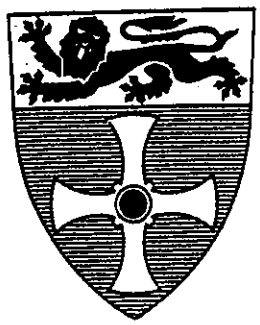

NON-AQUEOUS POLYVANADATE CHEMISTRY

BY

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A Thesis Submited in Partial Fulfilment of The Requirement for The Degree of Doctor Philosophy

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July 1998

ABSTRACT

The reaction between $VOCl_3$ and dme in CH_2Cl_2 produced red-brown crystals of $VOCl_3$.**dme**, **1**. Upon exposure to sunlight this compound produced green crystals of $VOCl_2$.**dme**, **2**. $[Ph_3BzP]_2VOCl_4$, **3**, has been produced by reaction of $VOCl_3$.**dme** with equimolar of $[Ph_3BzP]Cl$ in CH_2Cl_2. Sodium metavanadate was reacted with HCl (25%) and $[Bu^n_4N]Cl$ to produce $[Bu^n_4N]VO_2Cl_2$, **4**, in a high yield.

The $[VO_2(OMe)_2]^-$ anion has been produced from the attempted preparation of $Q[VO(OMe)_4]$ (Q= $[BzMe_3N]^+$, $[Bu^n_4N]^+$, $[Me_4N]^+$) and the crystal structure of $[BzMe_3N][VO_2(OMe)_2]$, **5**, is reported. $[Bu^n_4N][VO_2(OMe)_2]$, **6**, has also been produced in a high yield from the reaction of $[Bu^n_4N]VO_2Cl_2$ with two molar equivalents of NaOMe. The attempted synthesis of $[Bu^n_4N]_2[V_6O_{13}(OMe)_6]$ produced $[Bu^n_4N]_3V_5O_{14}$, **7**, whilst that of $[Bu^n_4N]_2[V_6O_{15}(OMe)_3]$ produced $[Bu^n_4N]_3V_5O_{14}$, **7** and $[Bu^n_4N]_4V_{12}O_{32}$, **8**.

$WO(OMe)_4$ was reacted with $VO(OMe)_3$ in the ratio of 1:1 in toluene to yield yellow needles of crystals of $[WVO_2(OMe)_7]$, **9**. Yellow microcrystalline $LiVO(OMe)_4$ **10** was prepared from equimolar amounts of $VO(OMe)_3$ and Li(OMe) in MeCN. The reaction between $VO(OMe)_3$ and NaOMe in the ratio of 1:1 and 3:1 in dme produced $[\{NaVO(OMe)_4\}_2]_n$, **11**, and $[\{NaV_2O_3(OMe)_5.dme\}_2]_n$, **12** , respectively. The structures of compound **11** and **12** are reported. The reactions between $[Bu^n_4N]_2MO_4$ (M= Mo, W) with $VO(OMe)_3$ did not proceed as expected and the products appear to be more complex than had been hoped.

$[Bu^n_4N]_3[HV_4O_{12}]$, **13** has been produced from the reaction between V_2O_5 and methanolic $[Bu^n_4N]OH$ in MeOH (2:3) and crystallized from cold acetone-toluene. $[Bu^n_4N]_3[V_5O_{14}]$, **7** has been produced from the reaction

