

## BEHAVIOUR OF TETRAPHENOXY NIOBIUM(V) AND TANTALUM(V) CHLORIDES IN THE PRESENCE OF LEWIS ACIDS

K. C. MALHOTRA, U. K. BANERJEE, K. C. MAHAJAN AND S. C. CHAUDHRY

Department of Chemistry, Himachal Pradesh University, Simla 171 005, India.

### ABSTRACT

Conductometric titrations of tetraphenoxy niobium(V) and tantalum(V) chlorides against  $\text{PCl}_5$ ,  $\text{AlCl}_3$ ,  $\text{FeCl}_3$  and  $\text{BiCl}_3$  in nitrobenzene show the formation of ionic compounds of composition  $\text{M}(\text{OPh})_4^+ \cdot \text{PCl}_6^-$ ,  $\text{M}(\text{OPh})_4^+ \cdot \text{AlCl}_4^-$ ,  $\text{M}(\text{OPh})_4^+ \cdot \text{FeCl}_4^-$  and  $\text{M}(\text{OPh})_4^+ \cdot \text{BiCl}_4^-$  where  $\text{M} \equiv \text{Nb or Ta}$ . These compounds have been isolated and characterized on the basis of elemental analysis, conductance and infrared spectral studies.

### INTRODUCTION

**P**ENTACHLORIDES of niobium, tantalum and antimony are known to act predominantly as chloride ion acceptors<sup>1-3</sup>. Compared to these pentachlorides, only a few examples are available in literature where phosphorus pentachloride acts as a chloride ion acceptor to form  $\text{PCl}_6^-$  ion, this ion being formed only when notably weak chloride ion acceptor is involved in the systems and the lattice energy favours its formation. Iodine(III) chloride is known to form a compound of composition  $\text{ICl}_3 \cdot \text{PCl}_6$  formulated as  $\text{ICl}_2^+ \cdot \text{PCl}_6^-$ .

The spectra of addition compounds of tetrachlorides of sulphur, selenium and tellurium with niobium(V) and tantalum(V) chlorides show the presence of pyramidal  $\text{MCl}_3^+$  and weakly perturbed octahedral  $\text{NbCl}_6^+$  and  $\text{TaCl}_6^+$  ions in the crystal<sup>5</sup>. Raman spectra of solidified  $\text{SbCl}_3$ - $\text{NbCl}_5$  mixtures have been explained on the basis of a dimer  $\text{SbNbCl}_{10}$ . Cationic complexes of the type  $\text{T}_4\text{Nb}^+$  and  $\text{T}_4\text{Ta}^+$  where T is tropolone cation have been stabilized by large symmetrical anions viz.  $\text{PF}_6^-$ ,  $\text{I}^-$ ,  $\text{I}_3^-$ ,  $\text{B}_{12}\text{Cl}_{12}^{2-}$  and  $\text{ClO}_4^-$  etc.<sup>6,7</sup> Recently we reported the formation of the cations of the type  $\text{M}(\text{OPh})_4^+$  ( $\text{M} = \text{Nb, Ta}$ ) by the large symmetrical anion  $\text{SbCl}_6^-$  from the reactions of tetraphenoxy niobium(V) and tantalum(V) chlorides with antimony(V) chloride<sup>8</sup>. We now report the stabilisation of these cationic species in the presence of other Lewis acids viz. phosphorus(V), aluminium(III), iron(III) and bismuth(III) chlorides.

### EXPERIMENTAL

Tetraphenoxy niobium(V) and tantalum(V) chlorides have been prepared by standard methods<sup>9,10</sup>. Lewis acids used were purified by standard methods given in literature. Compounds of composition  $\text{M}(\text{OPh})_4 \cdot \text{PCl}_6$  and  $\text{M}(\text{OPh})_4 \cdot \text{AlCl}_3$  were prepared by refluxing tetraphenoxy metal(V) chlorides and Lewis acids in exactly 1:1 molar ratio in carbon tetrachloride for 2-3 hr and cooling. While in the case

