PTU) Tl(I) bromide $C_{35}H_{40}BrN_{10}S_5Tl$	20.12 (19.27)	38.82 (39.60)	3.64 (3.77)	13.58 (13.20)	157	46.0
5.	Bromo Pentakis (PTU) mono-(dipy) Thallium (I) $C_{45}H_{48}BrN_{12}S_5Tl$	16.25 (16.79)	43.76 (44.38)	3.88 (3.94)	13.84 (13.80)	102	18.5
6.	Bromo Pentakis (PTU) mono-(o-phen) Thallium (I) $C_{47}H_{48}BrN_{12}S_5Tl$	16.84 (16.47)	44.94 (45.46)	3.72 (3.84)	13.56 (13.54)	138	7.6
7.	Mono (DPTU) Tl(I) chloride $C_{13}H_{12}ClN_2STl$	43.84 (43.65)	32.64 (33.32)	2.28 (2.56)	5.96 (5.98)	155	22.7
8.	Chloro mono (DPTU) mono (dipy) Thallium (I) $C_{23}H_{20}ClN_4STl$	31.25 (32.73)	44.52 (44.20)	3.18 (3.20)	8.98 (8.96)	135	3.4
9.	Chloro mono (DPTU) mono (o-phen) Thallium (I) $C_{25}H_{20}OClN_4STl$	31.48 (31.52)	47.02 (46.27)	3.22 (3.08)	8.98 (8.63)	135	3.4
10.	Mono (DPTU) T(I) bromide $C_{13}H_{12}BrN_2STl$	38.88 (39.86)	31.68 (30.43)	2.53 (2.34)	5.44 (5.46)	230	33.6
11.	Bromo mono (DPTU) mono (dipy) Thallium (I) $C_{23}H_{20}BrN_4STl$	30.68 (30.55)	40.84 (41.26)	2.98 (2.99)	8.44 (8.37)	134	14.3
12.	Bromo mono (DPTU) mono (o-phen) Thallium (I) $C_{25}H_{20}BrN_4STl$	24.52 (24.49)	42.82 (43.30)	2.84 (2.88)	8.12 (8.08)	180	6.7
13.	Bis (DPTU) Thallium (I) iodide $C_{26}H_{24}IN_4STl$	25.81 (25.93)	39.54 (39.59)	3.02 (3.04)	7.24 (7.10)	160	41.1
14.	Iodo bis (DPTU) mono (dipy) Thallium (I) $C_{36}H_{32}IN_6S_2Tl$	21.24 (21.64)	45.26 (45.75)	3.44 (3.38)	8.82 (8.89)	142	8.4
15.	Iodo bis (DPTU) mono (o-phen) Thallium (I) $C_{38}H_{32}IN_6S_2Tl$	20.94 (21.10)	47.44 (47.09)	3.46 (3.30)	8.62 (8.67)	175	5.9

Calculated values are given in parenthesis.
PTU = phenyl thiourea, DPTU = Diphenyl thiourea, dipy = 2, 2′-dipyridyl o-phen= 1, 10-phenanthroline.

in equimolar proportion. The mixed ligand complex precipitated and settled down. The precipitate was separated and washed several times with alcohol and was finally dried in vacuo over CaO.

The C, H and N analyses were carried out by microanalytical laboratory of this department and Tl was estimated gravimetrically as given by Furman (1962).

The molar conductances of the complexes were measured in DMSO using a Philips Conductivity Bridge model PR 9500 with a dip type conductivity cell.

Infrared spectra were recorded with a Beckman IR-20 for the range 3–16 μ using KBr pellets and in the far infrared range (16–50 μ) using a Beckman IR 5A fitted with a CsBr prism and using nujol mulls.

Results and Discussion

1 : 5 and 1 : 1 complexes are formed by the interaction of Tl(I) halides and PTU and DPTU respectively with the exception of Tl(I) iodide which gives a 1 : 2 product with DPTU. The mixed ligand complexes are insoluble in water and common organic solvents.

All the Tl(I) halide-substituted thiourea complexes have molar conductances (1×10^{-3}M in DMSO) in the range of 22 to 46 ohm^{-1} cm^2 $mole^{-1}$ suggesting 1 : 1 electrolytic behaviour. Molar conductances of the mixed ligand complexes in DMSO (1×10^{-3}M) fall in the range of 3 to 18 ohm^{-1} cm^2 $mole^{-1}$ possibly indicating a non-electrolytic nature and therefore the formation of 8 and 4 coordinate complexes of the type Tl (o-phen or dipy) $(PTU)_5$ × and Tl (o-phen or dipy) (DPTU) X. Geary (1971) has reported molar conductances for different electrolytes which have been used for comparison.

All the substituted thiourea complexes presumably show coordination through nitrogen which is inferred by the typical changes taking place in the regions of NH deformation and CN antisymmetric stretchings, C-S stretchings and the presence of a strong band at *Ca* 240 cm^{-1} assigned to Tl-N stretches. The i.r. spectra of the heterocyclic amines-substituted thiourea complexes show typical bands of coordinated amines as reported by Rahmani *et al.* (1976, 1977) earlier.

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