

Synthesis, Far-Infrared and Raman Spectra of Poly-Iodides of the Crown Ethers Main-Group Elements Encapsulates

Mervat M. El-Essawi

Department of Chemistry, Faculty of Science, Cairo University, Giza, Egypt.

SUMMARY

Polyiodide crown ether complexes of the general formula $[M(\text{crown ether})] I_n$ [$M = \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Cs}^+, \text{Tl}^{+++}, \text{Hg}^{++}, \text{Pb}^{++}, \text{Pd}^{++}$ and H_3O^+ , and $n = 2, 3, 5$ and 7] were prepared. The crown ethers used were 18 crown 6 (18C6), dibenzo 18 crown 6 (DB18C6) and dibenzo 24 crown 8 (DB24C8). The interhalogen complex $\text{Cs}(18\text{C}6)\text{I}_2$ was also synthesized. The structures of the compounds prepared have been elucidated by their Raman and Far-Infrared spectra.

INTRODUCTION

Polyhalide anions are usually formed by the addition of halogens or interhalide compounds to a halide ion⁽¹⁾. Polyhalide complexes of the type MI_n where $n = 3, 5, 7$ or 9 and M is a large alkali metal ion⁽²⁾, substituted ammo-nium⁽³⁾, phosphonium⁽⁴⁾, arsonium⁽⁵⁾, or organic cations such as N-alkyl urotropinium⁽⁶⁾, N-alkyl acridinium⁽⁷⁾, or a complex iodide transition metal ion, such as ion $\text{Cu}(\text{NH}_3)_4 \text{I}_3 \cdot \text{I}_3$ ⁽⁸⁾, are of interest because of their semi- and photo- conductive properties⁽⁹⁾.

A further extension of the field was the formation of polyiodides of crown ethers with encapsulated metal ions. Crown ethers have been re-

ported^(10,11) to chelate easily with metal salts and the interaction of the metal ion with crown ethers was shown to decrease their polarizing effect through interaction with oxygen donor functional groups of the crown, thus providing symmetrical encapsulates with larger diameters. Recently, we reported the isolation of polyiodide complexes of small metal ions such as Li⁺ and Na⁺ with 12 crown 4 in crystalline solid state⁽¹²⁾. In continuation of this work, we investigated the synthesis of polyiodide complexes of the main group elements, namely K, Cs, Tl, Pb and Hg with the crown ethers 18C6, DB18C6 and DB24C8. The Raman and Far-IR spectral characteristics of the complexes prepared are outlined. The crystal structures of some of such complexes are also determined⁽¹³⁾.

EXPERIMENTAL

Materials

Chemicals used were of AR grade. The crowns were obtained from Merck-Schuchardt, Germany.

Apparatus

Raman spectra of all compounds were scanned with a Laser $\lambda = 514.5$ using a spectrophotometer Model 2016 supplied by Jobin-Yvon Division Instruments. Far-Infrared spectra ($300-50 \text{ cm}^{-1}$) were obtained for solid pellets of samples in compressed polyethylene being recorded with Nicolet 2F vacuum spectrophotometer.

Synthesis of the metal-crown ether polyiodides

The complexes were prepared by mixing the metal iodide and iodine dissolved in the least amount of ethanol or methylene chloride in the molar ratio 1:1, 1:2, 1:3 and 1: excess. Equimolar amount of the appropriate crown ether was then added to the mixture. The solution was left overnight at 0°C. The crystalline complex precipitated was filtered off and thoroughly washed with ethanol. The analytical data, colour and melting points of the complexes prepared are given in Table I.

Preparation of thallium complexes: To a suspension of 0.331 g (1m mol) TlI in 20 ml ethanol 0.264 g (1m mol) 18 crown 6 was added. By addition of 0.254 g (1m mol) I₂ dissolved in the least amount of methylene chloride, the colour of iodine disappeared and TlI dissolved. The reaction mixture was left overnight at 0°C. The black crystals of [Tl (18 C6) I₂] I₇ were similarly prepared by the addition of 1g (4m mol) I₂.

The white crystals of Hg (18C6)I₂ were isolated by adding an excess amount of saturated iodine ethanolic solution to a mixture of 0.454 g (1m mol) HgI₂ and 0.264g (1m mol) [18 crown 6] dissolved in the least amount of ethanol . the reaction mixture was left overnight at 0°C.

Preparation of the lead compounds: Addition of 0.792 g (3m mol) of [18 crown 6] to a suspension of freshly prepared 0.461 g (1m mol) PbI₂ in 20 ml methylene chloride - ethanol mixture lead to its dissolution. When the solution was left to evaporate at room temperature white crystals of Pb (18 C6) I₂ was produced. The Pb (18 C6) I. I₃ complex was isolated by adding of 0.254 g (1m mol) I₂ to the previous solution. The green Pb (18C6) I.I₅ was

obtained by the addition of 0.762g (3m mol) I₂, whereas the addition of 1g I₂ gave the black polyiodide compound.

The black Pd (18 C6) I₃ complex was precipitated immediately by mixing aqueous solutions of 0.326 g (1m mol) K₂ Pd Cl₄ and 0.264 g (1m mol) [18 crown 6] followed by the addition of 0.254g (1m mol) I₂ dissolved in few drops of HI. The compound was soluble in methylene chloride.

