Electronic Supplementary Information for Dalton Transactions

Oxidation of *p*-chlorotoluene and cyclohexene catalysed by polymer-anchored oxovanadium(IV) and copper(II) complexes of amino acid derived tridentate ligands

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Supplementary material

Table - S1 Semi-quantitative (wt. %) information about the elements present on the surface of polymer beads obtained by EDAX.

Sample	C	N	O	V/Cu	Cl
Polymer bead	80.67	--	--	--	18.30
PS-H_2fsal-DL-Ala	68.72	1.99	8.35	--	0.34
PS-[VO(fsal-DL-Ala) H_2O]	62.97	1.22	11.99	3.34	0.15
PS-[Cu(fsal-DL-Ala) H_2O]	64.81	0.93	10.53	4.80	0.39
PS-H_2 fsal-L-Ile	70.93	2.12	8.27	--	0.30
PS-[VO(fsal-L-Ile) H_2O]	47.60	1.29	12.24	3.71	0.17
PS-[Cu(fsal-L-Ile) H_2O]	62.38	1.65	10.08	3.01	0.20

Table S2 - IR spectral data of ligands and complexes.

Name of sample	ν(C=N)	ν(V=O)
H_2fsal-DL-Ala, **I**	1635	
PS-H_2fsal-DL-Ala, **III**	1630	
PS-[VO(fsal-DL-Ala)(H_2O)], **1**	1602	984
PS-[Cu(fsal-DL-Ala)(H_2O)], **2**	1601	
H_2fsal-L-Ile, **II**	1638	
PS-H_2fsal-L-Ile, **IV**	1630	
PS-[VO(fsal-L-Ile)(H_2O)], **3**	1608	955
PS-[Cu(fsal-L-Ile)(H_2O)], **4**	1600	
[VO(fsal-DL-Ala)(H_2O)], **5**	1605	960
[Cu(fsal-DL-Ala)(H_2O)], **6**	1614	
[VO(fsal-L-Ile)(H_2O)], **7**	1610	977
[Cu(fsal-L-Ile)(H_2O)], **8**	1611	

Table S3 - Spin Hamiltonian parameters obtained from the experimental EPR spectra recorded for powdered samples of **2** and **4**, and of the corresponding non-polymer-bound complex **8** dissolved in DMF.

Catalyst	Sample	$g_{\parallel}$	$A_{\parallel}$ ($\times 10^{4}$cm^{-1})	$g_{\parallel}/A_{\parallel}$
PS-[Cu(fsal-DL-Ala)(X)], **2**	Fresh			
1st species		2.272	181	126
2nd species		2.295	171	134
PS-[Cu(fsal-DL-Ala)(X)], **2**-DMF	Fresh			
1st species		2.276	182	125
2nd species		2.305	178	130
PS-[Cu(fsal-DL-Ala)(X)], **2**	Used			
At least 3 distinct species present, one apparently corresponding to a highly distorted geometry. Approximate g values are given for this species.		$g_z \sim 2.34$ $g_y \sim 2.07$ $g_x \sim 1.94$		
PS-[Cu(fsal-DL-Ala)(X)], **2**-DMF	Used			
At least 3 distinct species present, one apparently corresponding to a highly distorted geometry. Approximate g values given for this species.		$g_z \sim 2.35$ $g_y \sim 2.07$ $g_x \sim 1.95$		
[Cu(fsal-L-Ile)(X)], **8**	In DMF			
1st species		2.285	175	130
2nd species		2.361	154	153
PS-[Cu(fsal-L-Ile)(X)], **4**	Fresh			
1st species		2.272	177	129
2nd species		2.314	160	144
3rd species		2.254	162	139
PS-[Cu(fsal-L-Ile)(X)], **4**-DMF	Fresh			
1st species		2.313	161	143
2nd species		2.274	183	124
PS-[Cu(fsal-L-Ile)(X)], **4**	Used			
At least 3 distinct species present, one apparently corresponding to a highly distorted geometry. Approximate g values are given for this species.		$g_z \sim 2.34$ $g_y \sim 2.07$ $g_x \sim 1.94$		
PS-[Cu(fsal-L-Ile)(X)], **4**-DMF	Used			
At least 3 distinct species present, one apparently corresponding to a highly distorted geometry. Approximate g values are given for		$g_z \sim 2.35$ $g_y \sim 2.07$ $g_x \sim 1.95$		

this species.

Table S4 - Vanadium-containing species (in ppm relative to VOCl$_3$) detected in the ^{51}V NMR spectra of 4 mM methanolic solutions (80% MeOH and 20% MeOD) of [V^{IV}O(fsal-DL-Ala)(H$_2$O)] (**5**) upon progressive additions of H$_2$O$_2$, followed by additions of styrene[a]

