

SOME STUDIES IN INORGANIC COMPLEXES*

XVI. THALLIUM(III) COMPLEXES OF 2-AMINOMETHYLPYRIDINE AND 6-METHYL-2-AMINOMETHYLPYRIDINE; TRIS(2,2'-BIPYRIDYL)ALUMINIUM(III) PERCHLORATE

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Water-stable ethylenediamine complexes of thallium(III) of the type $Tl en X_3$ and $Tl en_2 X_3$ ($X = Cl, Br, I$) were first described by Hieber and Sonnenkalb¹ and similar 1,10-phenanthroline and 2,2'-bipyridyl complexes were studied by Sutton.^{2,3} By means of conductance measurements the latter showed that these were ionic substances $[TlB_2X_2][TlX_4]$ and $[TlB_2X_2]X$ ($B =$ chelating base). The formation of the TlB_3^{3+} species was also established. The bronze-red iodo complexes are of particular interest since they show that the cation $[TlI_2(H_2O)_x]^+$ can be stabilized by chelation forming the ions $[TlB_2I_2]^+$. Kulba and Mironov⁴ extended this work including the isolation of the anhydrous salt $[Tlphenan_2][ClO_4]_3$ to which a four-coordinate structure was assigned from conductance measurements in water only. The possible formation of four-coordinate cationic thallium(III) was thought to be worthy of further investigation using the chelating ligands 2-aminomethylpyridine and 6-methyl-2-aminomethylpyridine. The latter ligand having increased donor capacity as well as giving rise to steric effects would enhance the likelihood of four-coordinate cation complex formation by virtue of the methyl group in the 6-position of the pyridine nucleus.

The isolation of the phenanthroline complex $[Alphenan_3][ClO_4]_3$ by Sutton⁵ prompted the present investigation with the ligand 2,2'-bipyridyl.

Results and Discussion

The addition of 2-aminomethylpyridine to thallium(III) halide in molar proportions in water resulted in lightly coloured precipitates of the type $[Tlpic_2X_2][TlX_4]$ in the case of the chloride and the bromide whereas the iodo complex was bronze-red due to $[TlI_4]^-$ ion. By using thallium nitrate with three molar proportions of the ligand in the presence of perchlorate the white salt $[Tlpic_3][ClO_4]_3$ was obtained. Reduction in the proportion of the ligand failed to give the $Tlpic_3^{3+}$ complex the tris complex $Tlpic_3^{3+}$ being obtained. By refluxing the latter in water one molecule of the ligand was replaced by aquo molecules with the formation of the green salt $[Tlpic_2(H_2O)_2][ClO_4]_3$, which because of its colour is probably the *cis*-isomer. Prolonged refluxing of the halido complexes also gave the green substance in dilute solutions. All the halido

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¹ Hieber, W., and Sonnenkalb, F., *Ber. dtsh. chem. Ges.*, B, 1928, **61**, 555.

² Sutton, G. J., *Aust. J. Sci. Res.*, A, 1951, **4**, 654.

³ Sutton, G. J., *Aust. J. Chem.*, 1958, **11**, 120.

⁴ Kulba, F. Ya., and Mironov, V. G., *Zh. neorg. Khim.*, 1959, **76**, 1392.

⁵ Sutton, G. J., *Aust. J. Chem.*, 1963, **16**, 278.

complexes were found to be soluble in ethanol or propanone from which they were crystallizable, the perchlorates being slightly soluble. Conductance measurements in nitrobenzene and nitromethane were in agreement with six-coordinate structures (Table 1), the conductances of uni-univalent electrolytes in these solvents usually being in the vicinity of 27 and 70 mhos $\text{cm}^2 \text{mole}^{-1}$ respectively. By adding aqueous 6-methyl-2-aminomethylpyridine (mepic) to thallium(III) nitrate in the presence of perchlorate and ethanol the white salt $[\text{Tlmepic}_2][\text{ClO}_4]_3$ was obtained. Conductance measurements in the aforementioned solvents showed that this substance was a ter-univalent electrolyte having no perchlorato bonding hence it was assumed to be a four-coordinate complex. No corresponding complex of 2-aminomethylpyridine was obtained even by prolonged refluxing in ethanol. It would therefore seem that thallium(III) is reluctant to form four-coordinate cationic complexes. However, this may be accomplished if the negativity of the donor atom is high enough or if the conditions for the corresponding trischelate complex be made less favourable by steric hindrance.

