Chemical Communications

(The Journal of The Chemical Society, Section D)

NUMBER 12/1970 24 JUNE

Non-repeatability of the Reported Preparation of Vanadium(V) Chloride

By I. M. GRIFFITHS and D. NICHOLLS*

(*Donnan Laboratories, The University, P.O. Box 147, Liverpool* L69 3BX)

Summary The reported preparation of vanadium(V) chloride is not confirmed; instead two novel complexes have been isolated from the $VOCl_3$–PCl_5 system.

SLAWISH AND JANNOPULOS[1] have claimed that the hitherto unknown vanadium(V) chloride can be prepared by the reaction

$$VOCl_3 + PCl_5 \rightarrow VCl_5 + POCl_3$$

in boiling 1,2-dichloroethane. The product was sublimed to give black crystals. This most unexpected thermal stability for the chloride, as well as our surprise at the reaction proceeding in the way indicated, led us to repeat the experiment under the conditions used by these authors and also at lower temperatures.

The reaction between equimolar quantities of $VOCl_3$ and PCl_5 in dry 1,2-dichloroethane at room temperature produces a dark brown precipitate. This when filtered off, washed with dichloroethane and dried *in vacuo* at room temperature has the composition PCl_8VO (by analysis). This product can be sublimed unchanged *in vacuo* at 80—90°; it is very readily hydrolysed to vanadium(V) oxide in moist air and is diamagnetic. Its reflectance spectrum shows absorption bands at 15,400, 18,100sh, 21,400, and 31,000sh cm^{-1}; with the exception of the band at 21,400 cm^{-1} these are the three lowest energy bands characteristic of the spectra of tetrachlorooxovanadates(V).[2] In nitromethane at 10^{-3}M the molar conductivity (Λ_M = 75·2 ohm^{-1} cm^2) indicates the compound to be a univalent electrolyte and we accordingly formulate it as $[PCl_4^+][VOCl_4^-]$. The infrared spectrum is in agreement with this formulation having a strong band which we assign to ν(V–O) at 1010 cm^{-1} and bands at 582s, 650s and 1304w cm^{-1} which are present in the spectrum of the PCl_4^+ ion.[3] Our spectrum does not show the weak bands reported for this ion at 1160 and 1215 cm^{-1} but contains weak bands at 1256, 1086, and 1030 cm^{-1}.

When the reaction is carried out under reflux in 1,2-dichloroethane, chlorine is evolved and upon cooling the resulting solution, black crystals of empirical formula PCl_9V (by analysis) are deposited. This compound has a room temperature magnetic moment μ_{eff} = 1·78 BM and an i.r. spectrum with absorptions at 1303s, 1010w, 640s and 600s cm^{-1} (the 1010 cm^{-1} band is almost certainly due to a trace of oxovanadium impurity). We therefore formulate it as $[PCl_4^+][VCl_5^-]$. Its electronic spectrum resembles that of $[PCl_4^+][VOCl_4^-]$ in having a strong band around 20,800 cm^{-1} which we attribute to a charge transfer transition involving the PCl_4^+ ion; it differs however in having low energy bands at 16,100 and 8300 cm^{-1} with a shoulder on this latter band at 6400 cm^{-1}. An octahedral arrangement in *e.g.* $[V_2Cl_{10}]^{2-}$ is thereby excluded (*Dq* for VCl_6^{2-} = 1,540 cm^{-1})[4] and a five co-ordinate VCl_5^- ion indicated. Two electronic transitions ($d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}, d_{xy}$ and d_{z^2}) are predicted for a trigonal bipyramidal d^1 system[5] and three ($d_{xy} \rightarrow d_{xz}, d_{yz}$; d_{z^2} and $d_{x^2-y^2}$) for a square pyramidal structure. In view of the small separation between the two lower energy bands the assignment of stereochemistry for the VCl_5^- ion is not possible since the 6,400 cm^{-1} band may arise as a Jahn–Teller distortion in the trigonal bipyramidal case.

The analogous reaction of $VOBr_3$ with PBr_5 in 1,2-dibromoethane under reflux yields largely vanadium(III) bromide.

(*Received, May* 6*th*, 1970; *Com.* 689.)

---

[1] A. Slawish and A. Jannopulos, *Naturwiss*, 1969, **56**, 369.
[2] D. Nicholls and D. N. Wilkinson, *J. Chem. Soc.* (*A*), 1970, 1103.
[3] T. C. Waddington and F. Klanberg, *J. Chem. Soc.*, 1960, 2339.
[4] P. A. Kilty and D. Nicholls, *J. Chem. Soc.*, 1965, 4915.
[5] P. C. Crouch, G. W. A. Fowles and R. A. Walton, *J. Chem. Soc.* (*A*), 1968, 2172.