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Coordination Behaviour of Thallium(I) towards Triazene-1-Oxides

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Results of coordination behaviour of thallium(I) towards variedly substituted monobasic bidentate/tridentate triazene-1-oxide (TH) are reported. The complexes have also been reacted with dipy/*o*-phen to probe the increase in the coordination number of thallium(I) complexes. The coordination number of thallium(I) is found to be four as well as six. Thallium(I), though a class (b) acceptor, has been found to give reasonably stable complexes with O- and N-donor ligands. The complexes are insoluble in common organic solvents, indicating thereby that they are polymeric in nature. It is believed that the polymerisation occurs through $\overset{1}{N} \rightarrow O$ oxygen leading to linear polymer with four coordination with (TH) and six coordination is case of mixed ligand complexes with dipy/*o*-phen through N-ArCl (*o*-chlorine)

INTRODUCTION

The Tl^+ ion has been proposed as a probe for the benaviour of K^+ ion in biological system[1]. The colourless Tl^+ ion has a radius of 1.54 Å comparable to those of K^+, Rb^+ and Ag^+ (1.44, 1.58 and 1.27 Å). In its chemistry Tl^+ ion, thus, resembles either the alkali or silver(I) ions. In crystalline salts, the Tl^+ ion is usually six or eight-coordinate. Thallium(I) chloride also resembles silver chloride in being photosensitive; it is found to darken in exposure to sunlight. Unlike AgCl, TlCl is insoluble in ammonia. Thallium(I) is found to give rather few complexes with exception of those with halide, oxygen and sulphur ligands. Organic ligands containing O-, N- and S-donor groups are coordinated to TlX. The Tl–X bond has been found to be more covalent compared to alkali metal ions in similar conditions.

Thallium compounds tend to be polymeric rather than ionic. Acetylacetonate has been found as linear polymer with four-coordinate thallium and alkoxides are found to be tetramers[2].

The unipositive state of thallium is quite stable; in aqueous solution it is distinctly more stable than thallium(III).

$$Tl^{3+} + 2e^- \rightarrow Tl^+ \quad (E° = +1.25\ V)$$

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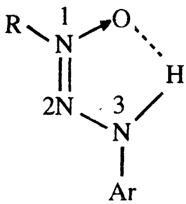
The redox potential has been found to be dependent on pH as well as the presence of complexing anions.

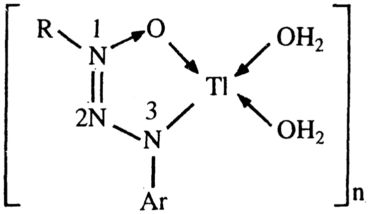
Thallium(III) gives aqua ions $[M(H_2O)_6]^{3+}$ both in solutions and in crystalline state. The ions are acidic.

$$M(H_2O)_6^{3+} \rightleftarrows M(H_2O)_5OH^{2+} + H^+; \quad K_a = 10^{-1}.$$

Our present investigation intends to compare the coordination behaviour of thallium(I) towards variedly substituted monobasic bidentate/tridentate triazene-1-oxides(TH) (I) and their complexes with Tl (I).



I



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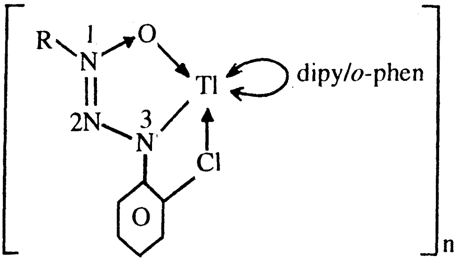