Treatment of complex **5**	^{51}V NMR signals[a]	Assignement of V species
Oxidation of **5** with air	–553 (~55%) [–562 and –566] (~45%)	[V^{V}O(fsal-DL-Ala)(MeO)(MeOH)]
Addition of 2 equiv. of H$_2$O$_2$. Global increase in intensity of the ^{51}V NMR signals.	–553 (~40%) [–562 and –566] (~60%)	[V^{V}O(fsal-DL-Ala)(MeO)(MeOH)]
Total of 4 equiv. of H$_2$O$_2$ added	–535 (15%) [–562 and –566] (~68%) –581 (~17%)	?[b] [V^{V}O(fsal-DL-Ala)(MeO)(MeOH)] [V^{V}O(fsal-DL-Ala)(O$_2$)(MeOH)]
Total of 6 equiv. of H$_2$O$_2$ added	–535 (10%) [–562 and –566] (~70%) –581 (~20%)	?[b] [V^{V}O(fsal-DL-Ala)(MeO)(MeOH)] [V^{V}O(fsal-DL-Ala)(O$_2$)(MeOH)]
Total of 7 equiv. of H$_2$O$_2$ added	–535 (8%) [–562 and –566] (~60%) –581 (~22%)	?[b] [V^{V}O(fsal-DL-Ala)(MeO)(MeOH)] [V^{V}O(fsal-DL-Ala)(O$_2$)(MeOH)]
Total of 8 equiv. of H$_2$O$_2$ added	[–562 and –566] (~15%) –581 (~77%) –658 (8%)	[V^{V}O(fsal-DL-Ala)(O$_2$)(MeOH)] [V^{V}O(fsal-DL-Ala)(O$_2$)(MeOH)] Product of alcoholysis[c]?
Total of 9 equiv. of H$_2$O$_2$ added	–581 (~53%) –658 (47%)	[V^{V}O(fsal-DL-Ala)(O$_2$)(MeOH)[
Addition of 2 equiv. of styrene (the global intensity of ^{51}V NMR decreases).	–581 (~48%) –658 (52%)	[V^{V}O(fsal-DL-Ala)(O$_2$)(MeOH)] Product of alcoholysis[c]?
Total of 3 equiv. of styrene up to 15 equiv. of styrene added (the global intensity of ^{51}V NMR decreased)	–581 (~65%) –658 (35%)	[V^{V}O(fsal-DL-Ala)(O$_2$)(MeOH)] Product of alcoholysis[c]?
From a total of 18 equiv. of styrene up to 35 equiv. of styrene(the global intensity of ^{51}V NMR decreased)	–553 (~25 to ~60%) –582 (~75 to ~40%)	V^{V}O(fsal-DL-Ala)(MeO)(MeOH) V^{V}O(fsal-DL-Ala)(O$_2$)(MeOH)
Total of 40 equiv. of styrene	Almost no ^{51}V NMR signal; very weak peaks at ca. –553 and –583	No vanadium(V) species

[a] The corresponding relative areas of the vanadium peaks detected are given in the bracket.

[b] The peak at ca. –553 ppm possibly corresponds to VO$_2^+$ (V$_1$), indicating some significant hydrolysis of the V^{V} complexes after one week of contact of the solution with air.

[c] The peak at –658 ppm in the ^{51}V NMR spectra may be a product of alcoholysis eg. V^{V}O(MeO)$_3$ or V^{V}O(O)$_2$(MeO).

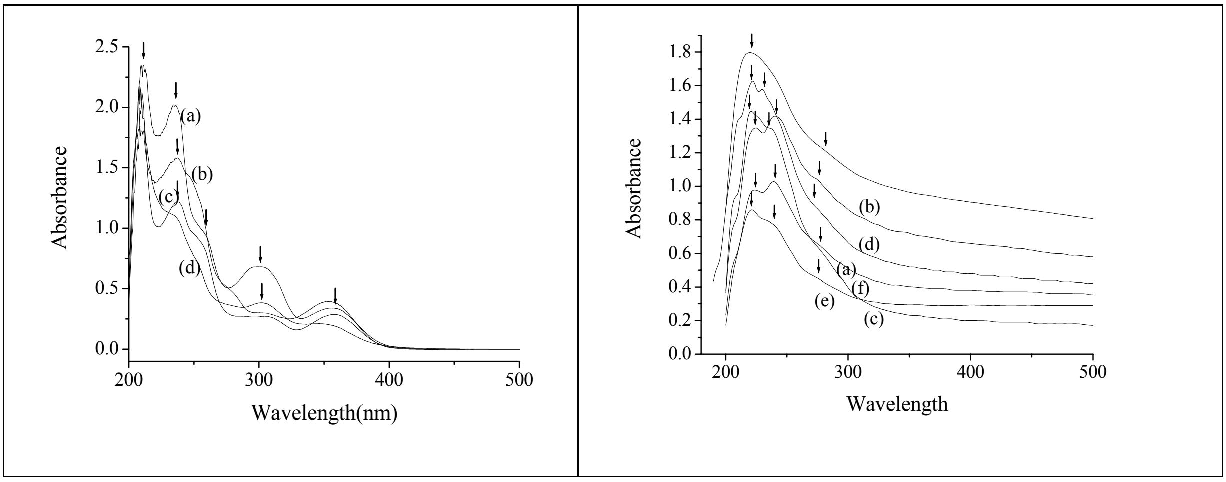

Fig. S1 Left: Electronic spectra of [VO(fal-DL-Ala)(H_2O)] (a), [Cu(fsal-L-Ile)(H_2O)] (b), [VO(fsal-L-Ile)(H_2O)] (c) and [Cu(fal-DL-Ala)] (d); right: Electronic spectra of polymer-bound ligands and metal complexes: PS-[Cu(fsal-L-Ile)(H_2O)] (a), PS-[Cu(fal-DL-Ala)(H_2O))] (b), PS-[VO(fal-DL-Ala)(H_2O)] (c), PS-H_2fsal-L-Ile (d), PS-[VO(fsal-L-Ile)(H_2O)] (e) and PS- H_2fsal-DL-Ala (f).