

# Metal Chloride-Phosphorus Chloride-Alkyl Chloride Complexes : Reactions with Gold(III), Zirconium(IV), Platinum(IV) and Oxouranium(VI) Chlorides

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Manuscript received 18 August 1981, revised 6 September 1982, accepted 3 August 1983

The reactions of anhydrous gold(III), zirconium(IV), platinum(IV) and oxouranium(VI) chlorides with trichloro and phenyl dichloro phosphines in presence of alkylating agents such as *t*-butyl chloride, *t*-amyl chloride, cyclohexyl chloride and trimethyl chloride have been carried out. Ionic solid products have been obtained and characterised by elemental analysis, ir and electronic spectra, thermogravimetric analysis, and conductivity and magnetic susceptibility measurement data.

KINNEAR and Perren<sup>1</sup> synthesised organophosphonium polychloroaluminates and used them for the preparation of new organophosphorus compounds by their hydrolysis or alcoholysis. Bullock *et al.*<sup>2,3</sup> initiated the synthesis and structural study of such polychlorometallates. Puri and Saini<sup>4-6</sup> also studied the reaction systems metal chloride-phenyldichloro- or trichloro-phosphine-alkyl chloride. These systems have also been studied by us using anhydrous cobalt(II)<sup>7</sup>, vanadium(III)<sup>8</sup>, oxovanadium(V)<sup>9</sup> and antimony(V)<sup>9</sup> chlorides. Syntheses and structural studies of the complexes, CsAuCl<sub>4</sub><sup>10</sup>, RbAuCl<sub>4</sub><sup>10</sup>, [Bu<sup>+</sup>PCl<sub>3</sub>][Zr<sub>2</sub>Cl<sub>9</sub>]<sup>11</sup>, M<sub>2</sub>[PtCl<sub>6</sub>] (M=K, Rb, Cs, Tl or Ag)<sup>12</sup> and M<sub>2</sub>[UO<sub>2</sub>Cl<sub>4</sub>]<sup>13</sup> (M is singly charged cation) have been reported. In continuation of our work on organophosphonium chlorometallate, we report here the reaction systems gold(III), zirconium(IV), platinum(IV) or oxouranium(VI) chloride-phenyl dichloro or trichlorophosphine-alkyl chloride.

## Experimental

### Materials and method :

HAuCl<sub>4</sub>·xH<sub>2</sub>O (B.D.H.), UO<sub>2</sub>Cl<sub>2</sub>·xH<sub>2</sub>O (B.D.H.) and H<sub>2</sub>PtCl<sub>6</sub>·xH<sub>2</sub>O were dehydrated by known method<sup>14</sup>. Zirconium(IV) chloride (Fluka), triphenylmethyl chloride (Riedel) and trichlorophosphine (B.D.H.) were used as such. *t*-Butyl, *t*-amyl and cyclohexyl chlorides were prepared by known methods<sup>15</sup> and distilled before use. Phenyldichlorophosphine was prepared by known method<sup>16</sup>. Solvents (CS<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>CN and nitrobenzene) were purified by known methods. Chlorine and phosphorus were estimated by known methods<sup>7</sup>. The infrared spectra were recorded in the 4000-250 cm<sup>-1</sup> region using Beckman IR-20 spectrophotometer. Conductivity was measured with Elico CM-82T conductivity bridge in dry nitrobenzene.

### Syntheses of complexes :

The compounds from the metal chlorides, trichloro- or phenyldichlorophosphine and alkyl

chlorides were synthesised by the same method as reported for the reaction with antimony(V) chloride<sup>9</sup> and cobalt(II) chloride<sup>7</sup>. The amount of the reagents used, colour of the products and yields are given in Table 1. The compounds did not exhibit sharp melting points, decomposition accompanied by change in colour occurred.

