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Trisdimethoxyphosphato-Complexes of Titanium(III), Vanadium(III), and Chromium(III)

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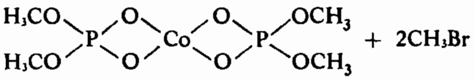
The trichlorides of titanium(III), vanadium(III) and chromium(III) were found to react with trimethylphosphate to give methyl chloride and trisdimethoxyphosphato-complexes of pseudooctahedral or octahedral structures.

It has been found recently that the dibromides of cobalt(II), nickel(II), and manganese(II) react with trimethylphosphate (TMP) with liberation of methyl chloride to give complex compounds,[1] *e.g.*:

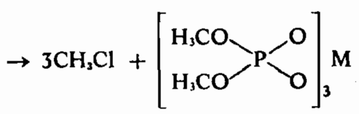
$CoBr_2 + 2(H_3CO)_3PO \rightarrow$



Such reactions explain the anomalous behaviour of the metal halide solutions in trimethylphosphate.[2] Since TMP-solutions of the perchlorates of titanium(III), vanadium(III), and chromium(III) in the presence of chloride ions show similar properties,[3,4] it was of interest to study the reactions of the respective trichlorides in TMP solution in more detail.

While titanium and vanadium trichlorides showed very low solubilities in TMP, chromium trichloride was readily dissolved in this solvent. The former chlorides were therefore converted into the acetonitrile-solvates, which were then used to prepare the respective solutions in TMP. All solutions were found to react at 60°C with trimethylphosphate with evolution of methylchloride, which was isolated as a byproduct and identified by its NMR-spectrum. From each of the solutions a residue was obtained which did not melt at 350°. The solid products were found to be insoluble in acetone, acetonitrile, benzene, 1,2-dichloroethane, nitromethane, and TMP. The products were free from chloride and gave analytical data in agreement with:

$MCl_3 + 3(CH_3O)_3PO \rightarrow$

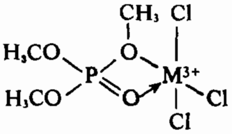


The reflection spectra of the compounds showed the presence of octahedral or pseudooctahedral coordination forms. This is indicated by the resemblance of the spectra to those of the hexaaquometal(III) species. Thus the spectrum of the titanium compound is characterized by a broad, unsymmetrical band with a maximum near 20000 cm^{-1}, while the chromium compound showed maxima at 21500 and 15000 cm^{-1} showing a lower D_q-value than for the chromium(III) hexaaquocomplex.

The infrared spectra of the solid compounds showed that the P=O frequency, which is found in TMP at 1280 cm^{-1}, is shifted to 1190 cm^{-1}. This allows the conclusion that the coordination is achieved through the oxygen atoms of the P–O groups.

It is thus apparent that trisdimethoxyphosphates of titanium(III), vanadium(III), and chromium(III) have been obtained. The dimethoxyphosphate group acts as a bidentate ligand through two of its oxygen atoms allowing the metal ions to achieve hexacoordination in the tris methoxyphosphato-compounds.

The high donor number of TMP ($DN_{SbCl_5} = 23$) suggests the coordination of TMP at the trichloride as the first step. The steric conditions will enable the TMP molecule to use also the oxygen atom of one of the methoxy-groups for coordination at the metal ion. This leads to a loosening of the O–CH_3 bond and also to an increased stability of the new complex with bidentate ligands (chelate-effect).



In this way the chlorine positions at the metal ion are replaced by coordination of the bidentate dimethoxyphosphate groups with simultaneous formation of methyl chloride.

Experimental Section

All operations were carried out in the absence of moisture. TMP (Ethyl Corporation, Detroit, Mich.) was refluxed over CaH_2 for several hours and after distillation *in vacuo* distilled over anhydrous sodium carbonate and fractionated; water content below 10^{-3} mol/l, $\varkappa = 10^{-9}$ Ohm^{-1} cm^{-1} at 20°. Acetonitrile

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(1) V. Gutmann and K. Fenkart, *Mh. Chem.* 99, 1452 (1968).
(2) V. Gutmann and K. Fenkart, *Mh. Chem.* 98, 1 (1967).
(3) V. Gutmann, A. Scherhaufer and H. Czuba, *Mh. Chem.* 98, 619 (1967).
(4) V. Gutmann, « Coordination Chemistry in Non Aqueous Solutions », Springer-Verlag Wien - New York, 1968.

(Sohio Chemical Co., Ohio, Mich.) was refluxed over P_2O_5 and fractionated; water content below 10^{-4} mol/l, $\varkappa = 10^{-8}$ Ohm^{-1} cm^{-1}.

$TiCl_3$ (Stauffer Chemical Co.), water content below 10^{-3} mol/l. VCl_3, water content below 10^{-3} mol/l; $CrCl_3$ was prepared by refluxing the hydrated chloride with thionyl chloride.

$TiCl_3$ is nearly insoluble in TMP. It was dissolved at 60° in acetonitrile and by partial evaporation the solvate was precipitated. This was dissolved in TMP to give a pink precipitate after a few minutes. In a vacuum a gas was evolved, which was frozen out and identified as CH_3Cl by the NMR-spectrum in CCl_4 (peak at 2.99 ppm). From the solution the solvent was removed in a vacuum at 60°, the residue washed with CCl_4 and exposed to the vacuum. It did not melt at 350° and was insoluble in acetone, acetonitrile, benzene, 1,2-dichloroethane, nitromethane and TMP.

Likewise VCl_3 was dissolved in acetonitrile and treated in an analogous manner. Again CH_3Cl was identified as the volatile product. The residue was isolated and showed similar properties to the titanium compound.

$CrCl_3$ gives in TMP a wine-red solution. After several hours a green precipitate is formed, while CH_3Cl collects in the cooled trap. The precipitate was isolated and analyzed.

Analytical. To determine the metal content the samples were treated in a microbomb with 3 g Na_2O_2 in the presence of a few drops ethylene glycol.[5] The metal contents were then determined photometrically, titanium as titanyl peroxotitanate, vanadium as heteropolytungstate and chromium as chromate. Chlorine was determined by the potentiometric method, and P as ammoniumphosphomolybdate.

Calcd. for $TiP_3O_{12}C_6H_{18}$: Ti, 11.3; P, 22.0; C, 17.0; H, 4.3; Cl, 0%. Found: Ti, 12.0; P, 20.1; C, 16.1; H, 4.7; Cl, 0.04%.

Calcd. for $VP_3O_{12}C_6H_{18}$: V, 12.0; P, 22.0; C, 17.0; H, 4.2; Cl 0%. Found: V, 14.0, P, 19.7; C, 17.7; H, 5.1; Cl 0.006%.

Calcd. for $CrP_3O_{12}C_6H_{18}$: Cr, 12.2; P. 21.8; C, 16.9; H, 4.3; Cl 0%. Found: Cr 12.1; P, 20.7; C, 17.4; H, 4.6; Cl, 0.04%.

The ^{1}H-NMR spectra were taken in CCl_4-solution with TMS as internal standard. The reflection spectra were recorded on a Beckmann DU-spectrophotometer with MgO-powder as a white standard. The solids were fairly well protected from hydrolysis by sealing the glass plates with silicone grease. For the infrared spectra a Perkin-Elmer Infracord 237 was used. TMP was taken by the capillary technique and the solid compounds in nujol.

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(5) H. Vodicka, Dissertation, Technische Hochschule, Wien, 1968.