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# CYCLOOCTATETRAENETHALLIUM(III) CHLORIDE AND POTASSIUM SALT OF CYCLOOCTATETRAENETHALLIUM(I)

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## SUMMARY

Interaction of the dipotassium salt of cyclooctatetraene with dipyridinium thallium(III) pentachloride in tetrahydrofuran yields cyclooctatetraenethallium(III) chloride which, upon treatment with potassium metal, yields the potassium salt of cyclooctatetraenethallium(I). IR spectra, thermal characteristics and some physical properties of the compounds are reported.

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## INTRODUCTION

Cyclopentadienyl, indenyl and fluorenyl complexes of thallium(III)[1,2] and thallium(I)[3,4] have already been reported. However, there is no reference in the literature regarding the preparation of cyclooctatetraene complexes of either thallium (III) or thallium(I). This paper describes the preparation and characterization of cyclooctatetraenethallium(III) chloride and potassium salt of cyclooctatetraenethallium(I) formed by the reaction of dipotassium salt of cyclooctatetraene with dipyridinium thallium(III) pentachloride and by treating cyclooctatetraenethallium(III) chloride with potassium metal in tetrahydrofuran respectively:

$$(C_5H_6N)_2TlCl_5 + K_2C_8H_8 \rightarrow C_8H_8TlCl + 2C_5H_6NCl + 2KCl$$

$$C_8H_8Tl^{III}Cl + 2K \rightarrow KC_8H_8Tl^{I} + KCl$$

## EXPERIMENTAL

All operations were carried out under anhydrous conditions. Tetrahydrofuran of good grade was further purified by distillation from lithium aluminium hydride. Infrared spectra (in KBr) were recorded on Perkin Elmer Model-137 Spectrophotometer. Thallium was estimated as thallic oxide, potassium as dipotassium sodium cobaltinitrite, chlorine as silver chloride and carbon and hydrogen by microanalytical methods.

Dipyridinium thallium(III) pentachloride was prepared as previously described[5].

### *Preparation of cyclooctatetraenethallium(III) chloride*

Finely dispersed potassium (0.78 g, 0.02 mole) was added to freshly distilled cyclooctatetraene (1.04 g, 0.01 mole) in tetrahydrofuran (150 ml) and the mixture was stirred vigorously for 6–8 h at room temperature. Dipyridinium thallium(III) pentachloride (5.4 g, 0.01 mole) in tetrahydrofuran (75 ml) was gradually added with constant stirring to this solution and the mixture was subsequently boiled under reflux for 10–12 h at 80–85°. It was then filtered through a G-4 sintered glass disc and the residue was washed with tetrahydrofuran. The filtrate, plus washings, on evaporation to dryness under reduced pressure (20–25 mm), gave a dark yellow residue which upon recrystallization from petroleum ether (60–80°) yielded dirty orange $C_8H_8TlCl$ (nc) (60%). (Found: C, 27.64; H, 2.29; Cl, 9.72; Tl, 58.88. $C_8H_8ClTl$ calcd.: C, 27.93; H, 2.34; Cl, 10.31; Tl, 59.42%.)

The compound melted at ca. 120° and is insoluble in most of the common organic solvents. Its IR spectrum shows the following frequencies: 3500 s, 3250 w, 3000 w, 1610 m, 1520 m, 1475 m, 1400 w, 1370 w, 1195 m, 1155 m, 1035 m, 1000 m, 742 m, 700 w $cm^{-1}$.

*Preparation of potassium salt of cyclooctatetraenethallium(I)*

To finely dispersed potassium (0.39 g, 0.1 mole) in tetrahydrofuran (100 ml) was gradually added cyclooctatetraenyl thallium (I) chloride (1.72 g, 0.005 mole) in tetrahydrofuran (50 ml). The other operations were carried out in a manner similar to that described above. The product obtained by recrystallization of the residue from hot petroleum ether was bright orange; $KC_8H_8Tl$, (yield 46%) dec. 95°. (Found: C, 27.01; H, 2.21; K, 10.72; Tl, 57.8. $C_8H_8KTl$ calcd.: C, 27.64; H, 2.32; K, 11.25; Tl, 58.79%.) The product is soluble in benzene, toluene, carbon tetrachloride, chloroform and dichloromethane but is insoluble in alcohol and acetone. The IR spectrum shows the following frequencies: 3500 s, 2930 s, 2350 m, 2200 w, 1650 m, 1600 w, 1550 m, 1455 m, 1390 s, 1190 w, 1095 w, 1030 w, 1005 w, 920 w, 818 m $cm^{-1}$.

## DISCUSSION

The IR spectrum of cyclooctatetraenethallium(III) chloride does not show any absorption in the region 3000–2900 $cm^{-1}$ characteristic of C–H stretching as does uranocene[6] whereas the other absorptions of the $C_8H_8$ moiety are observed *viz.*, 1520, 1475 $cm^{-1}$ (C–C stretching); 1195, 1155, 1035, 1000 $cm^{-1}$ (C–H deformation) and at 742, 700 $cm^{-1}$ (C–H out-of-plane deformation)[7]. Furthermore the appearance of a band at 1610 $cm^{-1}$ indicates the presence of a free C=C bond and hence suggests the tub configuration for cyclooctatetraene in this complex reminiscent of the complex $(C_8H_8)Co(C_5H_5)$[8]. In addition the appearance of a band at 700 $cm^{-1}$ (C–H out-of-plane deformation) suggests ionic character in the bonding between thallium and cyclooctatetraene in the complex.

The IR spectrum of the potassium salt of cyclooctatetraenethallium(I) shows the usual peaks of cyclooctatetraene as discussed above in addition to the absorption band (C–H stretch) at 2930 $cm^{-1}$. A shift in the C–H out-of-plane bending frequencies at 818 $cm^{-1}$ is observed. From the study of the IR spectra of this compound and its tendency to dissolve in organic solvents, we conclude that the bond between the metal atoms and the cyclooctatetraene moiety is predominantly covalent.

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## REFERENCES

1 Narendra Kumar, B. L Kalsotra and R K Multani, *J. Inorg Nucl. Chem* , in press.
2 Narendra Kumar, B L. Kalsotra and R K. Multani, *Chem. Ind* (*Lond*), in press
3 H Meister, *Angew Chem.*, 69 (1957) 533, U S. Patent 2,007,831 (1958)
4 E. O Fischer, *Angew. Chem* , 69 (1957) 207
5 Narendra Kumar, B L. Kalsotra and R. K Multani, *Curr Sci.* (*India*), 41 (1972) 785
6 A Streitweiser Jr and Muller-Westerhoff, *J Amer Chem Soc* , 90 (1968) 7364
7 H P Fritz, *Advan. Organometal. Chem* , 1 (1964) 305
8 A Nakamatra and N Hagihara, *Bull Chem Soc Jap* , 32 (1959) 880