



METAL DERIVATIVES OF ORGANO – PHOSPHOROUS COMPOUNDS: ZIRCONIUM (IV) DERIVATIVES

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ABSTRACT

Some new complexes of compositions have been isolated from the reaction of Zirconium (IV) chloride with dialkyl/diaryl phosphites in different molar ratios and under varying condition of temperature and solvent. The complexes have been characterized on the basis of elemental analysis infrared spectral data and magnetic susceptibility measurement. The lowering of the frequency in the spectra of complexes is a indicative of octahedral environment around the central of Zirconium metal ion and of the polymeric nature of complexes. All the complexes are expected to be octahedral.

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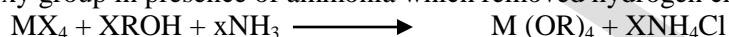
Schwarzenbach¹ compared the stability of organophosphonic acid and carboxylic acid complexes and suggested that organophosphonic acid have been found to be forming more stable complexes in comparison to carboxylic acid. Attempts have been made to synthesize new class of organopolyphonic acids as chelating agents. KabaChnik et al.² synthesized ethylenediamine–N, N'–bis (isopropyl phosphonic) acid (EDBIP) and ethylene diamine–N, N'–bis (dimethyl methylene phosphonic) acid (EDBMMP) by condensation of ethylene diamine with acetone and dialkyl phosphites followed by the hydrolysis of the obtained ester. Bersworth³, Bank and Yerick⁴ synthesized ethylene diamine–N, N, N', N'–tetrakis (methylene phosphonic), acid (EDTMP) and 1, 2–cyclo–hexylenediamine–N, N', N'–tetrakis (methylene phosphonic) acid by using the method suggested by Schwarzenback et al.⁵ Moedritzer and Irani⁶ reported that hydroxymethyl phosphonic acid is formed in a side reaction which interferes in the separation of pure aminophosphonic acid. This method was used by Westuback et al.⁷ and other researchers³⁻⁴ in reactions with poly amines. Isbell and chambers⁸ synthesized α -amino-ethyl phosphonic acid by curtius reaction. α -amino alkyl phosphonic acids were synthesized by Kabachnik et al⁹⁻¹⁰ in reactions of dialkyl phosphates with ammonia and a carboxyl compound.

The reactions of anhydrous Zirconium (IV) chloride with di-isopropyl methyl phosphonate were studied similar to reactions with anhydrous tin(IV) chloride and observed that isopropyl chloride and hydrogen chloride were evolved on heating the adduct¹¹. $TiCl_4 \cdot DIMP$. Lahe's et al.¹² studied the structure containing two phosphonate groups trans to each other. Similarly the reaction

of Zirconium (III) chloride was carried out with di-isopropyl methyl phosphonate (DIMP) at elevated temperature in benzene under reduced pressure. The complex tris(isopropyl methyl phosphonate) Zirconium (III) was obtained which was found to be soluble in all common organic solvents. On the basis of IR spectral studies a hexa coordinated polymeric structure, has been suggested to the complex¹³.

RESULT AND DISCUSSION

The reactions between Zirconium tetrachloride and dialkyl / diaryl phosphites were carried out in different molar ratios taking benzene as solvent. Some reactions were also carried out in absence of benzene solvent. Hydrogen chloride gas was evolved in the reactions. To avoid side reaction between evolved hydrogen chloride and dialkylphosphite, the reactions were carried out under reduced pressure (~20mm). The reaction between Zirconium tetrachloride with excess of dialkyl phosphite or in 1:4 molar ratio under refluxing at an oil bath temperature 110 – 120⁰C under reduced pressure (~20mm) yielded a product of the type Zr [OR(O) (OR) (R)]₄ in which all the four chlorine atoms of ZrCl₄ was replaced. This result does not resemble with the results reported by Jennings et al¹⁴ and Puri and Mehrotra¹⁷ in their studies on the reactions of Zirconium tetrachloride with alcohols and β-diketones respectively where even in excess of ligands only two chlorine atoms from ZrCl₄ could be replaced but the results obtained by all the resemble with the results obtained by Nelles¹⁵. Where all the four chlorine atoms were replaced by alkoxy group in presence of ammonia which removed hydrogen chloride from the reaction mixture.