between $[Bu^n_4N]_3[H_3V_{10}O_{28}]$ and methanolic $[Bu^n_4N]OH$ (1:3) ; V_2O_5 and a methanolic or an aqueous solution of $[Bu^n_4N]OH$ in the ratio of 5:6. The hydrolysis of $[VO(OMe)_3]$ in the presence of a methanolic solution of $[Bu^n_4N]OH$ with H_2O in the ratios of 5:3:6 ; 6:2:11 and 10:3:15 did not proceed as expected. The first and the third hydrolysis reaction produced a mixture of noncrystalline products, and the second produced $[Bu^n_4N]_4[V_{12}O_{32}]$, **8**. A new synthesis of $[Bu^n_4N]_3[V_{13}O_{34}]$, **14** has been discovered from the reaction of $[Bu^n_4N]_3[H_3V_{10}O_{28}]$ and $[VO(OMe)_3]$ in the ratios of 1:1 and 1:2, and from the reaction between $[Bu^n_4N]_3[H_3V_{10}O_{28}]$, $[VO(OMe)_3]$ and H_2O in the ratio of 1:3:3. $[Bu^n_4N]_4[V_{12}O_{32}]$, **8** was also produced when $[Bu^n_4N]_3[H_3V_{10}O_{28}]$ was reacted with an equimolar amount of p-toluidine, $[Bu^n_4N]OH$ solution in MeCN, or three molar equivalents of triethylamine.

An attempted preparation of $[Bu^n_4N][VO(OMe)_2(PhPO_3)]$, from the reaction of $VO(OMe)_3$ and $[Bu^n_4N][PhPO_3H]$ produced a mixture of non-crystalline purple compounds. $[Bu^n_4N]_2[V_2O_4(PhPO_3)_2]$, **15,** has been produced from the equimolar reaction of $VO(OMe)_3$, $PhPO_3H_2$ and $[Bu^n_4N]OH$ in acetonitrile, and the structure of **15** is also reported. $[Bu^n_4N][VO_2Cl_2]$, **4**, has been obtained from the reaction between $VOCl_3$.dme, $PhPO_3H_2$ and $[Bu^n_4N]OH$ in the ratio of 1:1:1 and 3:1:2. $[Bu^n_4N]_2[KV_3O_3(PhPO_3)_6.thf]$, **16**, had been produced from the reaction of **4** and $PhPO_3H_2$ in MeOH, and structurally characterised, although the source of K^+ has not been identified. In an attempt to prepare $[Bu^n_4N]_2[V_3O_5(OMe)_5(PhPO_3)]$, $VO(OMe)_3$ was reacted with $PhPO_3H_2$ and $[Bu^n_4N]OH$ to yield $[Bu^n_4N]_3[V_5O_{14}]$, **7**. The reaction of **7** and $[Bu^n_4N][PhPO_3H]$ (1:2) produced $[Bu^n_4N]_3[V_3O_8(PhPO_3)]$, **17**, and the compound has been structurally characterized. $[Bu^n_4N]_4[V_{12}O_{32}]$, **8**, has also

been obtained from the reaction of $[Bu^n_4N]_2[V_2O_4(PhPO_3)_2]$, $VO(OMe)_3$ and H_2O (1:2:3) ; **7**, $VO(OMe)_3$ and $PhPO_3H_2$ (1:1:1) ; and from the equimolar reaction of $[Bu^n_4N]_3[H_3V_{10}O_{28}]$, $PhPO_3H_2$ and $[Bu^n_4N]OH$. $[Bu^n_4N]_3[V_6O_{11}(PhPO_3)_5].0.5CH_3CN.0.5(CH_3CH_2)_2O$, **18** has been produced from the reaction of $VO(OMe)_3$ and **15** (2:1) ; $VOCl_3$.dme, $[Bu^n_4N][PhPO_3H_2]$ and $[Bu^n_4N]OH$ (1:1:2) ; and from the reaction of **15**, $[Bu^n_4N]Br$, $VO(OMe)_3$ and H_2O (2:1:6:9). The reaction of $VOCl_3$.dme, Na_3VO_4 and $[Bu^n_4N][PhPO_3H]$ in acetonitrile at room temperature produced $[Bu^n_4N]_2[V_9O_{19}Cl(PhPO_3)_4].2CH_2Cl_2$, **19** and the X-ray crystal structure of **19** is reported. In the attempt to synthesize $[Bu^n_4N]_5[V_{13}O_{26}(PhPO_3)_9]$, $[Bu^n_4N]_3[V_{13}O_{34}]$ was reacted with $PhPO_3H_2$ and $[Bu^n_4N]OH$ to yield $[Bu^n_4N]_3[H_3V_{10}O_{28}]$.