Functionalization of polyoxometalates: from Lindqvist to Keggin derivatives. 2. Investigation of the reactivity of anilines, organo-hydrazines and tolylisocyanate towards $[PW_{12-x}M_xO_{40}]^{n-}$ Keggin anions

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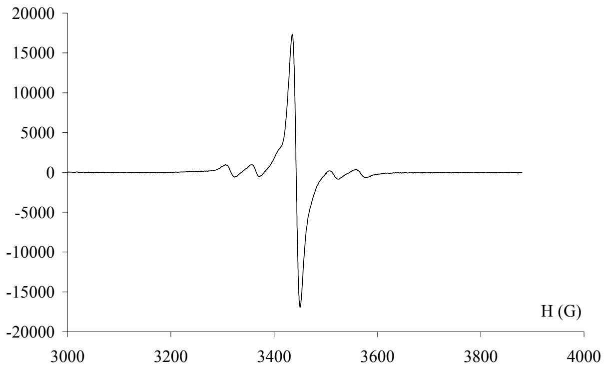
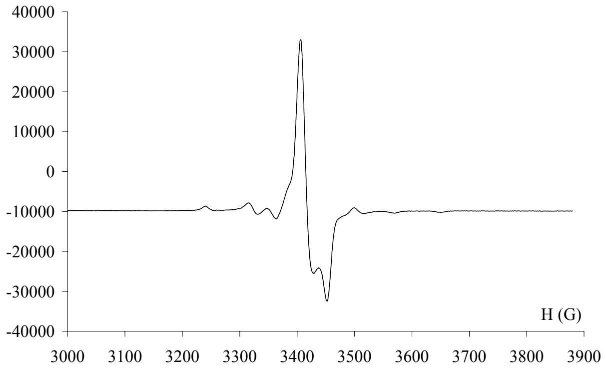
Supporting Information

EPR characterization of $\mathbf{2_I}$. The X band EPR spectra of $(Bu_4N)_4[\alpha\text{–}PW_{11}O_{39}\{Mo^VO\}]$ ($\mathbf{2_I}$) at room temperature were obtained in acetonitrile, with sample concentration of 10^{-2} M, in a 1 mm capillary tube. The X band EPR spectra at 77 K were obtained in acetonitrile, with sample concentration of 10^{-3} M, in a 3 mm quartz tube. The spectra are consistent with an axial Mo^V, as already observed by Pope *et al.*[1] on polycrystalline samples of $\mathbf{2_I}$ or by Launay *et al.* on a DMF solution of $[\alpha\text{-}SiW_{11}O_{39}\{Mo^VO\}]^{5-}$.[2] At room temperature, we thus observe the characteristic pattern for Mo^V with the central signal assigned to non-magnetically active molybdenum nuclei (Σnatural abundance = 75%) and six low-intensity satellites resulting from hyperfine coupling with the magnetically active molybdenum isotopes ^{95}Mo and ^{97}Mo ($I = 5/2$; Σnatural abundance = 25%). The spectrum at 77 K is consistent with a C_{4v} symmetry : $g_{//} = 1.912$, $g_\perp = 1.920$, $A_{//} = 74.29$ G and $A_\perp = 37.63$ G values are close to the ones obtained by Pope *et al.*[3b] ($g_{//} = 1.918$, $g_\perp = 1.937$, $A_{//} = 81.3$ G and $A_\perp = 33.24$ G)

Fig. 1 EPR spectra of $(Bu_4N)_4[\alpha\text{-}PW_{11}O_{39}\{Mo^VO\}]$ ($\mathbf{2_I}$) (in CH_3CN) at room temperature (top) and at 77 K (bottom).





ESI-mass Spectrometry in the positive mode. Positive mode ESI-mass spectra recorded on the products of reaction between **2** and N,N-methylphenylhydrazine, N,N-dimethylhydrazine, in refluxing acetonitrile, or 2,6-diisopropylaniline and 2,6-dimethylaniline, under microwave irradiation, have evidenced the formation of new cations, thus accounting for the unidentified signals observed by ^{1}H NMR. Indeed, in addition to the signal of the $(Bu_4N)^+$ cations (m/z 242), peaks are observed at m/z 329, m/z 267, m/z 384 and m/z 328 in the respective cases of N,N-methylphenylhydrazine, N,N-dimethylhydrazine, 2,6-diisopropylaniline and 2,6-dimethylaniline. These peaks have been attributed to the cations depicted on Figure 2, formed by condensation of the hydrazines or arylamines on dicyclohexylcarbodiimide. These attributions are confirmed by further collision induced dissociation (CID) experiments, whose results are shown in Table 2.