## Results and discussion

On the basis of elemental analyses, infrared spectral study and conductivity measurements, the complexes of Au(III), Zr(IV), Pt(IV) and UO(VI) may be formulated as [R'RPCl<sub>3</sub>]<sup>+</sup>[AuCl<sub>4</sub>]<sup>-</sup>, [R'RPCl<sub>3</sub>]<sup>+</sup>[Zr<sub>2</sub>Cl<sub>9</sub>]<sup>-</sup>, [R'RPCl<sub>3</sub>]<sub>2</sub><sup>2+</sup>[PtCl<sub>6</sub>]<sup>2-</sup> and [R'RPCl<sub>3</sub>]<sub>2</sub>[UO<sub>2</sub>Cl<sub>4</sub>], respectively (R'=Bu<sup>+</sup>, Am<sup>+</sup>, C<sub>6</sub>H<sub>11</sub><sup>+</sup> or Ph<sub>3</sub>C<sup>+</sup> and R=Ph or Cl).

The molar conductance of the complexes (1×10<sup>-3</sup>M) in nitrobenzene was found to be in the range of 15.88-24.26 mhos cm<sup>2</sup> mole<sup>-1</sup> for gold(III) and zirconium(IV) complexes, suggesting 1:1 electrolytic nature of these complexes, while the molar conductance values of platinum(IV) and oxouranium(VI) complexes were 40.08-49.36 mhos cm<sup>2</sup> mole<sup>-1</sup>, suggesting their 2:1 electrolytic nature<sup>17</sup>.

**Cationic spectra :** The infrared spectra of alkyl trichlorophosphonium [RPCl<sub>3</sub>]<sup>+</sup> and alkyl phenyl dichlorophosphonium [RPhPCl<sub>2</sub>]<sup>+</sup> species show weak absorption at 770-800 cm<sup>-1</sup>, assignable to ν(P-C) (alkyl) vibrations<sup>2-9</sup>. ν(P-Cl) vibrations were observed<sup>4-9</sup> as very strong bands between 620-590 cm<sup>-1</sup> and 530-490 cm<sup>-1</sup>. Very strong bands at 1450-1430 cm<sup>-1</sup> and 1020-990 cm<sup>-1</sup> could be due to ν(P-Ph) in analogy with similar bands observed at 1439 and 998 cm<sup>-1</sup>, respectively in Ni(PF<sub>3</sub>C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>, PCl<sub>2</sub>C<sub>6</sub>H<sub>5</sub> and Ni(PCl<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>4</sub> by Seel *et al.*<sup>18</sup> and at 1440 cm<sup>-1</sup> and 998 cm<sup>-1</sup> in [RPhPCl<sub>2</sub>][SbCl<sub>6</sub>] by Sneh *et al.*<sup>9</sup>.

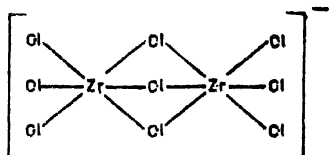
**Anionic spectra :** In the anion [AuCl<sub>4</sub>]<sup>-</sup>, bands at 350 and 355 cm<sup>-1</sup> could be assigned to ν<sub>g</sub>(E<sub>g</sub>) (Au-Cl) which were comparable to the values 362