Attempts to synthesize polyiodides of crown ether encapsulated transition metal ions such as Cu⁺ , Cu⁺⁺, Co⁺⁺ and Ni⁺⁺ using ethanol and methylene chloride as solvents were unsuccessful. However, the reddish brown H₃O⁺ (18 C6) I₃, the green H₃O⁺(18C6). I₅ and the black H₃ O⁺(18 C6) I₇ were formed.

The red brown H₃O⁺ (18 C6) I₃ was precipitated immediately by mixing a solution of 0.264g (1m mol) [18 crown 6] dissolved in 10 ml of water and 0.254 g (1m mol) I₂ dissolved in the least amount of HI. The green H₃O⁺ (18C6) I₅ and the black H₃O⁺(18C6) I₇ compounds were obtained by increasing the iodine concentration 0.508 g (2m mol) and 0.762 g (3m mol) I₂.

The yellow Cs (18C6) I Cl₂ compound was obtained by mixing 0.264 g (1m mol) [18 crown 6] and a saturated ethanolic solution of 0.168 g (1m mol) Cs Cl. The addition of about 0.16 g (1m mol) ICl gave immediately a yellow precipitate, which dissolved by the addition of few drops of methylene chloride. After 15 minutes yellow crystals were obtained. The experiment was carried out in a dry atmosphere of nitrogen.

RESULTS AND DISCUSSION

Polyiodides are known to exhibit various degrees of catenation and a wide variety of geometric arrangements. These generally depend on interaction with neighboring ions as well as the size and type of associated cation. The presence of a large cation would stabilize association of polyiodides in the form of I_2 and the situation in which more than one I_2 can be coordinated to Γ is limited to large cations. The interatomic distances in polyiodides ranging from 2.66 (bond length of I_2) to 4.30 Å (Van der Waals distance). Depending on the interatomic distance polyiodides may be considered as I_n^- . For example $[Cd(NH_3)_4 I_6]^{(14)}$, $I_3 \cdot n I_2$ [(Pyridinium- Pentaiodide,⁽¹⁵⁾ (Phenacetin)₂ H I₅ (16)], $I_5 \cdot n I_2$, $(C_2 H_5)_4 \cdot NI_7$, $(CH_3)_4 NI_9$ ⁽¹⁶⁾, or authentic I_3^- [1], I_5^- (16) or I_7^- ⁽¹⁷⁾ ions. From the spectroscopic point of view polyhalide species containing I_2 components would show bands at 170 - 180 cm^{-1} , in good agreement with the Raman bands in solid I_2 180 and 190 cm^{-1} , as well as bands characteristic of the other units incorporated in compounds under study.

The Far-ir and Raman bands of the triiodide compounds studied are listed in Table II. The strong asymmetric stretching band which is observed in the ir spectra, being absent in the Raman spectra, together with the existence of very weak shoulders due to the symmetric stretching vibrations in the ir spectra, would confirm that the triiodide ion in the studied complexes deviate slightly from $D_{\infty h}$ symmetry.

Triiodide ions are either linear or slightly bent, with equal or unequal I-I bonds. Generally they deviate slightly from $D_{\infty h}$ symmetry even with large cations such as $(C_6 H_5)_4 As^+$ and $CH_3 (C_6 H_5)_3 P^+$. Triiodide ions are shown

to be totally symmetric when the central iodine atom reside on a crystallographic center of symmetry such as in $\text{Cu}(\text{NH}_3)_4 \text{I}_3 \cdot \text{I}_3$ or $(\text{C}_2 \text{H}_5)_4 \text{NI}_3$. The triiodid species were reported to show Raman shifts near 110 and 75 cm^{-1} corresponding to the symmetric stretching vibration (ν_s) and deformation vibration (δ); the asymmetric stretching vibration (ν_{as}) would be active only in the ir spectrum for linear undistorted I_3^- and occur near 140 cm^{-1} .

Authentic I_5^- species showed strong bands between 145- 160 cm^{-1} ⁽¹⁶⁾. They might be of linear or bent structure depending on the cation. Most of the pentaiodides seem to acquire bent structures and are characterized by bands at 155, 145 cm^{-1} for the outer stretching vibrations and 112 and 76 cm^{-1} for inner stretching vibrations. Linear I_5^- ions have been seldom reported for example the pentaiodide of trimesic acid is characterized by bands at about 160 cm^{-1} for the outer stretches and 75 and 90 cm^{-1} for the inner stretches.

The data observed in Table III reveal, that all of the pentaiodide complexes studied are of the authentic V-shaped type except that of Li which might be $\text{I}_3 \cdot \text{I}_2$. The spectrum of the latter shows a band at 169 cm^{-1} , which may be considered to be due to associated I_2 molecule. It also exhibits the bands characteristic of the I_3^- moiety.

The reaction of TII and iodine could lead to the formation of a polyiodide, for example TII_3 (2) while in the presence of a suitable ligand might lead to the oxidation of thallium for example $\text{Cu}(\text{NH}_3)_4 (\text{TII}_4)$ ⁽¹⁸⁾. Addition of I_2 to TII, suspended in alcohol, in the presence of the crown ether 18C6 gave two complexes, namely a red $[\text{TI}(\text{18C6})\text{I}_2] \text{TII}_4$ (1) and the black hep-