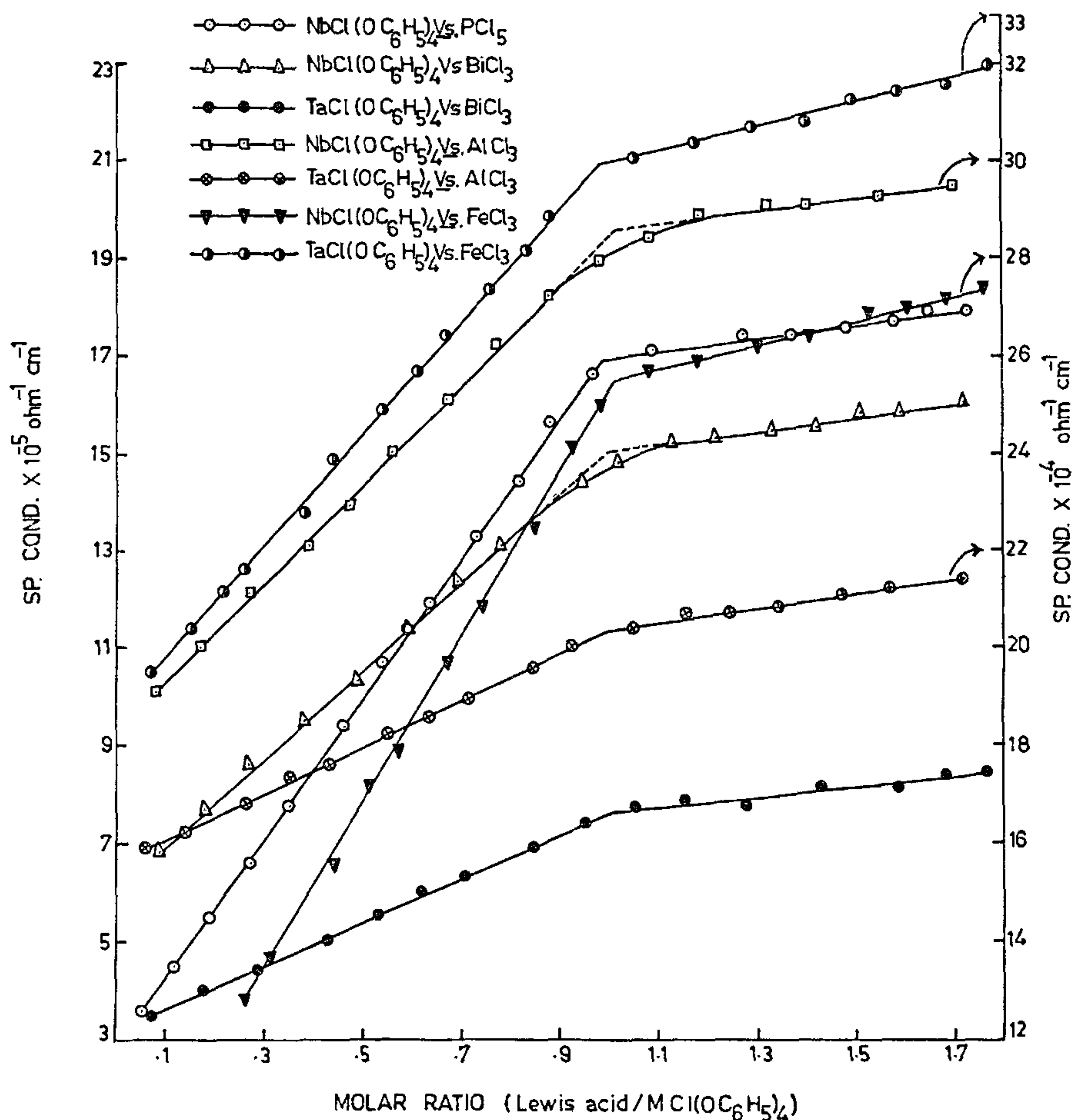
of compound of composition  $\text{M}(\text{OPh})_4 \cdot \text{AlCl}_3$ , crystalline compound separated out on cooling, in the case of compound  $\text{M}(\text{OPh})_4 \cdot \text{PCl}_6$  petroleum ether had to be added to extract the compound. Compounds of composition  $\text{M}(\text{OPh})_4 \cdot \text{BiCl}_3$  and  $\text{M}(\text{OPh})_4 \cdot \text{FeCl}_3$  were however prepared in nitromethane by a similar procedure. The compounds so obtained were filtered, washed 2-3 times with petroleum ether and finally dried under vacuum.

Niobium and tantalum in the presence of aluminium were estimated by the method reported earlier<sup>11</sup> while in the presence of iron, they were estimated by a different method<sup>12</sup>. Antimony and bismuth however do not interfere in the estimation of these metals by the usual methods<sup>8</sup>.

Chlorine was determined by Volhard's method. Molar conductance values of  $10^{-3}$  M solutions of the compounds were determined in nitrobenzene. Conductometric titrations were carried out in a specially-designed Y-shaped cell. Infrared spectra of the complexes were examined in KBr pellets or as Nujol mulls films using Perkin Elmer 337 and 621 infrared spectrophotometer.