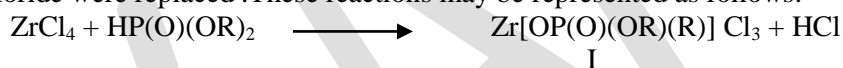
The reaction of Zirconium tetrachloride with dialkyl / diaryl phosphite may be represented as follows:



(R = ethyl, n-propyl, iso-propyl, n-butyl, diphenyl methyl)

Similar results have been reported by Peds et al¹⁶ in the reactions studied between Zirconium tetrachloride and diphenyl phosphonate.

The reactions of Zirconium (IV) chloride with dialkyl / diaryl phosphites were also studied in 1:1, 1:2 and 1:3 molar ratios in benzene solvent medium under reflux condition and reduced pressure (~20mm) at an oil –bath temperature 110-120⁰C. In the reaction one, two and three chlorine atoms from Zirconium tetrachloride were replaced. These reactions may be represented as follows:



In absence of benzene solvent.



III
↓



V

The product (I-V) are violet or yellow solids. These are moisture sensitive and become sticky on exposure to moist air. They are insoluble in common organic solvents, hence are polymeric in nature. They do not melt at higher temperature (300⁰C).

The structure of the Zirconium derivatives of dialkyl/ diaryl phosphites have been characterized by infra-red spectral studies (Table-1). In IR-spectra of Zirconium (IV) derivatives of various dialkyl / diaryl phosphites absorption bands have been observed in IR-spectral region 1125-1070 cm⁻¹. These have been assigned to phosphoryl group (P = O). The IR-absorption band due to free phosphoryl group (P=O) in dialkyl phosphites is observed in the region 1250-1220 cm⁻¹. The observed shift (νP=O) to lower frequency in Zirconium (IV) complexes may be attributed to the coordination of the phosphoryl oxygen to the Zirconium atom of the neighbouring molecules⁷. Strong absorption bands in the range 1020-1010 cm⁻¹ have been assigned to ν(P – O – C) absorption frequencies of these complexes. In IR-spectra of Zirconium derivatives weak bands were observed at 2460-2430 cm⁻¹ which could be due to ν(P – H)

frequencies. These could be present due to partial hydrolysis of the products during mixing the sample with nujol for recording IR-spectra of the complexes.

The IR-absorption bands observed in far IR region 600-560 cm^{-1} show characteristic absorption of (Zr – O – P) bonding in Zirconium derivatives⁵. The IR-absorption bands appearing in the far IR region 420-370 cm^{-1} could be attributed to $\nu(\text{Zr} - \text{Cl})$ frequencies 21 in complex is where chlorine atoms are partially replaced by ligand groups. The presence of an IR-absorption band in the region 1125-1170 cm^{-1} indicates the presence of P=O. The plausible mechanism of the formation of Zirconium derivatives of dialkyl / diaryl phosphite could be suggested in which two structures A and B are possible for these complexes.

EXPERIMENTAL CHEMICALS

Zirconium (IV) chloride (Fluka, AG) was used after analysis. Diethyl phosphite, Di-n-propyl phosphite, Di-is-propyl phosphite, Di-n-butyl. Phosphite (Both Fluka, AG) Di phenyl methyl phosphite (Aldrich, AG) were used after distillation under reduced pressure.

ANALYSIS OF INSTRUMENTS

Estimations of Chlorine, Phosphorus was done grammatically by standard wet analysis. Infra-red spectra of compounds was scanned on Beckman IR-20 spectrophotometer, in nujol mull by taking care of atmospheric moisture. Magnetic susceptibility measurements were done on Gouy's balance taking copper sulphate as calibrant.