TABLE 1—CHARACTERISATION DATA OF COMPLEXES

Sl. No.	Reactants			Product and yield (g)	Colour and state	Analysis % ; Found/(Calcd)		m. p. °C	Molar conductance of 10 <sup>-3</sup> M soln. in C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> (mho cm <sup>2</sup> mol <sup>-1</sup> )
	MCl <sub>3</sub>	R'PCl <sub>2</sub>	RCl			Cl	P		
Gold(III) compounds									
1.	0.30	0.12	0.098	[Bu <sup>+</sup> PCl <sub>2</sub> ] <sub>2</sub> [AuCl <sub>4</sub> ] (0.44)	Greenish brown Solid	45.25 (46.58)	5.58 (5.81)	201	16.24
2.	0.25	0.11	0.078	[Am <sup>+</sup> PCl <sub>2</sub> ] <sub>2</sub> [AuCl <sub>4</sub> ] (0.36)	Yellowish brown Solid	44.66 (45.39)	5.34 (5.66)	204	16.88
3.	0.30	0.14	0.12	[C <sub>6</sub> H <sub>11</sub> PCl <sub>2</sub> ] <sub>2</sub> [AuCl <sub>4</sub> ] (0.45)	Brown Solid	43.55 (44.42)	5.62 (5.54)	210	18.28
4.	0.32	0.15	0.30	[Ph <sub>2</sub> CPCl <sub>2</sub> ] <sub>2</sub> [AuCl <sub>4</sub> ] (0.60)	Greenish yellow Solid	34.28 (34.53)	4.59 (4.31)	208	24.26
5.	0.50	0.29	0.090	[Bu <sup>+</sup> PhPCl <sub>2</sub> ] <sub>2</sub> [AuCl <sub>4</sub> ] (0.70)	Brown Solid	36.50 (37.10)	5.09 (5.40)	204	22.38
6.	0.23	0.14	0.081	[Am <sup>+</sup> PhPCl <sub>2</sub> ] <sub>2</sub> [AuCl <sub>4</sub> ] (0.34)	Brown Solid	35.39 (36.23)	5.12 (5.27)	206	20.40
7.	0.30	0.18	0.12	[C <sub>6</sub> H <sub>11</sub> PhPCl <sub>2</sub> ] <sub>2</sub> [AuCl <sub>4</sub> ] (0.48)	Brown Solid	34.52 (35.50)	4.87 (5.16)	212	18.84
8.	0.20	0.12	0.17	[Ph <sub>2</sub> CPhPCl <sub>2</sub> ] <sub>2</sub> [AuCl <sub>4</sub> ] (0.37)	Brown Solid	27.86 (28.02)	3.83 (4.08)	205	19.30
Zirconium(IV) compounds									
9.	0.48	0.14	0.096	[Bu <sup>+</sup> PCl <sub>2</sub> ] <sub>2</sub> [Zr <sub>2</sub> Cl <sub>9</sub> ] (0.54)	White Solid	60.83 (61.16)	3.98 (4.45)	210	16.44
10.	0.30	0.088	0.068	[Am <sup>+</sup> PCl <sub>2</sub> ] <sub>2</sub> [Zr <sub>2</sub> Cl <sub>9</sub> ] (0.34)	White Solid	58.28 (59.96)	4.09 (4.36)		17.82
11.	0.46	0.14	0.11	[C <sub>6</sub> H <sub>11</sub> PCl <sub>2</sub> ] <sub>2</sub> [Zr <sub>2</sub> Cl <sub>9</sub> ] (0.60)	White Solid	58.13 (58.96)	4.56 (4.29)		15.88
12.	0.54	0.16	0.42	[Ph <sub>2</sub> CPCl <sub>2</sub> ] <sub>2</sub> [Zr <sub>2</sub> Cl <sub>9</sub> ] (0.83)	Creamish Solid	48.75 (48.27)	3.17 (3.51)		19.28
13.	0.45	0.17	0.088	[Bu <sup>+</sup> PhPCl <sub>2</sub> ] <sub>2</sub> [Zr <sub>2</sub> Cl <sub>9</sub> ] (0.54)	White Solid	51.48 (52.99)	4.33 (4.20)	210	20.48
