Metal Organophosphonates

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Unexpected Reactions of $[Ag(NCCH_3)_3][(V_2O_3)_2(RPO_3)_4{\subset}F]$ Cage Compounds with H_2 and NO**

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We report herein a strategy for the preparation of a new type of inorganic–organic hybrid materials that offer unique possibilities for tuning their properties and exhibit unexpected redox behavior with respect to NO and H_2. The strategy involves the use of a fluoride-templated vanadium cage $[(V_2O_3)_2(RPO_3)_4{\subset}F]^-$ as a building block linked by coordinated transition-metal fragments to give $[M^{n+}L_x][(V_2O_3)_2(RPO_3)_4{\subset}F]_n$ (M = metal ion, L = ligand, R = organic group). For example, the compound $[Ag(NCCH_3)_3][(V_2O_3)_2(PhPO_3)_4{\subset}F]$ (**1**; Figure 1), in contrast to most mixed-metal organophosphonates,[1–3] is soluble in polar organic solvents such as CH_3CN, acetone, and DMSO, which makes possible not only its characterization by advanced analytical methods but also its use as a precursor compound for the preparation of new materials that are otherwise impossible or difficult to prepare. A simple protocol for the synthesis of such hybrid materials on the basis of metal and/or ligand exchange is shown in Scheme 1.

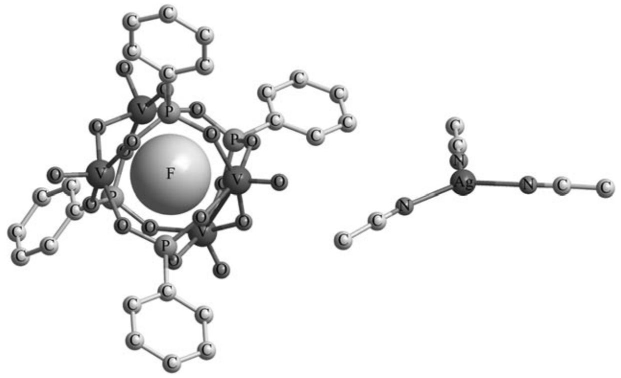
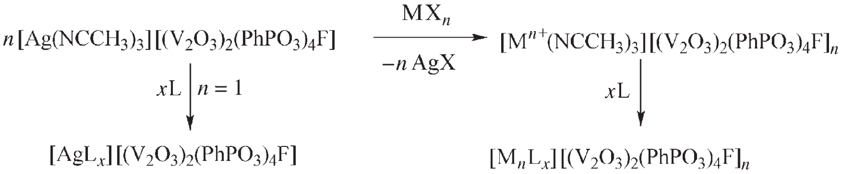


Figure 1. Crystal structure of **1** (F^- shown with van der Waals radius).

For example, the following compounds with the general formula $[ML_x][(V_2O_3)_2(PhPO_3)_4{\subset}F]_n$ ($[ML_x]^{n+}$ = [Ag(1,10-phenanthroline)$_2$]$^+$, [Ag(4,4′-bipyridine)]$^+$, [Ag(1-methylimidazole)$_2$]$^+$, $[Cu(NCCH_3)_6]^{2+}$, and [Cu(4,4′-bipyridine)$_2$($NCCH_3$)$_2$]$^{2+}$) have been prepared and characterized to show the utility of this approach in the preparation of new hybrid materials. In principle, by appropriate selection of M and L, any kind of metal complex can be incorporated into the cage compound. The cage structure itself with different ammonium or phosphonium ions as cations was the subject of some investigations.[4–6]



Scheme 1. Synthesis of inorganic–organic hybrid compounds with $[(V_2O_3)_2(RPO_3)_4{\subset}F]^-$ cages. X = Cl, Br.

A further advantage of the solubility of the title compound is the possibility to deposit it on the surface of a catalytic supporting material by adsorption from solution. In contrast to many other catalytic materials, this procedure makes use of the molecular structure of the unit, which could be determined separately beforehand together with its chemical properties.

The multinuclear NMR (^{19}F, ^{31}P, and ^{51}V) spectra of the diamagnetic cage structure $[(V_2O_3)_2(PhPO_3)_4{\subset}F]^-$ (Figure 2) nicely confirmed the existence and the geometry of the cage compound in solution. The ^{51}V NMR spectrum shows only one signal at $\delta \approx -582$ ppm. The ^{31}P NMR spectrum (in [D$_6$]DMSO) shows a doublet with a coupling constant of $^1J \approx 14$ Hz resulting from the coupling with the ^{19}F nucleus. The ^{19}F NMR spectrum of the fluoride anion appears as a quintet at $\delta = -176$ ppm and confirms the coupling effect with the four phosphorus atoms ($^1J \approx 15$ Hz).

