

Thallium(I) Complexes with Some Macrocyclic “Crown” Polyethers

M. E. FARAGO

Chemistry Department, Bedford College, Regent's Park, London NW1 4NS, U.K.

Received October 21, 1976

Complexes of some thallium(I) salts with macrocyclic crown ethers have been prepared. Complexes of benzo-15-crown-5 (I) and 4,5-dibromo-benzo-15-crown-5, (II), appear to have a sandwich structure where two molecules of the ligand are co-ordinated to one thallium ion. Complexes of 18-crown-6, (IV) have a 1:1 crown to metal ratio.

Introduction

Thallium(I) ions will replace potassium in the activation of certain enzymes [1]. Following a suggestion [2] that thallium could be used as a probe for potassium in biological systems, investigations were made into the comparative behaviour of these two ions with potentially chelating anions and with macrocyclic crown ethers [3]. The latter compounds are well known for their ability to form complexes with alkali and alkaline earth metal ions [4]. The crown ethers used in this study are shown in Figure 1.

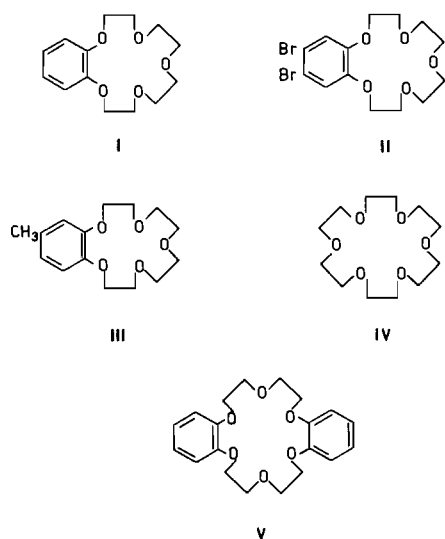


Fig. 1. Structural formulae of macrocyclic crown ethers: I, benzo-15-crown-5; II, 4,5-dibromobenzo-15-crown-5; III, methylbenzo-15-crown-5; IV, 18-crown-6; V, dibenzo-18-crown-6.

A complex of thallium(I) with dibenzo-18-crown-6, V, and 2,4-dinitrophenolate has been reported [3c], but there are no other reports of solid crown ether complexes of the thallium(I) ion, although there are reports of solution studies with crown ethers [4], and with similar macrocycles [5, 6].

In this paper the preparation of complexes of thallium(I) salts with macrocycles I, II and IV are reported. Attempted preparations with III were not successful.

Experimental

Preparation of the Compounds (Table I)

A warm solution of the thallium salt in water was added to a warm solution of the crown ether in acetone. The mixture was set aside until crystals appeared. The compounds were collected on fluted filter papers and air dried. Infrared spectra were measured on a Perkin-Elmer 457 recording spectrophotometer using nujol mulls between KBr plates.

Results

Thallium(I) like potassium [7], strontium, and barium [8] yielded 1:2 complexes with benzo-15-crown-5. In contrast to calcium [8] which yields only 1:1 and sodium [7] which gives both 1:1 and 1:2 complexes. With thallium(I) and 18-crown-6 only 1:1 complexes were found.

The infrared spectrum of the coordinated ligand in $\text{TlSCN}(\text{I})_2$ is almost identical to those of $\text{KBPh}_4(\text{I})_2$ [7a] and $\text{KI}(\text{I})_2$. The X-ray structure of the potassium iodide complex shows a sandwich structure [9] in which the conformation of the macrocycle allows the oxygen atoms to be near the metal ion, and all methylene groups on the side away from the metal ion. The similarity of the infrared spectra of all three benzo-15-crown-5 thallium complexes indicates that they have this structure. That all three complexes show bands expected for non-complexed anions provides additional evidence for this type of structure. $\text{Tl}(\text{SCN})(\text{I})_2 \cdot 2\text{H}_2\text{O}$ shows $\nu(\text{C-N})$ at 2037 cm^{-1} and $\nu(\text{C-S})$ at 745 cm^{-1} . $\text{Tl}(\text{ClO}_3)(\text{I})_2 \cdot \text{H}_2\text{O}$

TABLE I. Analytical Data.