14.	0.34	0.13	0.078	[Am <sup>+</sup> PhPCl <sub>2</sub> ] <sub>2</sub> [Zr <sub>2</sub> Cl <sub>9</sub> ] (0.43)	White Solid	50.27 (52.00)	4.01 (4.13)	214	18.84
15.	0.40	0.15	0.10	[C <sub>6</sub> H <sub>11</sub> PhPCl <sub>2</sub> ] <sub>2</sub> [Zr <sub>2</sub> Cl <sub>9</sub> ] (0.49)	White Solid	49.28 (50.25)	3.75 (4.07)	208	20.84
16.	0.35	0.13	0.21	[Ph <sub>2</sub> CPhPCl <sub>2</sub> ] <sub>2</sub> [Zr <sub>2</sub> Cl <sub>9</sub> ] (0.49)	Creamish Solid	42.57 (42.31)	2.90 (3.35)	208	17.68
Platinum(IV) compounds									
17.	0.15	0.12	0.082	[Bu <sup>+</sup> PCl <sub>2</sub> ] <sub>2</sub> [PtCl <sub>6</sub> ] (0.30)	Orange Solid	52.48 (53.44)	6.84 (7.77)	154	40.08
18.	0.17	0.14	0.11	[Am <sup>+</sup> PCl <sub>2</sub> ] <sub>2</sub> [PtCl <sub>6</sub> ] (0.35)	Orange Solid	50.62 (51.63)	7.29 (7.51)	150	42.84
19.	0.20	0.16	0.14	[C <sub>6</sub> H <sub>11</sub> PCl <sub>2</sub> ] <sub>2</sub> [PtCl <sub>6</sub> ] (0.42)	Orange Solid	49.26 (50.17)	6.42 (7.30)	152	44.28
20.	0.12	0.097	0.20	[Ph <sub>2</sub> CPCl <sub>2</sub> ] <sub>2</sub> [PtCl <sub>6</sub> ] (0.35)	Orange Solid	34.88 (36.43)	4.83 (5.30)	148	41.12
Oxouranium(VI) chloride complexes									
21.	0.30	0.24	0.16	[Bu <sup>+</sup> PCl <sub>2</sub> ] <sub>2</sub> [UO <sub>2</sub> Cl <sub>4</sub> ] (0.56)	Light green Solid	44.93 (44.07)	7.58 (7.78)	205	46.24
22.	0.42	0.34	0.27	[Am <sup>+</sup> PCl <sub>2</sub> ] <sub>2</sub> [UO <sub>2</sub> Cl <sub>4</sub> ] (0.92)	Yellowish green Solid	42.31 (42.82)	7.36 (7.47)	210	
23.	0.58	0.45	0.32	[C <sub>6</sub> H <sub>11</sub> PCl <sub>2</sub> ] <sub>2</sub> [UO <sub>2</sub> Cl <sub>4</sub> ] (1.84)	Light green Solid	40.93 (41.61)	7.45 (7.26)	203	48.82
24.	0.63	0.51	1.04	[Ph <sub>2</sub> CPCl <sub>2</sub> ] <sub>2</sub> [UO <sub>2</sub> Cl <sub>4</sub> ] (1.84)	Light green Solid	29.88 (30.26)	5.22 (5.28)	206	
25.	0.42	0.44	0.23	[Bu <sup>+</sup> PhPCl <sub>2</sub> ] <sub>2</sub> [UO <sub>2</sub> Cl <sub>4</sub> ] (0.89)	Light green Solid	30.91 (32.20)	6.69 (7.03)	201	47.78
26.	0.53	0.56	0.34	[Am <sup>+</sup> PhPCl <sub>2</sub> ] <sub>2</sub> [UO <sub>2</sub> Cl <sub>4</sub> ] (1.04)	Light green Solid	32.56 (31.20)	6.61 (6.81)	208	
27.	0.57	0.60	0.40	[C <sub>6</sub> H <sub>11</sub> PhPCl <sub>2</sub> ] <sub>2</sub> [UO <sub>2</sub> Cl <sub>4</sub> ] (1.30)	Light green Solid	29.40 (30.40)	6.36 (6.63)	208	
28.	0.55	0.58	0.91	[Ph <sub>2</sub> CPhPCl <sub>2</sub> ] <sub>2</sub> [UO <sub>2</sub> Cl <sub>4</sub> ] (1.30)	Light green Solid	21.73 (22.64)	5.09 (4.95)	210	49.36