taiodide $[\text{Tl}(\text{18C6})\text{I}_2]\text{I}_7$ (2). The structures of both thallium compounds were confirmed by x-ray diffraction^(13,19). The former compound seems to be composed of a complex anion $[\text{TlI}_4]^-$ and a cation $[\text{Tl}(\text{18C6})\text{I}_2]^+$. Tl (III) lies in the center of the crown surrounded by 6 oxygen atoms of the crown, two iodide atoms being coordinated to Tl above and below the crown ring. The anion $[\text{TlI}_4]^-$ might be conceived as a slightly distorted tetrahedron (Fig. 2). Also the red complex exhibits three strong far-infrared bands at 150.86 (F_2), 139.61 (A) and 53.28 (δ),⁽²⁰⁾ most likely are due to the tetrahedral arrangement in the anion. Only one Raman shift is observed due to the symmetric Tl-I stretching vibration at (123 cm^{-1}) in the nearly centrosymmetric cation. Compound (2) has been crystallographically characterized. It is composed of the cation $[\text{Tl}(\text{18C6})\text{I}_2]^+$ and the anion I_7^- . The hepta-iodide ion ($\text{I}_5^- \cdot \text{I}_2$) (Fig. 3) is composed of infinite chains of penta-iodide ions and iodine molecules. Its Raman and far-ir spectra are consistent with the x-ray structural parameters. They clearly showed the presence of both I_2 and I_5^- moieties. The I_2 unit had a bond length of 2.78 \AA producing a Raman shift at 172 cm^{-1} . Bands assigned to the bent I_5^- unit have also been observed (Table IV).

The reaction of HgI_2 and I_2 in presence of the crown ether 18C6 gave $\text{Hg}(\text{18C6})\text{I}_2$ which is identical with that previously reported⁽²¹⁾. The x-ray analysis showed, that Hg^{++} ion fitted in the crown ring being coordinated by its oxygen atoms and two iodine atoms situated above and below the ring and revealed centrosymmetric character (Fig. 4). The Raman and far-ir spectra show the following characteristic bands

R 75w , 135 vs and 164.5 vw
 ir 52.08s , 67.54 m , 163.97s and 194.84 m

The very strong Raman shift observed at 135 cm^{-1} may be due to the Hg-I symmetric stretching vibration. The very strong far-ir band at 163.97 is due to the Hg-I asymmetric stretching vibration.

The Raman shifts and far-ir spectra of the lead complexes are listed in Table V. From the numerous Raman shifts observed in the spectrum of Pb(18C6)I_2 it is concluded that it is of asymmetric nature. X-ray crystal structure analysis has shown, that Pb(18C6)I_3 (13) was built up of triiodide ion (with $d(\text{I-I}) = 289.4(2)$ and $292.2(2)$ pm and with an (I-I-I) angle of $178.09(4)^\circ$) and a complex cation $[\text{Pb(18C6)I}]^+$ in which Pb lies in the center of the ring surrounded by the 6 oxygens of the non planar ring, which is similar to $\text{Pb Cl(18C6)(Sb Cl}_6)^{(22)}$, $[\text{Pb(18C6)(CH}_3\text{CN)}_3(\text{Sb Cl}_6)_2]$, $[\text{Pb(18C6)(NO}_3)_2]$ ⁽²³⁾ and $\text{Pb(18C6)(CCl}_3\text{COO), HOCCl}_3$ ⁽²⁴⁾. The coordination sphere is completed by I^- $d(\text{Pb-I}) = 290,1(2)$ pm from one side of the ring and by the iodide atoms of the I_3^- $d(\text{Pb-I}) = 381.4(2)$ pm (Fig. 5). The Raman and far-ir spectra (Table II) are consistent with the X-ray structural parameters. A band at 85 cm^{-1} due to the Pb-I vibrations in the cation was observed. The bands observed in the spectrum of the green Pb(18C6)I_5 compound indicate the presence of the V shaped I_5^- moiety. Only one weak Raman band was observed at 161.5 cm^{-1} , which shifts to higher frequency by increasing the iodine concentration. The black compound Pb(18C6)I_7 exhibits in its spectrum a broad band at $170 - 150\text{ cm}^{-1}$

and a strong band at 133 cm^{-1} , which seem to be due to the association of iodine molecules to a triiodide moiety.

The palladium complex Pd (18C6) I.I₃ dissolved in methlene chloride. The line at 163 (e/m) which was observed in the mass spectrum of the compound, confirmed the presence of Pd in the compound. Raman and IR spectra showed, that is a triiodide, which is most probably similar to the lead compound Pb (18C6) I.I₃.

The Raman and far-ir spectra of H₃O⁺ (18C6) I₅ compound exhibit bands at $163, 145\text{ cm}^{-1}$ (outer stretches) 115 and 67 cm^{-1} (inner stretches). Therefore, it could be concluded that the pentaiodide is of the authentic V shaped type. The Raman and far-infrared spectra of compound H₃O⁺ (18C6) I₇ exhibit the following bands R : 168.5 v s , 115 s and 78.9 s whereas its IR spectrum shows bands at 170 v s , 135 v s , 110 sh , 100 m and 75 m (cm^{-1}). Also it exhibits an overtone at 200 cm^{-1} due to 2vs vibrations of the I₃⁻ moiety. It is clear from the strong Raman band at 168 cm^{-1} and the bands at 133 , 115 and 78.9 cm^{-1} , that the compound is composed of I₂ associated with the I₃⁻ unit.

The spectra of Cs (18C6)I Cl₂ and Cs ICl₂ compounds are very similar (25). A strong broad band of 225 cm^{-1} (due two the symmetric stretching vibration) with two shoulders at 265 and 255 cm^{-1} (assigned to the asymmetric stretching vibration) were observed in the ir spectra. A strong Raman shift due to the symmetric stretching vibration was observed at 267 cm^{-1} . The crystal structure of this compound will be reported soon.