Reactions between Zirconium (IV) chloride and diethyl phosphite in different molar ratios: IN BENZENE SOLVENT

To a known amount of ice cooled Zirconium (IV) chloride in benzene was added calculated amount of respective diethyl phosphite and di-n-propyl phosphite in benzene under anhydrous conditions, Heat and hydrogen chloride were evolved in the reaction. After cooling the reaction mixture to room temperature it was refluxed under reduced pressure and at oil bath temperatures of 110-120 $^{\circ}\text{C}$. After 8-10 hrs of refluxing a yellowish orange product was formed which increased in amount on further refluxing till the completion of reaction. It took 30-40 hrs in each case. The excess of benzene was distilled off and its traces were removed in vacuo at 80 $^{\circ}\text{C}$. The product was washed with dry benzene and dried again in vacuo. White or yellowish white solid product was obtained. Analytical results have been reported in Table 1.

Table 1 Preparation and Analysis of Zirconium (IV) Chloride Derivatives with diethyl phosphite and di-n-propyl phosphite

Sl. No.	ZrCl ₄	Reactants	Compound	Colour	Ratio	C	H	P	Cl
1	2.33	1.38	Zr [OP(O)(OC ₂ H ₅) ₂ Cl] ₃	light green solid	1:1	14.34	2.98	9.26	31.84
2	2.33	2.76	Zr [OP(O)(OC ₂ H ₅) ₂ Cl] ₂	light green solid	1:2	22.02	4.58	14.22	16.28
3	2.33	4.14	Zr [OP(O)(OC ₂ H ₅) ₂ Cl] ₃	light green solid	1:3	26.76	5.57	17.28	6.59
4	2.33	5.52	Zr [OP(O)(OC ₂ H ₅) ₂ Cl] ₄	light green solid	1:4	34.72	6.75	14.95	-
5	2.33	1.66	Zr [OP(O)(OC ₃ H ₇) ₂ Cl] ₃	light green solid	1:1	19.83	3.85	8.54	29.33
6	2.33	3.32	Zr [OP(O)(OC ₃ H ₇) ₂ Cl] ₂	light green solid	1:2	29.67	5.69	12.60	14.43
7	2.33	4.98	Zr [OP(O)(OC ₃ H ₇) ₂ Cl] ₃	light green solid	1:3	34.72	6.75	14.59	5.70
8	2.33	6.64	Zr [OP(O)(OC ₃ H ₇) ₂ Cl] ₄	light green solid	1:4	34.72	6.75	14.95	-

WITHOUT SOLVENT

To a known amount of Zirconium (IV) chloride was added calculated amount of dialkyl / triethyl phosphite dropwise in dry conditions by keeping the flask in ice. The reaction is exothermic so heat and hydrogen chloride evolved very fastly. The reaction mixture was heated at an oil bath temperatures of 50-60°C and 110-125°C and reduced pressure. The reaction was very fast in beginning. After 3-4 hrs of heating the reaction mixture turned to a solid form. It was heated upto 10-15 hrs till the reaction was over. In the end the product was washed with benzene and dried in vacuo at 80°C. White or yellowish solid obtained as a product. The analytical results have been shown in Table 2.

Table 2 Infra-Red spectra of diethyl phosphite and di-n-propyl phosphite of Zirconium IV