### RESULTS AND DISCUSSION

Conductometric titrations between tetraphenoxy niobium(V) and tantalum(V) chlorides and phosphorus(V) chloride have been carried out at  $25 \pm 0.1^\circ \text{C}$  in nitrobenzene. The solutions of tetraphenoxy niobium(V) and tantalum(V) chlorides in nitrobenzene are very low conducting. However, addition of Lewis acids results in a rise in conductance of the solution. The conductance composition curves (figure 1) reveal sharp breaks at 1:1 molar ratio suggesting the possibility of formation of 1:1 stoichiometry. The continuous increase in conductance followed by the dissolution of the parent phenoxides has been attributed to the formation of ions in solution, thus excluding the formation of non-conducting compounds of the type  $\text{PMCl}_6(\text{OPh})_4$ . Possible ions responsible for the conductance of the solution may be formulated as:



**Figure 1.** Conductometric titrations of tetraphenoxy niobium(V) and tantalum(V) chlorides against Lewis acids in nitrobenzene at  $25 \pm 0.1^\circ \text{C}$ .



thus suggesting the stabilization of the cation  $\text{M}(\text{OPh})_4^+$  by the large symmetrical anion  $\text{PCl}_6^-$  which with earlier observations<sup>6-8</sup>. Compounds of composition  $\text{M}(\text{OPh})_4^+ \text{PCl}_6^-$  have been actually isolated in separate experiments, analytical data being reported in table 1. These compounds are crystalline solids and have high melting points. They are fairly soluble in nitrobenzene and molar conductance values of milli-

molar solutions of these compounds in nitrobenzene suggest their ionic nature<sup>13</sup>.

Information on the structure of these compounds has been obtained from their infrared spectra. The bands present around  $350 \text{ cm}^{-1}$  in  $\text{NbCl}(\text{OPh})_4$  and around  $335 \text{ cm}^{-1}$  in  $\text{TaCl}(\text{OPh})_4$  due to terminal  $\nu(\text{M}-\text{Cl})$ <sup>8</sup> have been found to be missing in the complexes. Instead new and sharp bands observed at 448 and  $362 \text{ cm}^{-1}$  in the spectra of the complexes of these phenoxides with phosphorus pentachloride may be



TABLE I

*Analytical data of the compounds of tetraphenoxy niobium(V) and tantalum(V) Chlorides with Lewis acids*

Compound	Colour	m.pt. °C	Elemental analysis				Molar conductance in nitrobenzen (ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> )
			% Found		% Req'd.		
			Nb or Ta	Cl	Nb or Ta	Cl	
Nb(OC <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> . PCl <sub>6</sub>	Yellow	> 220	12.81	29.81	13.11	30.04	22.7
Ta(OC <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> . PCl <sub>6</sub>	Light Yellow	> 220	22.43	26.37	22.71	26.72	22.1
Nb(OC <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> . BiCl <sub>4</sub>	Light Brown	> 220	11.01	17.12	11.39	17.40	22.4
Ta(OC <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> . BiCl <sub>4</sub>	Dark pink	> 220	19.81	15.37	20.02	15.70	23.2
Nb(OC <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> . AlCl <sub>4</sub>	Maroon	211	14.43	21.89	14.66	22.39	24.1
Ta(OC <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> . AlCl <sub>4</sub>	Red	110(d)	24.87	19.43	25.06	19.66	23.6
Nb(OC <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> . FeCl <sub>4</sub>	Brown	> 220	13.77	21.17	14.04	21.45	21.8
Ta(OC <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> . FeCl <sub>4</sub>	Dark	> 220	23.75	18.58	24.13	18.93	23.2

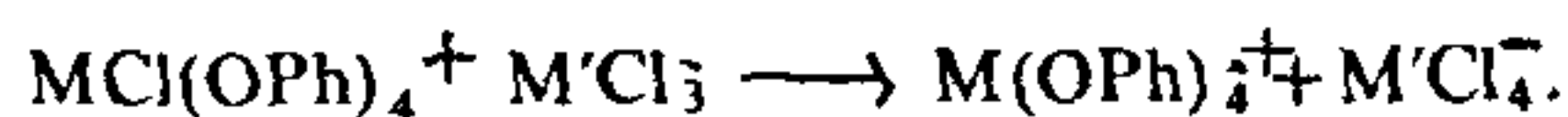
d = decompose

assigned to  $\nu(\text{P—Cl})$  stretching modes in an octahedral environment<sup>14</sup> resulting from change of symmetry from PCl<sub>5</sub> to PCl<sub>6</sub><sup>-</sup>. Besides a lowering of about 8–10 cm<sup>-1</sup> has been observed in the  $\nu(\text{M—O})$  stretching modes of the phenoxy derivatives on complexation with PCl<sub>5</sub> which may be attributed to change in symmetry around the metal. Apart from these important bands the other important bands present at 1596, 1498, 1472, 1384, 1182, 1167, 884, 825 and 688 cm<sup>-1</sup> assigned to  $\nu(\text{C} \equiv \text{C})$ ,  $\nu(\text{=CH})$ ,  $\nu(\text{C—C})$  ring vibrations present in phenol<sup>15</sup> shift to lower spectral regions suggesting the presence of positive charge on the metal surrounded by phenoxy groups.