One of the interesting chemical properties of these materials is the ability of the cage structure to change reversibly its oxidation state between the singlet ($4V^V$) and the doublet ($3V^V/1V^{IV}$) states accompanied by internal structural relaxation. The doublet state can easily be generated by one-electron chemical reduction of the diamagnetic cage, for example, by I^- or H_2/Pt at 300 K in CH_3CN. Generally, the EPR spectra of the mixed-valence state ($3V^V/1V^{IV}$) in CH_3CN solutions show a hyperfine multiplet resulting from the interaction of the unpaired electron with

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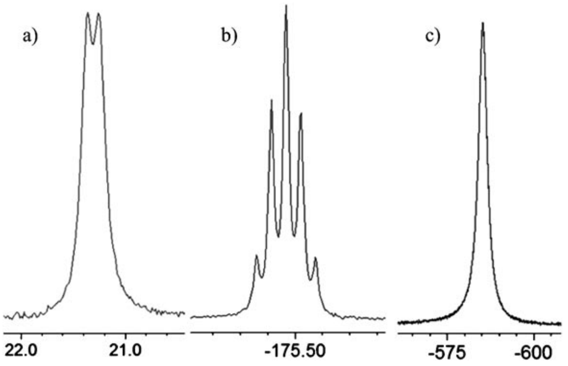

Figure 2. Multinuclear NMR spectra of **1** in [D_6]DMSO: a) ^{31}P, b) ^{19}F, c) ^{51}V (chemical shift in ppm).

four equivalent ^{51}V nuclei ($I={}^{7}/_{2}$) of the cage, accompanied by a rapid tumbling of the cage.[5,7,8] However, any factor reducing the tumbling rate , owing for example to the specific interactions, will simultaneously cause the spin density to be in part localized at one or more vanadium atoms. For example, lowering the temperature of the CH_3CN solution of the cage compound ($S={}^{1}/_{2}$) down to the frozen state at 77 K leads to the reduction of the hopping rate of the electron[9] and to a partial deformation of the cage, which together cause a localization of spin density. This process is reversible and is evidenced by the change from the 29-line spectrum (Figure 3) to an anisotropic eight-line spectrum typical for the localization of spin density at one ^{51}V nucleus. The reversibility of the redox process could be evidenced by the reaction of the cage ($S={}^{1}/_{2}$) with NO, whereby the singlet state could be recreated (see the Supporting Information).

To obtain a theoretical model for the cages and their EPR responses, quantum-mechanical calculations based on the hybrid version of the DFT method using the B3LYP functional in connection with the G-311G bases set[8] were carried out on singlet and doublet states of the cage. The calculations showed that the doublet state is more stable than the singlet state. Furthermore, larger V–OP and V–F bond lengths result in comparison to the singlet structure, which means that the volume of the reduced cage is enlarged as a result of an increase of the antibonding character of bonding orbitals between the V atoms and the O_3PR (R = H) fragments.

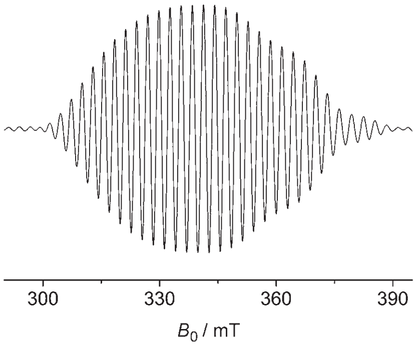

Figure 3. X-band EPR spectrum (after subtraction of a broad line) of **1** in CH_3CN solution treated with H_2/Pt at ambient temperature ($g_{iso}=1.968$, $A_{iso}=28.6$ G).

The most interesting and, in part, unexpected chemical properties become apparent if the solid materials are involved in redox reactions. To demonstrate this, the systems (a)–(d) in Figure 4 were chosen to show how it would be possible that the structure modification of the molecular cationic as well as anionic components can result in a remarkable change of the redox behavior of the vanadium ions. As a criterion for the redox ability of these materials, the temperature T_a for the first appearance of a V^{IV} EPR signal under a flow of H_2 or NO gases was used. The experimental results will be discussed below under the aspect of reactivity.