Compound	Molar Proportions M:L Used in Prepn.	Analyses Found			Calc. %		
		C	H	N	C	H	N
Tl(SCN)(I) ₂ ·2H ₂ O	1:1	42.6	5.2	1.5	42.2	5.3	1.6
Tl(SCN)(I) ₂ ·2H ₂ O	1:2	42.3	5.1	1.6	42.2	5.3	1.6
Tl(ClO ₃)(I) ₂ ·H ₂ O	1:2	40.2	5.0	—	40.0	5.0	—
Tl(ClO ₄)(I) ₂	1:2	40.0	4.8	—	39.9	4.8	—
Tl(SCN)(II) ₂	1:2	31.0	3.2	1.2	31.25	3.25	1.25
Tl(SCN)(II) ₃	^a	33.6	3.5	0.8	33.5	3.5	0.9
Tl(ClO ₃)(II) ₂	1:2	30.2	3.1	—	29.5	3.2	—
Tl(benzoate)(II) ₃	1:2	37.1	3.7	—	26.3	4.4	—
Tl(ClO ₄)(IV)	1:1	25.8	4.2	—	26.3	4.4	—
Tl(SCN)(IV)	1:1	29.5	4.6	2.5	29.6	4.6	2.6

^aFrom filtrate.

shows $\nu_4(\text{ClO}_3)$ at 465 cm^{-1} and $\text{Tl}(\text{ClO}_4)(\text{I})_2$ has a strong sharp band $\nu_4(\text{ClO}_4)$ at 621 cm^{-1} . The hydrated compounds show bands around 3500 cm^{-1} and at 3480 and 1630 cm^{-1} .

The infrared spectrum of $\text{Tl}(\text{SCN})(\text{II})_2$ in the region $1000\text{--}1200\text{ cm}^{-1}$ is very similar to that of $\text{Tl}(\text{SCN})(\text{I})_2\cdot 2\text{H}_2\text{O}$ and probably has a similar sandwich structure. $\text{Tl}(\text{SCN})(\text{II})_3$ has a similar infrared spectrum but with additional bands near 900 , 990 and 1220 cm^{-1} , all of which are apparent in the spectrum of the free ligand. This compound thus has two coordinated crown ether groups and one of crystallisation. In both $\text{Tl}(\text{SCN})(\text{II})_2$ and $\text{Tl}(\text{SCN})(\text{II})_3$ the C–N stretching and C–S stretching modes are at 2055 and 755 cm^{-1} respectively, indicating ionic thiocyanate. $\text{Tl}(\text{ClO}_3)(\text{II})_2$ also probably has a sandwich structure with ionic chlorate, $\nu_4(\text{ClO}_3)$ being at 470 cm^{-1} .

The two compounds with 18-crown-6 are anhydrous 1:1 complexes. The thiocyanate complex $\text{Tl}(\text{SCN})(\text{IV})$ has bands from thiocyanate which indicate S-bonding. $\nu_1(\text{C–N})$ is at 2065 cm^{-1} [5], 2055 cm^{-1} (sh) and $\nu_3(\text{C–S})$ is at 718 cm^{-1} . The position of the C–S stretching band has been found to be a useful guide to the bonding of the thiocyanate ligand [10]. Although there is some slight splitting of the C–N stretching band it seems more likely that this is due to site symmetry rather than to two types of coordination of the type found in $\text{Ca}(\text{NCS})_2(\text{I})$ [7b, 8b]. Two kinds of thiocyanate coordination could only be brought about by some kind of bridging. The anhydrous $\text{Tl}(\text{ClO}_4)(\text{IV})$ shows a very strong band at 625 cm^{-1} which can be assigned to $\nu_4(\text{ClO}_4)$ which indicates [8] ionic ClO_4^- . There is, however, a very weak band at 462 cm^{-1} which could be assigned to $\nu_2(\text{ClO}_4)$ which becomes infrared active when the symmetry of the ClO_4^- group is lowered from T_d to C_{3v} . There is possible some weak interaction between the perchlorate group and the thallium ion in this complex.

Discussion

The thallium(I) ion has a pair of anti-bonding s electrons and is expected to form few complexes [3a, 11]. Compounds are known in which this lone pair plays a stereochemical role. In both Tl_3PO_4 [12] and Tl_3BO_3 [13] the coordination about the thallium atom is such that it lies at the apex of a pyramid with three nearest neighbours. The thallium atom is similarly found at the apex of a distorted pentagonal pyramid [14] in the thallium hydroxobenzonic acid complex with phenanthroline.

