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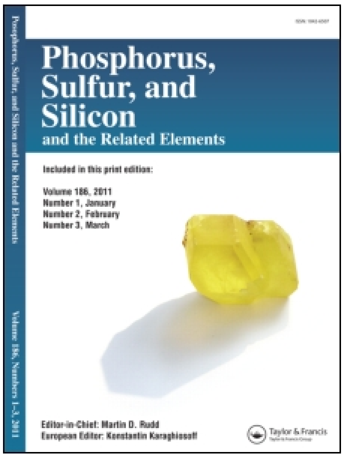

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New Vanadium Phosphonate Clusters and Coordination Polymers

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The solvothermal synthesis of vanadyl phosphonates has been studied under different conditions. Starting from dichlorovanadate, $M[V^VO_2Cl_2]$ ($M = PPh_4$, $MePPh_3$), or decavanadate and phosphonic acids, RPO_3H_2 (R = Me, *t*Bu, Ph), the formation of oxovanadium clusters under the directing influence of templates as well as of different solvents has been investigated. It is also shown that the cation M influences the formed oxovanadium structures as well as the rests in the phosphonic acids because of their different steric behaviour.

Keywords: oxovanadium phosphonates; oxovanadium clusters

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INTRODUCTION

The system $V/O/RPO_3^-$ has been studied intensively within the last decade not only because of its varied molecular chemistry reaching from binuclear species to compounds with „supramolecular architecture" but also in view of the fact that these compounds could be of interest for different applications e.g. as layered materials, sorbents or as precursors of catalysts (for a review see [1]). In recent years we studied the catalytical properties of oxovanadium phosphates in oxidation catalysis[2,3] as well as the preparation of improved vanadium phosphate catalysts[4] and new crystalline phases in the V/P/O system[5].

Now we extended our investigations to include oxovanadium phosphonates with the aim to obtain some new phases which are suited as potential precursors of oxidation catalysts. Furthermore we were interested in obtaining knowledge about the conditions of formation of the different oxovanadium clusters to be able to influence the structures of the desired products.

Zubieta et al. has been studied the formation of oxovanadium phenyl and t-butyl phosphonates from $[PPh_4][VO_2Cl_2]$ and $PhPO_3H_2$ or $t$$BuPO_3H_2$ under solvothermal conditions in Acetonitril[6]. We have modified the reaction conditions especially by carrying out the reaction in the presence of silver salts to influence the chloride ion concentration in the reaction mixture and by changing the cation of the dichlorovanadate.

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RESULTS AND DISCUSSION

In the system $[MePPh_3][VO_2Cl_2]/AgNO_3/PhPO_3H_2/MeCN$ depending on the silver concentration, i.e. the remaining Cl/V ratio in the reaction mixture different compounds are obtained. In the range Cl/V = 0.6 to 1.4 only $[MePPh_3][(VO)_6(PhPO_3)_8 \subset Cl^-]_3$ (1) is formed, the structure of which is built up by a honeycomb-like arrangement of spherical $[(VO)_6(PhPO_3)_8 \subset Cl^-]$ particles with hexagonal channels which includes the $[MePPh_3]$ cations.

In the presence of an excess of Ag^+ ions the following new silver containing oxovanadium phosphonates has been prepared:

$$[\{(V^V{}_3O_5)(V^{IV}O)(PhPO_3)_5\}_4(OV^{IV}...OV^{IV}..OH_2) \subset 4\,Ag^+]^{4-}\ (\underline{2})$$

$$[\{(V^V{}_2O_3)(V^VO_2)\}_4(PhPO_3H)_2(PhPO_3)_{14} \subset 4\,(Ag_2)^{2+}.\,H_2O]^{2-}\ (\underline{3})$$

$$[\{(V^V{}_3O_5)(V^V{}_2O_3)(V^VO_2)_2(PhPO_3)_6 \subset Ag(MeCN)_2\}_2]^{2-}\ (\underline{4})$$

$$Ag_3(V^VO_2)(PhPO_3)_2\ (\underline{5})$$

In addition a vanadium-free silver diphosphonate, $Ag(Ag\text{-}MeCN)[PhP(O)_2OP(O)_2Ph]$ (6), has been isolated.