There are examples in literature where aluminium(III) iron(III) and bismuth(III) chlorides are also known to be chloride ion acceptors<sup>1,16</sup>. Blatt and coworkers<sup>17-19</sup> have reported the preparation of a few tetrachloroferrate(III) with heterocyclic cations. The tetrachloroferrate(III) anion exists in concentrated HCl solution<sup>20</sup>. These anions may also be stabilised in solvents such as triethylphosphate and phosphorus oxychloride<sup>21</sup>. In the present studies, therefore, in order to ascertain the composition of the compounds formed by iron(III) aluminium(III) and bismuth(III) chlorides with tetraphenoxy niobium(V) and tantalum(V) chlorides, conductometric titrations of these phenoxides versus trichlorides of iron, aluminium and bismuth have been carried out in nitrobenzene at 25 ± 0.1° C. Conductance composition curves (figure 1) show sharp breaks at 1:1 molar ratio possibly because of the formation of a compounds of composition M(OPh)<sub>4</sub><sup>+</sup>. FeCl<sub>4</sub><sup>-</sup>, M(OPh)<sub>4</sub><sup>+</sup>. AlCl<sub>4</sub><sup>-</sup> and M(OPh)<sub>4</sub><sup>+</sup>. BiCl<sub>4</sub><sup>-</sup> as the case may be. These compounds have been isolated in separate experiments and their

stoichiometric compositions have been established by elemental analysis (table I).

Low frequency infrared spectra of these compounds show no band in the region 330–350 cm<sup>-1</sup> which suggest the absence of bands of the type Nb—Cl or Ta—Cl in these compounds. Instead new sharp bands at 385 cm<sup>-1</sup> in iron(III) chloride, at 492 cm<sup>-1</sup> in aluminium(III) chloride and at 298 cm<sup>-1</sup> in bismuth(III) chloride complexes have been observed and may be assigned to  $\nu(\text{Fe—Cl})$ ,  $\nu(\text{Al—Cl})$  and  $\nu(\text{Bi—Cl})$  stretching vibration in FeCl<sub>4</sub><sup>-</sup><sup>22,23</sup>, AlCl<sub>4</sub><sup>-</sup><sup>24</sup> and BiCl<sub>4</sub><sup>-</sup><sup>25</sup> respectively due to change in symmetry from MCl<sub>3</sub> to MCl<sub>4</sub><sup>-</sup>. These observations may be rationalised in terms of the following equation:



It can be concluded that in the presence of strong chloride ion acceptors, tetraphenoxy niobium(V) and tantalum(V) chlorides behave as chloride ion donor thus forming large symmetrical anions of the type PCl<sub>6</sub><sup>-</sup>, BiCl<sub>4</sub><sup>-</sup>, FeCl<sub>4</sub><sup>-</sup>, AlCl<sub>4</sub><sup>-</sup> which help in stabilizing the large cation M(OPh)<sub>4</sub><sup>+</sup>.

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## ANNOUNCEMENT

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### NATIONAL CONFERENCE ON 'LEAD, ZINC & CADMIUM AT WORKPLACE— ENVIRONMENT AND HEALTH CARE,' UDAIPUR—14-16 DECEMBER, 1982

Indian Lead Zinc Information Centre, the Indian Branch Officers of the world renowned Lead, Zinc and Cadmium Associations of London, is organizing a seminar on 'Lead, Zinc and Cadmium at Workplace—Environment and Health Care' at Udaipur from 14-16 December 1982.

Prevention of pollution hazards both to the environment and to the workplace engaged in lead, zinc and cadmium industry will be the major theme of the seminar which would be the first of its kind to be held in India with particular reference to the three non-ferrous metals. Over 40 technical papers dealing with diverse aspects of the subject will be presented and discussed at the three day deliberations. A number

of experts from foreign countries are expected to participate in the conference. Yet another attraction for the participants would be the plant visit programme to the mines and smelters of HZL where elaborate pollution control systems have been installed in recent times.

For details in regard to the seminar, please contact

Indian Lead Zinc Information Centre,  
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