References

- (1) K-F. Tebbe: Polyhalogen cations and polyhalide anions, <<Homoatomic rings, chains and macromolecules of main group elements>> AL Rhein-gold, Elsevier, Amsterdam, Oxford, New York, p 551 (1977).
- (2) K-F. Tebbe and U. Georgy; *Acta Crystallogr.*, **C 42**, 1675 (1980).
- (3) H. R. Luss and D. L. Smith; *Acta Crystallogr.*, **B 36**, 1580 (1980).
- (4) M. El Essawi, S. Abd El Khalik, H. J. Berthold and R. Wartchow *Z. Naturforsch.*, **45b**, 703 (1991).
- (5) J. Runsink, S. Swen-Walska and T. Migchelsen; *Acta Crystallogr.*, **B 28**, 1331 (1972).
- (6) H. Stegemann, G. Jabs, H. Mittag, L. Schmidt; H Füllbier, P. Cikmacs G. Petrovskis, A. Lulis and A. S. Orliukas *Z. Anorg. Allg. Chem.*, **555** 183 (1987).
- (7) S. Kusabayashi and H. Milawa, *Bull. Chem, Soc Japan*, **38**, 1410 (1965).
- (8) K-F. Tebbe, *Z. Anorg. Allg. Chem.*, **489**, 93 (1982).
- (9) P. J. Trottr and P. A. White; *Appl. Spectrosc.*, **32**, 323 (1978).
- (10) A. V. Bajaja, N. S. Poonia, *Coord. Chem. Rev.*, **87**, 55 (1988).
- (11) C. J. Pedersen, *J. Am. Soc.*, **89**, 7017 (1967), **92**, 391 (1970).
- (12) M. El Essawi and S. Abd El Khalik, *Egypt J. Chem.*, **37**. 559 (1994).
- (13) K-F. Tebbe, M. El Essawi and S. Abd El Khalik; *Z Naturforsch* **11**, 1429 (1995).
- (14) K-F. Tebbe and M. Plewa, *Z. Anorg. Allg. Chem.*, **489**, 111 (1982).
- (15) A. EL-Koli, U. Müller, R. Christophersen and K. Dehnicke, *Acta Cryst-allogr.* **C44** (1988).
- (16) E. M. Nour, L. H. Chen and J. Laane, *J. Phys. Chem.*, **90**, 2841 (1986).

- ⁽¹⁷⁾. M. Poli, J.C. Gordon, R. K. Kamara and S. E. Fanwick, *Inorog. Chem.*, **31**, 3165 (1992).
- ⁽¹⁸⁾. K-F. Tebbe, *Acta Crystallogr.*, **45**, 180 (1989).
- ⁽¹⁹⁾. M. El Essawi, S. Abd El Khalik and K-F. Tebbe (will be published soon).
- ⁽²⁰⁾. T. G. Spiro, *Inorg. Chim.*, **6**, 569 (1967).
- ⁽²¹⁾. H. Von Arnim, K. Dehnicke, K. Maczek and D. Fenske, *Z. Anorg. Allg. Chim.*, **619**, 1704 (1993).
- ⁽²²⁾. D. A. Pears and J. F. Stoddart, *Acta Crystallogr., C*, **42**, 51 (1986).
- ⁽²³⁾. R. D. Rogers, A. H. Bond, *Inorg. Chim. Acta.*, **192**, 163 (1992).
- ⁽²⁴⁾. S. T. Malinovskii, Yu. A. Simonov and Yu. Nazarenko, *Kristallografiya* **35**, 1410 (1990).
- ⁽²⁵⁾. W. Gabes and U. H. Gerding, *J. Molec Struct.*, **14** 267 (1972).

Table 1 Analytical data, colour and melting points for complexes.

Complex	↑ M.p. °C	↑ Colour	Anal. Found (calc.)		
			C, %	H, %	I, %
Li (18C6) I ₃	45	black	21.9 (22.12)	3.5 (3.71)	57.4 (58.35)
Li (18C6) I ₅	75	green black	16.4 (15.91)	3.3 (2.67)	69.5 (70.05)
Na (18C6) I ₃	80	brown	21.8 (21.58)	3.7 (3.62)	56.6 (56.99)
Na (18C6) I ₅	115	green	15.9 (15.64)	2.8 (2.62)	68.4 (68.83)
K (18C6) I ₃	178	brown	21.9 (21.07)	3.6 (3.54)	55.1 (55.89)
K (DB 18C6) I ₃	260	brown	31.1 (30.79)	3.9 (3.10)	48.7 (48.98)
K (DB 18C6) I ₅	-	dark brown	24.5 (23.23)	2.5 (2.34)	62.0 (61.54)
K (DB 24 C8) I ₃	118	brown	33.2 (33.20)	3.4 (3.68)	49.1 (49.49)
K (DB 24 C8) I ₅	90	dark brown	25.8 (25.69)	3.0 (2.87)	61.5 (62.02)
Cs (18 C6) I ₃	130	brown	18.2 (18.53)	3.1 (3.11)	48.2 (48.94)
Cs (18 C6) I ₅	140	green	13.8 (13.97)	2.5 (2.34)	60.9 (61.50)
Hg (18 C6) I ₂	-	white	21.1 (20.04)	3.4 (3.33)	35.3 (35.31)
[Ti (18 C6) I ₂] Ti I ₄	-	red	11.0 (10.05)	1.8 (1.69)	53.5 (53.08)
[Ti (18 C6) I ₂] I ₇	-	black	9.1 (8.95)	1.7 (1.5)	65.5 (65.46)
Pb (18 C6) I ₁₃	-	red	16.0 (14.72)	2.5 (2.47)	50.6 (51.85)
Pb (18 C6) I ₁₅	-	green	11.2 (11.69)	200 (1.96)	57.2 (57.37)
Pb (18 C6) I ₁₇	-	black	10.2 (9.69)	1.8 (1.63)	65.4 (65.33)
Pb (18 C6) I ₂	-	white	19.9 (19.87)	3.4 (3.34)	34.9 (34.99)
Pd (18 C6) I ₁₃	160	black	16.7 (16.41)	2.4 (2.75)	57.6 (57.79)
H ₃ O ⁺ (18 C6) I ₃	75	red brwon	20.9 (21.70)	4.9 (4.10)	56.5 (57.33)
H ₃ O ⁺ (18 C6) I ₅	125	green	16.1 (15.70)	2.8 (2.97)	69.3 (69.13)
H ₃ O ⁺ (18 C6) I ₇	55	black	11.9 (12.30)	2.2 (2.32)	75.9 (75.82)
Cs (18 C6) ICl ₂	125	yellow	24.2 (24.22)	4.1 (4.07)	