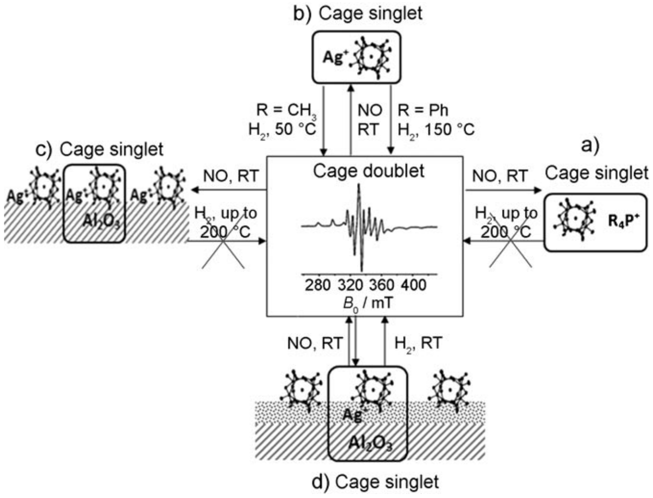

Figure 4. The doublet cage ($S={}^{1}/_{2}$) as a center in the reactivity circuit formed by: 1) the singlet cages undergoing different interactions and 2) the reactants NO and H_2. The spectrum in the center of the figure represents the X-band EPR response for the V^{IV} center. Details on the systems (a)–(d) are included in the text.

a) The first system deals with the cage $[(V_2O_3)_2(PhPO_3)_4\subset F]^-$ and a phosphonium[3] or Ag^+ counterion. It was found that the cage in the singlet state ($4V^{V}$) is unable to change its oxidation state to the doublet state ($3V^{V}/1V^{IV}$) under a flow of NO at 293 K. However, the $NO_{(g)}$ is able to reoxidize the cage in the doublet state (generated, for example, by reduction with I^-) to the singlet state, regardless of the type of counterion, which means that the doublet cage is itself also reoxidized in the solid state. Concerning the reduction of the cage under a flow of H_2, it was found that the cage in the singlet state with a phosphonium counterion could not be reduced by H_2 at temperatures below 200 °C (Figure 4a), while the compound consisting of the cage and silver cations is reduced to the doublet state with $T_a=150$ °C (see Figure 4b). This low T_a value for the silver complex should be attributed to the high ability of the Ag^+ ion to interact with H_2.[10–12]
b) The second system is related to the effect of the structure modification (by substitution) of the cage itself on the redox process. Using the cage $[(V_2O_3)_2(RPO_3)_4\subset F]^-$ (R =

CH_3, Ph) with Ag^+ as the counterion, it was found that under a flow of NO there is only a very small difference in the reaction ability of the doublet cage with Ph or CH_3 substituents. However, a drastic change in T_a was found under a flow of H_2: $T_a = 150\,°C$ for R = Ph, $T_a = 50\,°C$ for R = CH_3. This unexpected large shift in T_a should be caused by the large steric hindrance of the electron transfer in the case of Ph substitution.

c) To gauge possible applications, it was of interest to study the reactivity of **1** on the surface of supporting materials such as γ-Al_2O_3. It is of interest to note that the same results were found as in the case (a), in which phosphonium was the counterion for the reactions with H_2 and NO. The Ag^+ ions and the cages in (c) are adsorbed on different sites of the alumina surface, which should result in a larger separation between the cages and the Ag^+ ions and therefore in a diminishing of the effect of the Ag^+ ions.

d) The fourth system concerns the redox process of $[(V_2O_3)_2(RPO_3)_4\subset F]$ (R = CH_3 or Ph) supported on the surface of $AgNO_3$ which is deposited on γ-Al_2O_3. In this case, the unexpected result was found that the cage in the singlet state has the ability to be reduced to the doublet state under a flow of NO at room temperature. However, the EPR signal (spectrum in Figure 4) of the cage in the doublet state diminished with time, which means that the observed V^{IV} concentration represents a net effect. This result can be attributed to the fact that the cage in the doublet state is active toward oxidation to the singlet state under a flow of NO, which was shown by separate experiments. The second and also unexpected result was found when the cage in the singlet state was reduced to the doublet state under a flow of H_2 even at room temperature.

The mechanism by which the NO or H_2 promotes the redox process is obviously based on the combined action of different elementary processes. However, it has been demonstrated that $[Ag^+]_n$ clusters that are formed during the reduction of Ag^+ by H_2 are responsible for this activity in Ag-based catalysts.[13–15] The results presented here imply that at least one step in the reduction process of V^V centers should be the formation of polar Ag^+–H_2 intermediates.[10–12] There is obviously a synergetic effect caused by the silver species and the cage that is responsible for the activity of these materials. The electronic properties of the cage favor this behavior because from an energetics point of view the one-electron transfer in both directions is favored,[8] not least because of simple internal structural relaxation processes like spin-density delocalization and changes of the bond lengths (e.g. V–O).

Experimental Section

Compound **1** was prepared from the solvothermal reaction of HVO_3, $PhPO_3H_2$, and $AgNO_3$ in CH_3CN and characterized by multinuclear NMR spectroscopy (^{19}F, ^{31}P, and ^{51}V), elemental analysis, TGA, and X-ray diffraction while further physical and chemical properties were studied by EPR spectroscopy by using V^{IV} as monitors (for more details, see the Supporting Information).

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