and  $365\text{ cm}^{-1}$  reported by Sabatini *et al.*<sup>10</sup>. As suggested earlier<sup>10</sup>, the anion  $[\text{AuCl}_4]^-$  may have square planar structure with  $D_{4h}$  symmetry.

In the anion  $[\text{Zr}_2\text{Cl}_9]^-$ , the absorption at  $387\text{ (A}_g^-)$ ,  $368\text{ (E}^+)$ ,  $358$  and  $318\text{ cm}^{-1}\text{ (E}^+)$  were due to  $\nu(\text{Zr-Cl})$  terminal and at  $249$  and  $230\text{ cm}^{-1}$  were due to  $\nu(\text{Zr-Cl})$  bridging, as suggested by Bullock *et al.*<sup>11</sup> for  $[\text{Bu}^t\text{PCl}_3]_2^+[\text{Zr}_2\text{Cl}_9]^-$ . The anion could be suggested to have a face-shared bi-octahedral structure having  $D_{3h}$  symmetry



The anion  $[\text{PtCl}_6]^{2-}$  showed absorption peaks at  $345\text{ (}\nu_1\text{)}$ ,  $320\text{ (}\nu_2\text{)}$  and  $338\text{ cm}^{-1}\text{ (}\nu_3\text{)}$  due to Pt-Cl as suggested by Adams and Morris<sup>12</sup> for  $\text{M}_2\text{PtCl}_6$  at  $350\text{ (}\nu_1\text{)}$ ,  $320\text{ (}\nu_2\text{)}$  and  $341\text{ cm}^{-1}\text{ (}\nu_3\text{)}$ .

In the spectra of the  $[\text{UO}_2\text{Cl}_4]^{2-}$ , a band observed at  $270\text{ cm}^{-1}$  could be assigned to  $\nu(\text{U-Cl})$  and is comparable with the absorption bands observed at  $270\text{ cm}^{-1}$  by Day and Venanzi<sup>13</sup>.

The electronic spectrum of the compound  $[\text{Bu}^t\text{PCl}_3]_2[\text{PtCl}_6]$  exhibited weak bands at  $25000$  and  $29000\text{ cm}^{-1}$ , corresponding to the transition  $^1\text{A}_{1g} \rightarrow ^3\text{T}_{1g}$  and  $^1\text{A}_{1g} \rightarrow ^1\text{T}_{1g}$ . A strong band at  $38050\text{ cm}^{-1}$  is assigned to  $\pi$ -eg (metal-chloride) charge transfer transition<sup>20</sup>. The anion,  $[\text{PtCl}_6]^{2-}$ , can thus be assigned  $O_h$  symmetry.

A low intensity band at  $22100\text{ cm}^{-1}$  was observed in the electronic spectrum of  $[\text{Bu}^t\text{PCl}_3]_2[\text{UO}_2\text{Cl}_4]$  which could be due to  $1\text{ }\Sigma_g^+ - 3\pi_u$  transition for  $\text{UO}_2^{2+}$  moiety<sup>21</sup> and the anion  $[\text{UO}_2\text{Cl}_4]^{2-}$  may have  $D_{4h}$  symmetry.

Thermal analyses of  $[\text{Bu}^t\text{PCl}_3]_2[\text{UO}_2\text{Cl}_4]$  and  $[\text{Bu}^t\text{PCl}_3]_2[\text{Zr}_2\text{Cl}_9]$  have been studied. In the two complexes the first mass loss (23 and 12%, respectively) was observed between  $250$ - $350^\circ$  and corresponded to decomposition and removal of  $\text{Bu}^t\text{Cl}$  (theoretical 23.09 and 12.63%). The second step was a slow decomposition and oxidation between  $450$ - $600^\circ$ , after which the mass becomes constant. This corresponds to the final formation of uranyl or zirconium phosphates ( $\text{U}_3\text{O}_8 \cdot 3\text{P}_2\text{O}_5$  or  $\text{ZrO}_2 \cdot \text{P}_2\text{O}_5$ ), respectively.

Attempts to synthesise the complexes of platinum(IV) chloride with phenyldichlorophosphine

were unsuccessful. The failure of these reactions may probably be due to the reduction of Pt(IV) by phosphine as has been reported by Chatt<sup>22</sup> in the reactions of tertiary phosphines with Pt(IV) compounds.

#### Acknowledgements

The authors thank Prof. H. K. Pujari, Head, Chemistry Department, Kurukshetra University, Kurukshetra for facilities. One of the authors (S. L.) is also thankful to C.S.I.R., New Delhi for financial assistance.

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