Table 2 Far-Infrared and Raman Vibrational Spectra of the Triiodides in cm^{-1}

Compound	Mode of Observation	ν_{asym}	ν_{sym}	δ	tentative bands.
Li (18C6)I ₃	R		113.5 s	78 s	227 mvbr 2vs
	ir	129.25 v s	115-95 wbr sh	78 v w sh	167.8 lattice overtone 56 lattice mode
Na (18C6)I ₃	R		107 m	76 w sh	246.92 m v br
	ir	135 v s	112-100 br sh		54.12 lattice mode
K (18C6)I ₃	R		117 s	78.5 s	248.85
			115.48 vwsh	77.16m	229.56 2vs
			101.58 vwsh		61.52 lattice mode
K (DB18C6)I ₃	R	132.5 w	116.5 m	78 s	
K (DB24C8)I ₃	R		108 vs		424.5 4vs
	ir	135 v s br	108 wsh	73.81 w	322.15 3vs 21.6 2vs 241.13 w 56 lattice mode
Cs (18C6)I ₃	R		108.5 w		
	ir	136.96 s	112.6 w sh		246
			100 w sh		
Pb (18C6)I ₃	R		114.5 s	78.5 m	84.5 v Pb-I
	ir	138 s br	98 w br	70 sh	
Pd (18C6)I ₃	R		111 s	81 w	
	ir	140 s	107 w		217 2vs

Table 3 Raman and Far-Infrared Vibrations of the Penta-Iodide Compounds.

Compound	Mode of Observation	outer stretching vib.		Inner stretching vib.		bending	other bands
		ν_{sym} , outer	ν_{asym} , outer	ν_{sym} , inner	ν_{asym} , inner		
Li (18C6) I ₅	R	169 vs		111 m-w			
	ir	169 vs	135 s	103.96 m	67 m	50 m	
Na (18C6) I ₅	R	163.5 s		115 m	80 s	52.6 m	
	ir	160	140 - 130 w br sh	105.9 v w sh	68 m	52.6 m	253.98 w
Cs (18C6) I ₅	R	151 v w		105.79 v w	88.74 m br	53.88 m	
	ir	157 - 140 br sh	131.18 v s				221.84
K (DB18C6) I ₅	R	165 m		113.5 m	76 s -m	54 w	
	ir		140.82 vs	105 m	82.9 m br		204.48 2vs inner 331.8 2v s outer
K (DB24C8) I ₅	R	165 s		114 s -m	77 s -m	52.55 s	
	ir		140.82 vs	105.9 vw	68.1 s		
Pb (18C6) I ₅	R	161.5 w					
	ir	157 vs	150 sh 140 sh 130 sh	110 w s b	67 s	53	88 w v Pb - I
H3O ⁺ (18C6) I ₅	R	163 s					
	ir	165 vs	145 m sh	110 - 105 w sh	67 s	50 m	333.5 w 2vs outer 2055 2vs inner 270 m 327 m 2vs outer

Table 4 Vibrational Spectra of the Heptaiodide of Thallium.

Raman	Far-Infrared	Assignment
172 S		ν (I_2) vibration
	150.85 m sh	ν (sym. stretch outer) (I_5^-)
	140.61 broad m sh	ν (asym. stretch outer) (I_5^-)
	123.46 m	ν (Tl - I) Tl coordinated to the crown
119 m		(sym stretch inner) (I_5^-)
	76.5 m	ν (asym. stretch inner) (I_5^-)
	52.55 s	bending (I_5^-).

Table 5 Vibrational spectra of the lead compounds.