Sl. No.	Complex Compound	$\nu(\text{P}-\text{O}-\text{C})$ Cm^{-1}	$\nu(\text{P}=\text{O})$ m^{-1}	$\nu(\text{P}-\text{C})$ cm^{-1}	$\nu(\text{P}-\text{H})$ cm^{-1}	$\nu(\text{Ti}-\text{O}-\text{P})$ cm^{-1}	$\nu(\text{Ti}-\text{Cl})$ cm^{-1}
1	Zr [OP(O)(OC ₂ H ₅)(C ₂ H ₅)]Cl ₃	1015, 1020	1120,1125	750	2440	590	420,395
2	Zr [OP(O)(OC ₂ H ₅)(C ₂ H ₅)] ₂ Cl ₂	1010, 1015	1090	735	2450	585	400, 380
3	Zr [OP(O)(OC ₂ H ₅)(C ₂ H ₅)] ₃ Cl	1010, 1020	1080	730	2430	580	410, 380
4	Zr [OP(O)(OC ₂ H ₅)(C ₂ H ₅)] ₄	1005	1075	725	2420	570	-
5	Zr [OP(O)(OC ₃ H ₇)(C ₃ H ₇)]Cl ₃	1020	1090	750	2445	595-570	420
6	Zr [OP(O)(OC ₃ H ₇)(C ₃ H ₇)] ₂ Cl ₂	1015	1085	740	2440	590	400,375
7	Zr [OP(O)(OC ₃ H ₇)(C ₃ H ₇)] ₃ Cl	1015	1090	725	2450	590	395
8	Zr [OP(O)(OC ₃ H ₇)(C ₃ H ₇)] ₄	985	1075	720	2430	570	-

REFERENCES

- Schwarzenbach, G. and Flaschka, H.; "Complexometric Titration" Methuen & Co. London (1969).
- Kabachnik, M.I. Medved, T. Ya, Dyatlova, N.M. Rudomino, M.V. Churilling, N.V. Fitsulyak, I.D. Ussar 461, 106, 25 Feb. (1965) Chem. Abstr 87, 135936b (1977).
- Bersworth, F.C. U.S. Pat 2, 599, 807, (1952). Chem. Abstr. 47 43601 (1953).
- Banks, C.V. and Yerick, R.E. Anal Chim. Acta 20, 301 (1959).
- Schwarzenbach, G. Ackermann, H. and Ruchstul, P. Helv. Chim. Acta, 32, 1175 (1949) Chem. Abstr 44 547e (1950).
- Moedritzer, K. and Irani R.R. J. Org. Chem. 31(5), 1603 (1966).
- Westrerback, S. Rajan, K.S. and Martall, A.E.J. Am. Chem. Soc. 87, 2567 (1965).
- Chambers, J.R. and Isbell, A.F.J. Org. Chem. 28, 832 (1964).
- Kabachnik, M.I. and Medved, T.Ya. Dokl. Akad. Nauk SSSR. 84, 689 (1952).
- Kabachnik, M.I. and Medved T. Ya. Dokl, Akad, Nauk, SSSR 84, 717 (1952).
- Mikulaski, C.M., Karayannis, N.M., Minkiswicz, J.V. Pytowski, L.L. and Lober, M.M. Inorg., Khim. Acta 3 523 (1969), Chem. Abstr. 72, 85774c (1970).
- Arbusov, B.A. and Pudovik, A.N., J. Gen. Chem. USSR 17, 2158 (1947). Chem. Abstr. 42, 4522bdeg (1948).
- Osipov, O.A.; Golvoronski, V.I.; Shvets, A.A.; Priman, Mol. Spektrosk. Khim. Sb. Dokl. Sib 3rd. Krasnoyarsk. USSR Rub 1964 (1966), 117-21 (Russ.) chem. Abstr. 69, 6592r (1968).
- Osipov, O.A.; Golvoronski, V.I. and Shvets. A.A. Zh; Neorgan Khim. 8, 2190-3 (1963) (Russ.) chem. Abstr. 64, 16835C (1966).
- Molvor, R.A.; Grant, G.A. and Rubloy, C.E. Cand. J. Chem. 34, 1611 (1956).
- Jennings, J.A. Wardlaw, W and Way, W.J.R.; J. chem. Soc. 637 (1936). Chem. Abstr, 36, 51804 (1936).
- Mehrotra, R.C. and Puri, D.M.J. Less Common Metals 3, 253 (1961), 4, 393 (1962), J.Ind. Chem. Soc. 39, 447, 449 (1962).