III

EXPERIMENTAL

All chemicals used were of AnalaR grade unless otherwise specified. The ligands were synthesized by following published procedures[3]. Complexes were prepared by interacting AnalaR thallous nitrate, thallic oxide in aqueous-alcoholic medium in 1 : 2, 1 : 3 and 1 : 4 metal ion-ligand and molar ratios. The metal-ligand mixture was treated with sodium acetate buffer to control pH and refluxed on water bath for about 2 h. The contents were filtered and concentrated. On cooling colourless/pale yellow crystals of thallium complexes separated out. The solubilities of the complexes were examined and they were recrystallised from petroleum-ether. The complexes obtained were further treated with depyridyl/*o*-phenanthroline in acetone. The clear solution was filtered and concentrated to get the dipyridyl/*o*-phenanthroline adducts. Thallium was estimated as thallous chromate.[4]

RESULTS AND DISCUSSIONS

Table-1 gives the characterisation data while Table-2 presents the IR spectral band positions. The characterisation data confirms to the stoichiometries $TlT(H_2O)_2$, [TlT. dipy/*o*-phen]. The complexes were invariably white and pale yellow in case of nitro substituents. The complexes blacken after a few days—characteristic of photosensitiveness of thallium salts. Since thallium salts are extremely poisonous, the complexes were prepared in fuming cupboards and handled with gloves. On heating, the complexes did not melt, rather decomposed around 150–155°C. Complexes were found to be insoluble in common organic solvents. To ascertain whether the complexes are of definite composition, these were treated and washed with acetone, alcohols, petroleum ethers etc. before analysis and were found to give consistent analytical results.. The stability of the +1 oxidation state in Group III increases in the sequence Al < Ca < In < Tl. The occurrence of an oxidation state which is 2 less than the group valency is sometimes referred to as the *inert pair effect* but it is important to recognise that

TABLE-1
CHARACTERISATION DATA OF THALLIUM(I) COMPLEXES OF TRIAZENE-1-OXIDES

Ligand complex	Substituents		Analysis % Found (Calcd.)			
	R	Ar	Tl	C	N	H
$TlT_2(H_2O)_2$	CH_3	C_6H_5	51.87 (52.30)	21.32 (21.53)	10.68 (10.76)	2.98 (3.07)
$TlT(H_2O)_2$	C_6H_5	C_6H_5	44.81 (45.13)	31.69 (31.85)	9.17 (9.29)	2.96 (3.09)
$TlT(H_2O)_2$	CH_3	$C_6H_4CH_3$ (*p*)	50.37 (50.76)	23.58 (23.76)	10.28 (10.39)	3.37 (3.46)
$TlT(H_2O)_2$	C_6H_5	$C_6H_4CH_3$ (*p*)	43.46 (43.68)	33.17 (33.40)	8.86 (8.99)	3.59 (3.64)
$TlT(H_2O)_2$	C_6H_5	$C_6H_4NO_2$ (*p*)	40.89 41.04	28.81 (28.97)	11.19 (11.26)	2.57 (2.61)
$TlT(H_2O)_2$	CH_3	$C_6H_4NO_2$ (*p*)	46.73 (46.89)	19.27 (19.31)	12.73 (12.87)	2.46 (2.52)
TlT dipy	CH_3	C_6H_3	41.98 (42.14)	36.99 (37.19)	14.38 (14.46)	2.79 (2.89)
TlT *o*-phen	C_6H_3	C_6H_3	33.97 (34.22)	48.27 (48.32)	11.69 (11.74)	2.96 (3.02)
TlT dipy	CH_3	$C_6H_4CH_3$ (*p*)	40.81 (40.96)	38.48 (38.55)	13.97 (14.05)	3.10 (3.21)
TlT *o*-phen	C_6H_3	$C_6H_4CH_3$ (*p*)	33.06 (33.38)	48.91 (49.09)	11.38 (11.45)	3.38 (3.43)
TlT	CH_3	C_6H_4Cl (*o*)	47.95 (48.05)	19.60 (19.78)	9.80 (9.89)	2.50 (2.59)
TlT	C_6H_3	C_6H_4Cl (*o*)	41.89 (41.93)	29.53 (29.60)	8.59 (8.63)	2.58 (2.67)
TlT dipy	CH_3	C_6H_4Cl (*o*)	39.06 (39.34)	34.68 (34.71)	13.47 (13.50)	2.48 (2.56)
Tl T *o*-phen	CH_3	C_6H_4Cl (*o*)	35.68 (35.88)	39.97 (40.10)	12.29 (12.31)	2.59 (2.63)