Pb (18C6) I_2	Pb(18C6)I . I_3		Pb(18C6)I . I_5		Pb(18C6)I . I_7	
R	R	ir	R	ir	R	ir
287 w						
226 w				175 v w sh		
			161.5 v w		167 v w	170-150 m br
				157 v s		
149 w	138 v br			150 sh		133 m - s
				140 sh		
				130 sh		
	114.5 s	105 w sh				107 s
		95 w				
84.5 m		85 w		85 w		85 w - m
	78.5 m	75 sh		75		
69.5 s				53 w		54 s

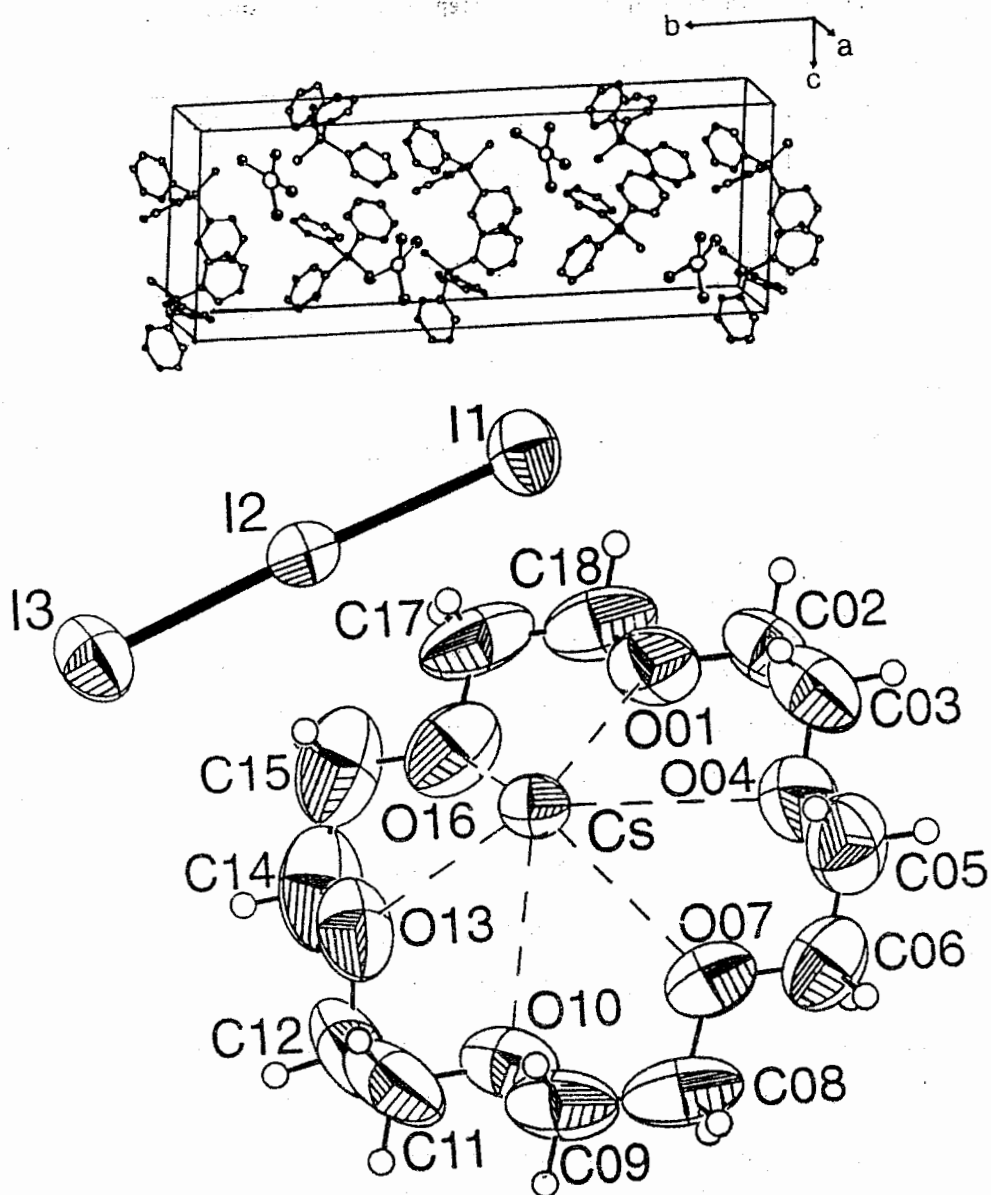


Figure (1) The [P Ph₃ Me] Cu Cl₄ complex
Cesium (18 Crown 6) Triiodide

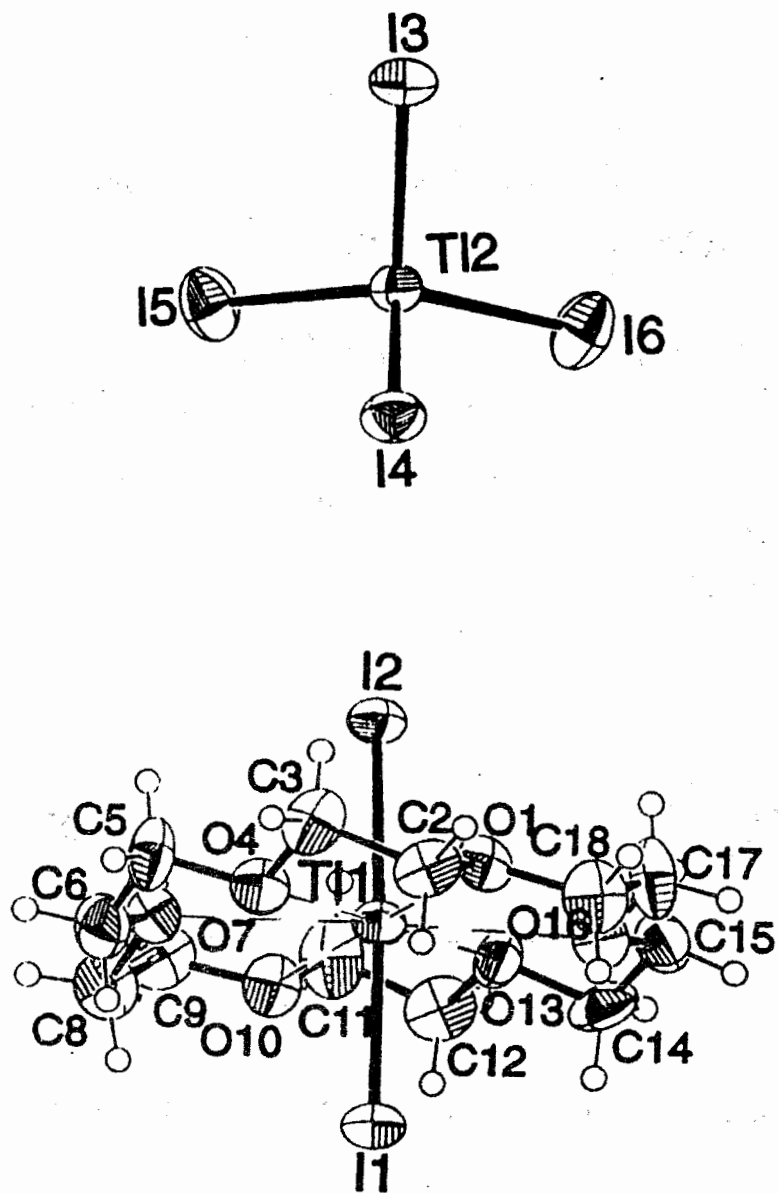


Figure (2) The Thallium Complex [Tl (18C6)I₂. TlI₄]