X-ray single-crystal structure analyses of 2-4 showed that not - as expected - the introduced nitrate anions but the silver cations in connection with $(V^{V}O_2)^+$ and $(V^{IV}O)^{2+}$ building groups replace the template function of the chloride ions. This resulted in macromolecular anionic complexes which are assembled from several small, together connected spherical vanadyl phosphonate building units. These complexes integrate in their architecture Ag^+ cations via donor acceptor bonds with bridging oxygen atoms and vanadyl oxygen atoms.

The anion 2 is isostructural with $[\{(V^{V}{}_3O_5)(V^{IV}O)\ (PhPO_3)_5\}_4(H_2O...V^{V}\text{-}O\text{-}V^{V}..OH_2) \subset 4Cl^-]^{4-}$ [6]. Both ions differ in the replacement of the four included Cl^- ions by four Ag^+ cations.

The structure of 5 shows monomeric VO_2^+ cations in a distorted trigonal-pyramidal coordination beeing part of a branched $1/\infty\ \{(VO_2)(PhPO_3)_3\}$ single-chain which remembers the tetrahedral chains in alkaline metavanadates or polyphosphates.

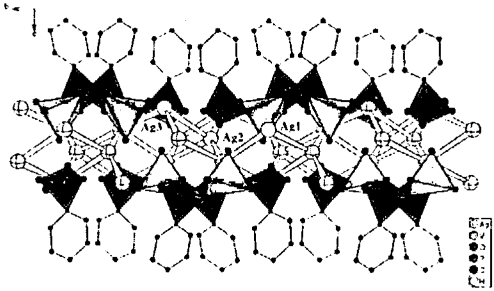

FIGURE 1 Oxovanadium phosphonate chains in $Ag_3(V^{V}O_2)(PhPO_3)_2$ showing the framework of Ag-Ag bonds

Linking of the chains via Ag3 leads to layers between two of them an only from Ag1 and Ag2 formed network of metal-metal bonds ($d_{(Ag\text{-}Ag)}$ = 3.13-3.43 Å) between Ag1 and Ag2 is included (FIG. 1).

In the System $[MePPh_3][VO_2Cl_2]/AgNO_3/tBuPO_3H_2/MeCN$ the influence of different templates (T = Cl^-, OH^-, NO_3^-) on the structure formed has been studied.

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These structures are belonging to the family $[(VO)_x(tBuPO_3)_8 \subset T^-]$ (x = 6-7). As shown in FIG. 2 the topology of the molecule with nitrate as template can be derived directly from $[(VO)_6(tBuPO_3)_8 \subset Cl^-]$. For this purpose one of the $\{V_2P_2O_4\}$ rings is opened and an {VO} unit fitted into the structure in such a way that a $\{V_3O_5\}$ trimer is formed.

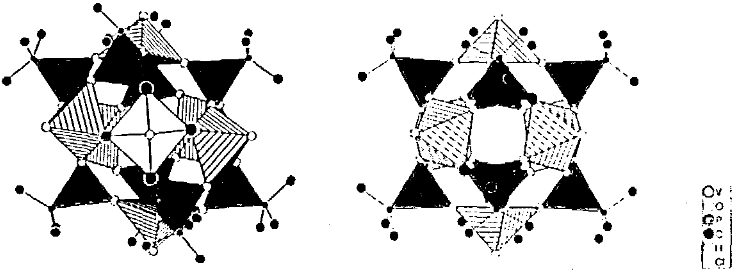

FIGURE 2 Molecules of $[(V^VO)_5(V^{IV}O)(tBuPO_3)_8 \subset Cl^-]$ (right) and $[(V^V{}_3O_5)(V^VO)_4(tBuPO_3)_8 \subset NO_3^-]$ (left); hatched circles show the oxygen atoms of P-O-V bonds which are opened for the insertion of the additional $[OVO_4]$ pyramid

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By thermal degradation from $[PPh_4][(VO)_4\{PhP(O)_2OP(O)_2PPh\}_4 \subset Cl^-]$ pure β-$(VO)(PO_3)_2$ and from $[(VO)_6(tBuPO_3)_8 \subset Cl^-]$ a mixture of V_xO_y and β-$(VO)(PO_3)_2$ have been obtained. These are active phases in oxidation catalysis.

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