However, crystal structures of some naturally occurring antibiotics [15] with thallium(I) show coordination patterns resembling those of the alkali metals. The thallium(I) salt of monensin [16] is isomorphous with the potassium salt, having 6-coordination about the metal, while that of grisorixin shows a coordination number of five [17]. The flexible diantennycin forms isomorphous sodium, potassium and thallium complexes, each with seven-fold coordination [18, 19].

In the complexes prepared here those of benzo-15-crown-5 and dibromo-benzo-15-crown-5 appear to contain sandwich structures which are very similar to the potassium analogues [7, 9]. The inert pair of electrons is thus not stereochemically active.

Acknowledgments

The author thanks the Director of Rothamstead Experimental Station, Harpenden, Hertfordshire, and Dr. M. Truter, Head of the Molecular Structures Department, Rothamstead for hospitality when this work was initiated. The members of the Molecular Structures Department, in particular Dr. D. G. Parsons and Dr. J. N. Wingfield are thanked for helpful discussions and advice and gifts of crown ether compounds. Miss M. F. Easton of Bedford College is thanked for carrying out microanalyses.

References

- 1 C. E. Interrisi, *Biochem. and Biophys. Acta*, **173**, 567, 630 (1969). A. T. Ivashchenko and B. S. Balmidhanov, *Izv. Akad. Nauk. Kaz. S.S.R. Ser. Biol.*, **12**, 73 (1974); *C.A.*, **82**, 106257x (1975); C. M. Grisham, R. K. Gupta, R. E. Barnett and A. S. Mildvan, *J. Biol. Chem.*, **249**, 6738 (1974).
- 2 R. J. P. Williams, *Quart. Revs. Chem. Soc.*, **24**, 331 (1970).
- 3 (a) A. G. Lee, *J. Chem. Soc. A*, 2007 (1971).
(b) N. S. Poonia and M. R. Truter, *J. Chem. Soc. Dalton*, 1791 (1972).
(c) N. S. Poonia and M. R. Truter, *J. Chem. Soc. Dalton*, 2062 (1973).
- 4 C. J. Pedersen, *J. Am. Chem. Soc.*, **89**, 7017 (1967).
- 5 J. M. Lehn, J. P. Savage and B. Dietrich, *J. Am. Chem. Soc.*, **92**, 2916 (1970).
- 6 For a review see J. J. Christiansen, D. E. Eatough and R. M. Izatt, *Chem. Rev.*, **74**, 351 (1974) and references therein.
- 7 (a) D. G. Parsons, M. R. Truter and J. N. Wingfield, *Inorg. Chim. Acta*, **14**, 45 (1975).
(b) D. G. Parsons and J. N. Wingfield, *Inorg. Chim. Acta*, **17**, L25 (1976).
- 8 (a) D. G. Parsons and J. N. Wingfield, *Inorg. Chim. Acta*, **18**, 263 (1976).
(b) J. D. Owen and J. N. Wingfield, *Chem. Commun.*, 318 (1976).
- 9 P. R. Mallinson and M. R. Truter, *J. Chem. Soc. Perkin II*, 1818 (1972).
- 10 M. E. Farago and J. M. James, *Inorg. Chem.*, **4**, 1706 (1965); J. L. Burmeister, *Coord. Chem. Revs.*, **1**, 205 (1966); C. Pecile, *Inorg. Chem.*, **5**, 210 (1966).
- 11 A. G. Lee, "The Chemistry of Thallium", Elsevier, London (1971) p. 284; F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3rd Edn., Interscience, London (1972) p. 281.
- 12 M. Ganne and M. Tournoux, *Compt. Rend.*, **276C**, 1755 (1973).
- 13 M. Marchand, Y. Piffard and M. Tournoux, *Compt. Rend.*, **276C**, 177 (1973).
- 14 D. L. Hughes and M. R. Truter, *J. Chem. Soc. Dalton*, 2214 (1972).
- 15 M. R. Truter, *Structure and Bonding*, **16**, 71 (1973).
- 16 A. Agtarap, J. W. Chamberlain, M. Pinkerton and L. K. Steinrauf, *J. Am. Chem. Soc.*, **89**, 5737 (1967); *J. Mol. Biol.*, **49**, 533 (1970).
- 17 M. Alleaume and D. Hickel, *Chem. Commun.*, 175 (1972).
- 18 E. W. Gzerwinski and L. K. Steinrauf, *Biochem. Biophys. Res. Commun.*, **45**, 1284 (1971).
- 19 D. M. Czakis-Sulikowska, *Roczniki Chem.*, **46**, 2315 (1972).