Fig. 2 Postulated structures of the cations obtained by refluxing $(Bu_4N)_3[PW_{11}O_{39}\{Mo^{VI}O\}]$ (**2**) with N,N-methylphenylhydrazine (a) or N,N-dimethylhydrazine (b) or under microwaves irradiation of **2** with 2,6-diisopropylaniline (c) or 2,6-dimethylaniline (d), in acetonitrile and in the presence of dicyclohexylcarbodiimide and pyridine.

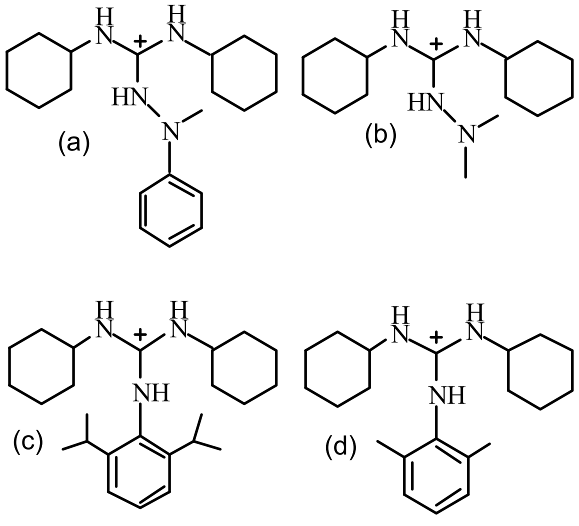


Table 2. MS^2 experiments on the cations obtained by refluxing $(Bu_4N)_3[PW_{11}O_{39}\{Mo^{VI}O\}]$ (**2**) with N,N-methylphenylhydrazine or N,N-dimethylhydrazine or under microwave irradiation in the presence of 2,6-diisopropylaniline or 2,6-dimethylaniline, in acetonitrile and in the presence of dicyclohexylcarbodiimide and pyridine.

m/z	Relative abundance	Postulated cation
With N,N-methylphenylhydrazine		
329	99%	$[C(NHC_6H_{11})_2(NHNC_7H_8)]^+$
247	1%	$[H_2NC(NHC_6H_{11})(NHNC_7H_8)]^+$
230	57%	$[(C_6H_{11}NH)C(N_2C_7H_8)]^+$
224	42%	$[H_2NC(NHC_6H_{11})_2]^+$
148	base peak	$[H_2NC(N_2C_7H_8)]^+$
131	15%	$[C(N_2C_7H_7)]^+$
107	10%	$[H_2NNC_6H_5]^+$
100	9%	$[H_3NC_6H_{11}]^+$
With N,N-dimethylhydrazine		
267	77%	$[C(NHC_6H_{11})_2(NHNC_2H_6)]^+$
185	1%	$[H_2NC(NHC_6H_{11})(NHNC_2H_6)]^+$
168	base peak	$[(C_6H_{11}NH)C(N_2C_2H_6)]^+$
125	1%	$[H_2NC(NC_6H_{11})]^+$
98	10%	$[H_3NC_6H_9]^+$
With 2,6-diisopropylaniline		
384	base peak	$[C(NHC_6H_{11})_2(NHC_{12}H_{17})]^+$
302	27%	$[H_2NC(NHC_6H_{11})(NHC_{12}H_{17})]^+$
285	28%	$[(C_6H_{11}NH)C(NC_{12}H_{17})]^+$
220	7%	$[(H_2N)_2C(NHC_{12}H_{17})]^+$

203	29%	$[H_2NC(NC_{12}H_{17})]^+$
188	38%	$[HC(NC_{12}H_{17})]^+$
186	91%	$[CNC_{12}H_{16})]^+$
170	6%	$[CNC_{11}H_{12}]^+$
146	18%	$[H_2NC_{10}H_{10}]^+$
131	1%	$[C_{10}H_{11}]^+$
With 2,6-dimethylaniline		
328	base peak	$[C(NHC_6H_{11})_2(NHC_8H_9)]^+$
246	26%	$[H_2NC(NHC_6H_{11})(NHC_8H_9)]^+$
229	40%	$[(C_6H_{11}NH)C(NC_8H_9)]^+$
164	8%	$[(H_2N)_2C(NHC_8H_9)]^+$
147	88%	$[H_2NC(NC_8H_9)]^+$
132	6%	$[HCNC_8H_9]^+$
100	6%	$[H_3NC_6H_{11}]^+$
98	1%	$[H_3NC_6H_9]^+$

References.

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