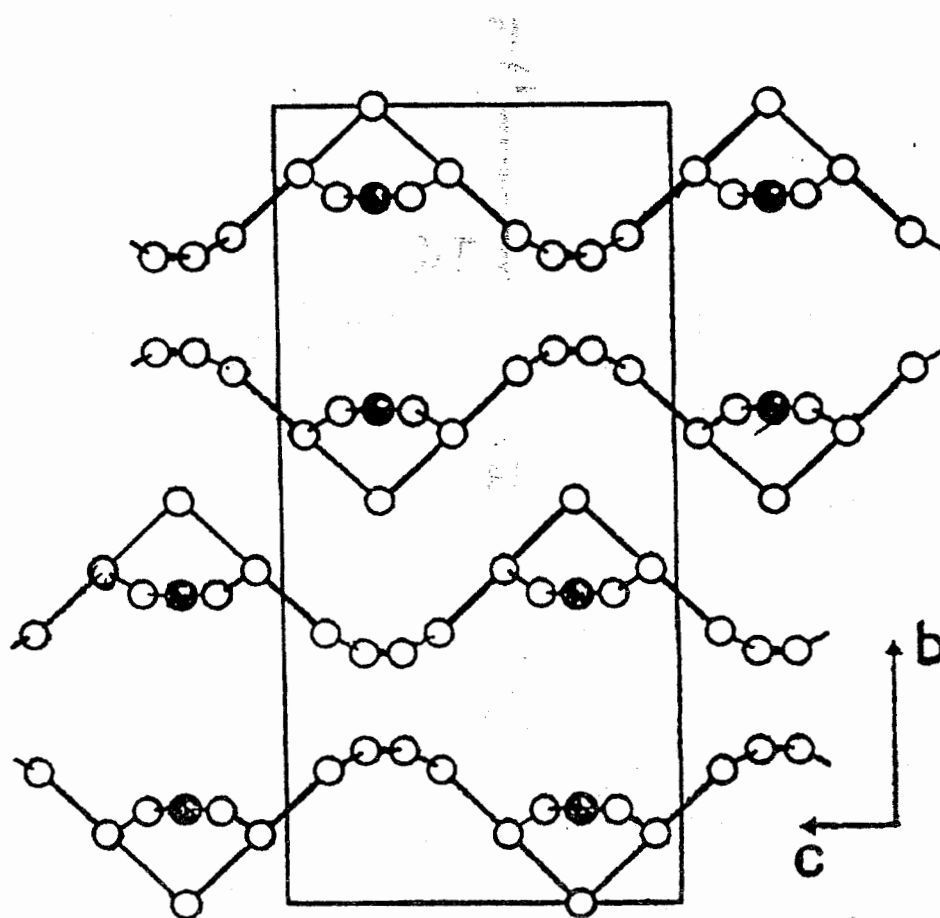


Figure (3) The Heptaiodide of Thallium [Tl (18C6) I₇] I₇

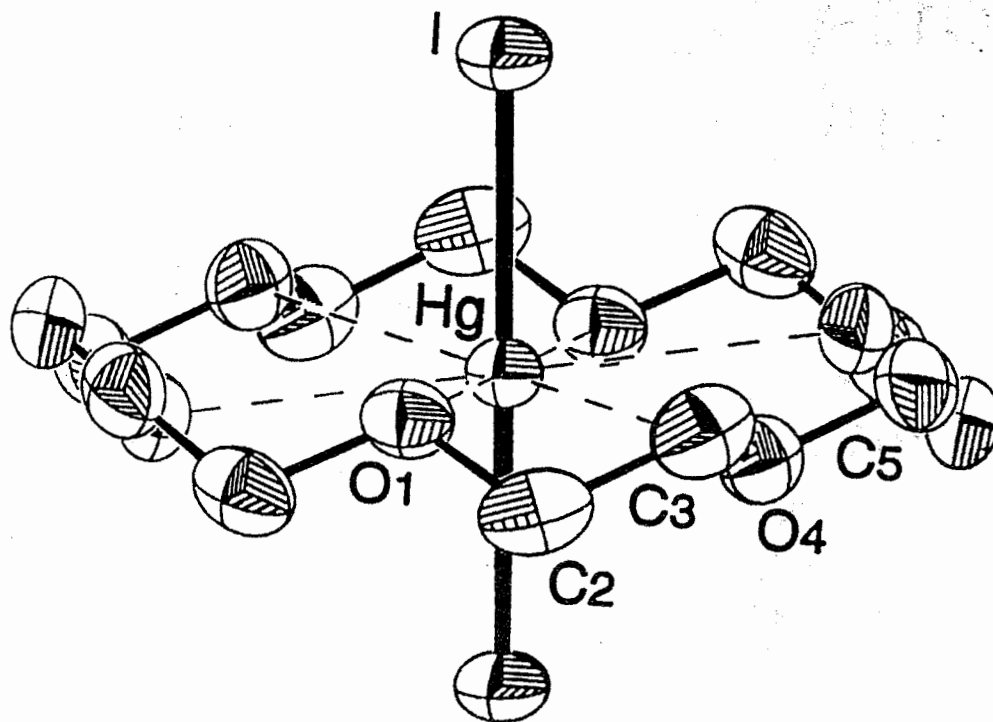


