Electronic Supplementary Material for PCCP


# Supplementary Material

### DFT Computations

In case of the $AlF_4^-$ surface model cluster four different surface models were investigated by DFT methods: $VO(acac)_2/AlF_4^-$ with axial coordination of the surface site (adduct I) and $VO(acac)_2/AlF_4^-$ with equatorial coordination of the surface site (adduct II). For the axial coordination of the surface site the influence of a proton coordinating with a chelating oxygen was examined. Two cases were distinguished, where the proton is either within the molecular plane of the acac ligand (adduct III) or out of plane (adduct IV). The converged geometries of the model complexes are illustrated in Figure S1. Some characteristic bond lengths and bond angles of the computed structures are summarized in Table S1. For the four converged geometries the $^{19}F$, $^{27}Al$, and $^{1}H$ ligand hfc were calculated and are summarized in Table SII.

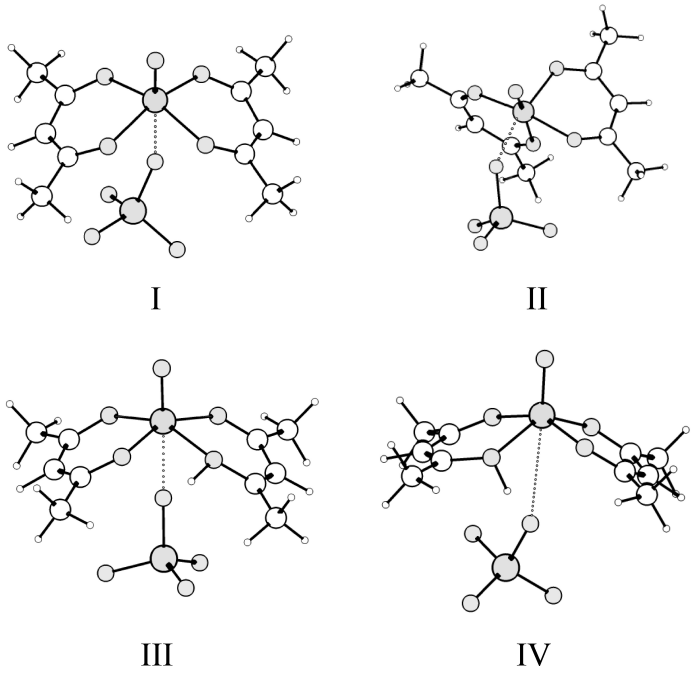


Figure S1: Optimized geometries for the model adducts I, II, III, IV, and IV. Large gray circles indicate F, medium gray circles V, small gray circles O, open circles C, and small open circles H atoms.

**Table S1:** Selected geometrical parameters of optimized $VO(acac)_2/AlF_3$ model adducts.

| adduct/ parameter | I | II | III | IV | $VO(acac)_2$[a] | exp.[b] |
|---|---|---|---|---|---|---|
| $R_{V=O}$[c] (Å) | 1.59 | 1.60 | 1.59 | 1.58 | 1.59 | 1.56 |
| $R_{V=O}$[d] (Å) | 2.02 | 2.02 | 1.96 | 1.93 | 1.99 | 1.97 |
| $R_{V=O}$[d] (Å) | 2.02 | 1.99 | 2.15 | 1,96 | 1.99 | 1.96 |
| $R_{V=O}$[d] (Å) | 2.01 | 1.96 | 1.94 | 1,97 | 1.99 | 1.98 |
| $R_{V=O}$[d] (Å) | 2.01 | 2.18 | 1.97 | 2.11 | 1.99 | 1.96 |
| $R_{V-F}$[e] (Å) | 2.50 | 2.09 | 2.25 | 2.99 | - | |
| $\angle O{=}V{-}O$[f] (°) | 101.8 | 100.0 | 101.5 | 106.7 | 106.7 | 104.5 |
| $\angle O{=}V{-}O$[f] (°) | 102.9 | 98.0 | 103.5 | 105.0 | 106.7 | 106.3 |
| $\angle O{=}V{-}O$[f] (°) | 102.1 | 99.0 | 99.5 | 102.9 | 106.7 | 108.2 |
| $\angle O{=}V{-}O$[f] (°) | 101.9 | 105.1 | 100.4 | 116.4 | 116.7 | 105.6 |
| $\angle O{=}V{-}F$[g] (°) | 179.5 | 96.4 | 176.2 | 168.0 | - | - |

[a] Computed values for an isolated $VO(acac)_2$ complex.[1] [b] Experimental values from an X ray single crystal structure of $VO(acac)_2$.[2] [c] Vanadyl bond length. [d] Bond lengths between V and O atoms of acac ligands. [e] Bond length between V and F atom of AlF surface model adduct. [f] Bond angles between vanadyl bond and O atoms of acac ligands. [g] Bond angles between vanadyl bond and F atom.

**Table S2:** Theoretically calculated $^{19}F$, $^{1}H$, and $^{27}Al$ hfc parameters $A_{ii}$, $A_{iso}$, and $T_{\perp}$ (in MHz) of $VO(acac)_2/AlF_3$ model adducts in comparison with experimental data.

| parameters/ model | | $A_{xx}$ | $A_{yy}$ | $A_{zz}$ | $A_{iso}$[a] | $T_{\perp}$[b] |
|---|---|---|---|---|---|---|
| I | $^{19}F$ | 0.34 | 0.76 | 12.70 | 4.60 | 4.05 |
| | $^{27}Al$ | -0.20 | -0.20 | 0.68 | 0.09 | 0.30 |
| II | $^{19}F$ | -34.45 | -29.63 | -37.92 | -8.72 | 23.32 |
| | $^{27}Al$ | -0.82 | -0.67 | 0.49 | -0.33 | 0.41 |
| III | $^{19}F$ | 2.44 | 5.60 | 16.14 | 8.16 | 4.14 |
| | $^{1}H$[c] | 7.43 | 8.31 | 20.80 | 12.22 | 4.36 |
| | $^{27}Al$ | -0.09 | -0.08 | 0.82 | 0.22 | 0.30 |
| IV | $^{19}F$ | 0.08 | 0.54 | 8.44 | 3.02 | 2.71 |
| | $^{1}H$[c] | -0.64 | -0.12 | 13.97 | 4.40 | 4.79 |
| | $^{27}Al$ | -0.03 | -0.02 | 0.66 | 0.20 | 0.23 |
| exp. | $^{19}F$ | 0.02 | 0.02 | 15.61 | 5.21 | 5.20 |
| | $^{1}H$[c] | 0.20 | 0.20 | 15.00 | 5.10 | 5.00 |
| | $^{27}Al$ | - | - | 2.2 | - | - |

[a] Calculated from $A_{iso} = 1/3(A_{xx} + A_{yy} + A_{zz})$. [b] Calculated from $T_{\perp} = ½ (A_{zz} - A_{iso})$. [c] Proton at chelating oxygen atom of acac ligand.

**References**

1 V. Nagarajan, B. Müller, O. Storcheva, K. Köhler and A. Pöppl, *Res. Chem. Intermed.*, 2007, **33**, 705.
2 P. Dodge, D. H. Templeton and A. Zalkin, *J. Chem. Phys*., 1961, **35**, 55.