Supporting Information

© Wiley-VCH 2007

69451 Weinheim, Germany
Metal-Oxide-Based Nucleation Process under Confined Conditions: Two Mixed-Valence $V_6$-Type Aggregates Closing the $W_{48}$ Wheel-Type Cluster Cavities

Achim Müller,* Michael T. Pope,* Ana Maria Todea, Hartmut Bögge, Joris van Slageren, Martin Dressel, Pierre Gouzerh, René Thouvenot, Boris Tsukerblat and Aidan Bell

Figure S1. UV-Vis spectrum of a freshly-prepared solution of 2.
Valence localization/delocalization and Intervalance Charge Transfer Transitions


![IR spectrum of 2](image)

**Figure S2.** IR spectrum of 2
Phosphorus NMR Spectra

Room temperature $^{31}$P solid-state NMR spectra were recorded at 162 MHz in the single-pulse mode using a Bruker Avance 400 spectrometer equipped with a 4 mm MAS NMR probe. Owing to the small chemical shift anisotropy of the samples, relatively low spinning rates (= 10 kHz) were sufficient to obtain spectra free of spinning side bands. Data were acquired with 10° flip angle of 1 ms length with a repetition time of 1 s. Chemical shifts are given with respect to 85% H$_3$PO$_4$ as external standard.

The $^{31}$P MAS NMR spectrum of 1 (Figure S4) displays three partially overlapping isotropic signals at ca. -7.7, -7.3 and - 7.1 ppm (fwhm ca. 160 Hz, ca. 1 ppm). This indicates the presence of at least three different phosphorus environments compatible
with the X-ray structural analysis showing the presence of four crystallographically-independent phosphorus atoms in the crystal.\(^5\) The \(^{31}\)P MAS NMR spectrum of 2 (Figure S5) displays a very broad isotropic feature centered at \textit{ca.} 0 ppm (fwhm \textit{ca.} 2 kHz, \textit{ca.} 12 ppm) which consists essentially of two overlapping signals with unequal width. According to the centrosymmetrical 2a, there should be four inequivalent phosphorus atoms. Due to the vicinity of the paramagnetic V\(^{IV}\) centers the individual signals are broadened with respect to 1 and overlap each other.

Figure S4. \(^{31}\)P MAS-NMR spectrum of 1
Figure S5. $^{31}$P MAS-NMR spectrum of 2