Figure (4) The Mercuric Complex [Hg (18C6) I₂]

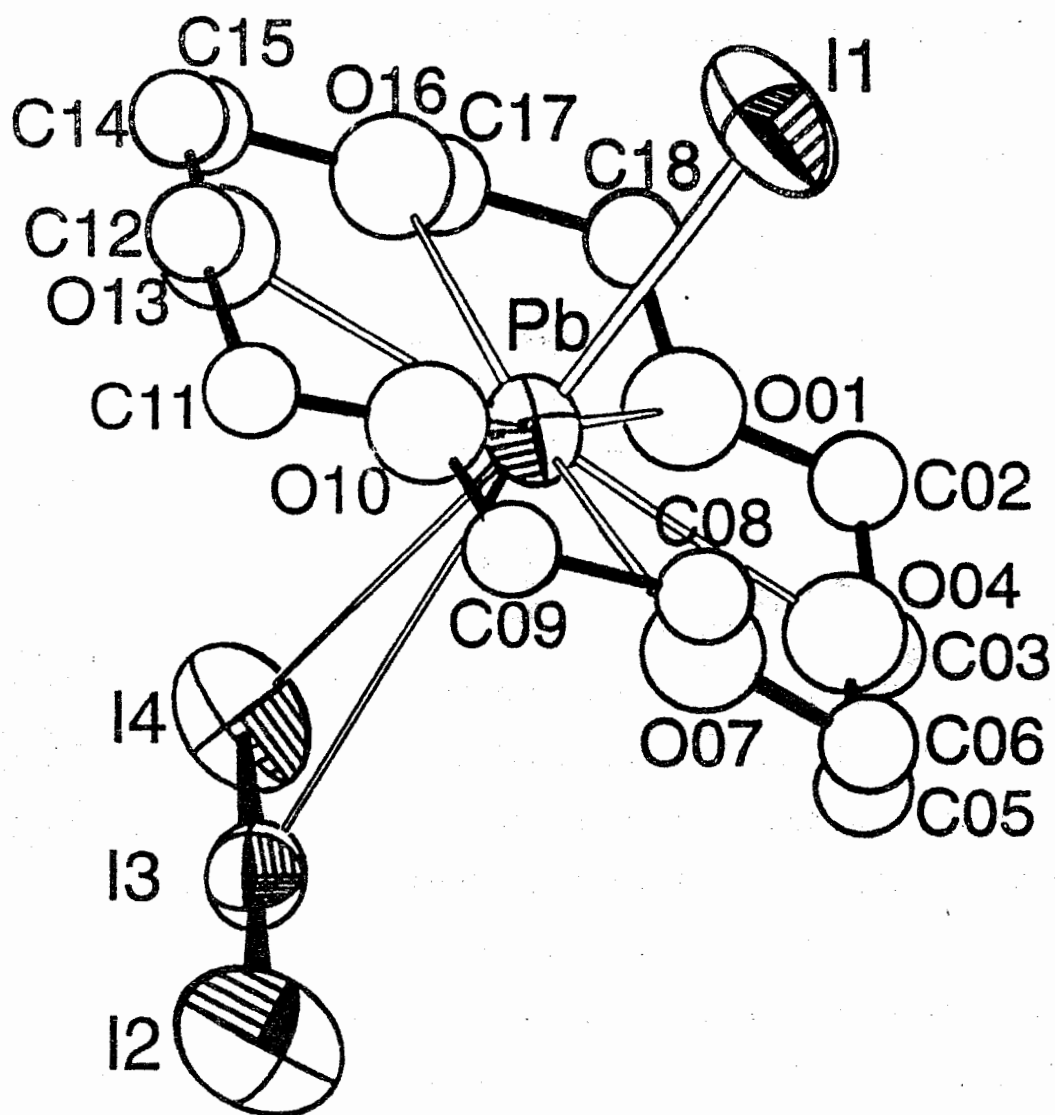


Figure (5) The Lead Triiodide Complex [Pb (18C6) I₃]