this is a description rather than an explaination. The phenomenon is quite general among the heavier elements of the *p*-block (*i.e.*, post-transition elements or B-subgroups). The term *inert pair effect* is sometimes misleading since it implies that the energy required to involve the ns^2 electrons in bonding increases in the sequence Al < Ga < In < Tl. But the sequence is, in fact, In < Al < Tl < Ga. The explaination lies in rather decrease in bond energy with increase in size from Al to Tl so that the energy required to involve the ns^2 electrons in bonding is not compensated by the energy released in forming the two additional bands.[5]

Complexing behaviour of thallium(I) and thallium(III) using sulphur ligands and comparison of the properties of complexes with those of analogous oxygen containing ligands are valuable guides in our present study.[6, 7] A four-coordinated complex with thiosalicylic acid and salicylic acid contained two coordinated water molecules. We have obtained complexes of the formula $[TlT{\cdot}2H_2O]$. The two water molecules have been replaced by chelating nitrogen donor ligands dipy/*o*-phen. The characterization data results have further been supported by infrared studies.

The presence of a strong band at 840 cm^{-1} in the complex indicates the presence of coordinated water.[9] The $\overset{3}{N}$—H stretch of the ligand completely disappears, indicating $\overset{3}{N}$—Tl bond. The $\overset{1}{N} \rightarrow O$ stretch at about 1300 cm^{-1} is considerably lowered to about 1240 cm^{-1}, indicating $\overset{1}{N} \rightarrow O \rightarrow Tl$ electron drainage[9–12]. The results indicate that though Tl(I) is expected to behave like class (b) acceptor, it does give fairly stable complexes with O- and N-donor ligands. The coordination of dipyridyl/*o*-phenanthroline has been confirmed by the identification of Tl(I) dipy/*o*-phen stretch[13, 14] around 730 cm^{-1}, 1170 cm^{-1} and 1420 cm^{-1}. Identification of (Tl—N) band 150 cm^{-1}, (Tl—O) band 330 cm^{-1} and (Tl—Cl) band around 310 cm^{-1} further support to our conclusions[15–17]. There are two expected modes of vibrations for thallium(I)-chlorine stretches: one for terminal chlorine and other for bridging chlorine. The observed thallium(I)-chlorine stretch indicates the presence of bridging chlorine (Table-2).[15] A

TABLE-2

KEY IR BANDS (cm^{-1}) OF THALLIUM(I) COMPLEXES

Ligands/ complexes	Substituents		$\nu(\overset{3}{N}$—H)	$\nu(\overset{1}{N} \rightarrow O)$	ν(Tl—N)	ν(Tl—O)	ν(Tl—Cl)
	R	Ar					
TH	CH_3	C_6H_5	3200 s	1300 s	—	—	—
$TlT(H_2O)_2$	CH_3	C_6H_5	—	1240 s	150 w	325 m	—
$TlT(H_2O)_2$	C_6H_5	C_6H_5	—	1235 s	150 w	330 m	—
TlT dipy	CH_3	C_6H_5	—	1240 s	150 w	330 m	840 s
TlT *o*-phen	CH_3	C_6H_5	—	1240 s	150 w	330 m	840 s
$TlT{\cdot}H_2O$	CH_3	C_6H_4Cl (*o*)	—	1240 s	150 w	330 m	—
TlT dipy	CH_3	C_6H_4Cl (*o*)	—	1240 s	150 w	330 m	840 s
TlT *o*-phen	CH_3	C_6H_4Cl (*o*)	—	1240 s	150 w	330 m	840 s

polymeric structure for complexes of the type [Tl(I)T·$2H_2O$], [Tl(I)T·dipy/*o*-phen] through oxygen bridging and bridging through chlorine atom in case of N-C(Ar)-*ortho*-chloro-substituted triazene-1-oxides has been proposed.

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