TABLE I
MOLECULAR CONDUCTANCES OF COMPLEXES AT 10^{-3}M CONCENTRATION

Substance	Nitrobenzene	Nitromethane
$[\text{Tlpic}_2\text{Cl}_2][\text{TlCl}_4]$	28.0	82.0
$[\text{Tlpic}_2\text{Br}_2][\text{TlBr}_4]$	29.6	83.8
$[\text{Tlpic}_2\text{I}_2][\text{TlI}_4]$	26.7	81.0
$[\text{Tlpic}_3][\text{ClO}_4]_3$	85.7	188.4
$[\text{Tlpic}_2(\text{H}_2\text{O})_2][\text{ClO}_4]_3$	88.8	195.2
$[\text{Tlmepic}_2][\text{ClO}_4]_3$	84.9	198.0
$[\text{Aldipy}_3][\text{ClO}_4]_3$	78.3	196.1

By the reaction of 2,2'-bipyridyl and absolutely anhydrous aluminium chloride and perchlorate in ethanol the complex $[\text{Albipy}_3][\text{ClO}_4]_3$ was ultimately formed. It was found to be more soluble than the corresponding phenanthroline complex but also solution stable. Its structure as a six-coordinate complex was verified by conductance measurements in the aforementioned solvents. The absorption spectrum of the complex (max. 2370, 2820 Å, $\log \epsilon$ 4.49, 4.61) was found to be similar to that of the ligand (max. 2370, 2810 Å, $\log 3 \epsilon$ 4.53, 3.48). This indicates little or no double bond character but the complex has a relatively high degree of both solution as well as thermodynamic stability (stable to above 300°) which must be due to strong σ -bond formation.

Experimental

Conductance measurements were made with a Philoscope model GM4249/01 and cell type GM4221. A.R. nitrobenzene was frozen and the crystals separated, treated with Na_2SO_4 and distilled. A.R. nitromethane was purified by drying over CaSO_4 and retaining the fraction boiling at $101\text{--}101.5^\circ$.

(a) *Dichlorobis(2-methylaminopyridine)thallium(III) Tetrachlorothallate(III)*

Thallium(III) chloride tetrahydrate (1.9 g; 5mm) in water (10 ml) was treated with the ligand (0.6 g; 5mm) in water and the white microcrystalline precipitate which formed, filtered, washed with water, and dried in a vacuum desiccator (yield 1.2 g) (Found: C, 16.9; H, 1.8; Tl, 48.8%. Calc. for $C_{12}H_{16}N_4Cl_6Tl_2$: C, 17.2; H, 1.9; Tl, 48.0%).

(b) *Dibromobis(2-picolyamine)thallium(III) Tetrabromothallate(III)*

Experimental procedure (a) was repeated in the presence of lithium bromide (2.0 g) when pale yellow prisms resulted (yield 1.8 g) (Found: C, 13.2; H, 1.0; Tl, 36.7%. Calc. for $C_{12}H_{16}N_4Br_6Tl_2$: C, 13.1; H, 1.4; Tl, 37.1%).

(c) *Di-iodobis(2-aminomethylpyridino)thallium(III) Tetraiodothallate(III)*

Procedure (a) was repeated in the presence of lithium iodide (3 g) when bronze-red microcubes resulted (yield 2.7 g) (Found: C, 10.4; H, 1.0; Tl, 29.1%. Calc. for $C_{12}H_{16}N_4I_6Tl_2$: C, 10.4; H, 1.2; Tl, 29.5%).

(d) *Tris(2-aminomethylpyridino)thallium(III) Perchlorate*

Thallium(III) nitrate trihydrate (2.2 g; 5mm) together with lithium perchlorate (3.0 g) in water (10 ml) was treated with the ligand (1.7 g; 15mm) when white microcrystals resulted (yield 3.6 g) (Found: C, 26.8; H, 3.7; Tl, 25.0%. Calc. for $C_{18}H_{24}N_6Cl_3O_{12}Tl$: C, 26.2; H, 3.1; Tl, 24.8%).

(e) *Diaquobis(2-aminomethylpyridino)thallium(III) Perchlorate*

Procedure (d) was repeated and the product refluxed in water until a bright green colour had developed. The solution was then evaporated (20 ml), filtered, and set aside to crystallize (yield 1.6 g) (Found: C, 19.0; H, 2.6; Tl, 27.1%. Calc. for $C_{12}H_{20}N_4Cl_3O_{14}Tl$: C, 19.0; H, 2.6; Tl, 27.2%).

(f) *Bis(6-methyl-2-aminomethylpyridine)thallium(III) Perchlorate*

Procedure (d) was repeated with the ligand 6-methyl-2-aminomethylpyridine (1.2 g; 10mm) and refluxing the precipitate which formed in ethanol (50 ml) for 1 hr. The pale yellow tetragonal crystals were dried (yield 1.2 g) (Found: C, 22.6; H, 2.8; Tl, 27.7%. Calc. for $C_{14}H_{20}N_4Cl_3O_{12}Tl$: C, 22.5; H, 2.7; Tl, 27.4%).

(g) *Tris(2,2'-bipyridyl)aluminium(III) Perchlorate*

Anhydrous aluminium chloride (1 g) and sodium perchlorate (3 g) were added to anhydrous ethanol (10 ml) at 50° with stirring. The crystalline precipitate which formed was filtered and portion of the filtrate (1.5 ml) added dropwise to a solution of excess bipyridyl (0.5 g) in anhydrous ethanol (4 ml) when only a faint precipitate occurred. It was necessary to evaporate the solution to half-volume and set aside in a freezer to form the white acicular microcrystals. The product was found to be stable to above 300° (yield 0.4 g) (Found: C, 45.0, 45.8; H, 2.7, 3.4; Al, 3.1%. Calc. for $C_{30}H_{24}N_6Cl_3O_{12}Al$: C, 45.4; H, 3.4; Al, 3.4%).

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