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New oxidovanadium(IV) complex with redox-active acenaphthene-1,2-diimine ligand: synthesis, structure, redox properties and catalytic activity in alkane oxidations with hydrogen peroxide †

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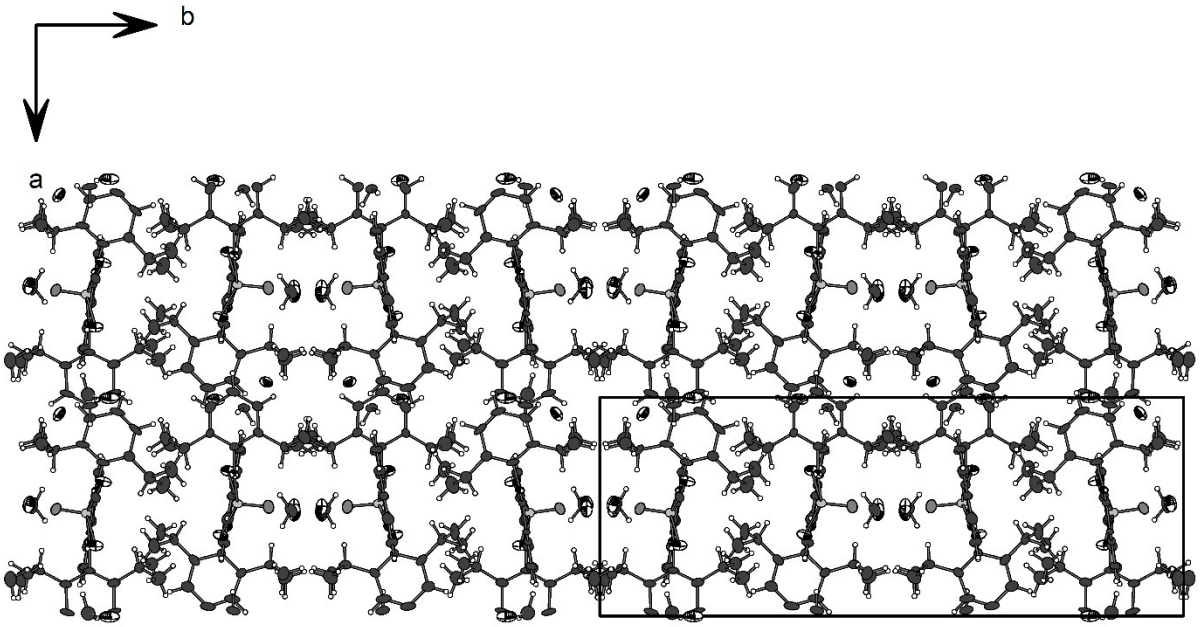


Fig. S1. Crystal packing of **1**·1.7CH_2Cl_2

Table S1. Kinetic parameters for the competitive oxidation of cyclohexane and acetonitrile with various systems based on H_2O_2.[a] The data are taken from ref[1].

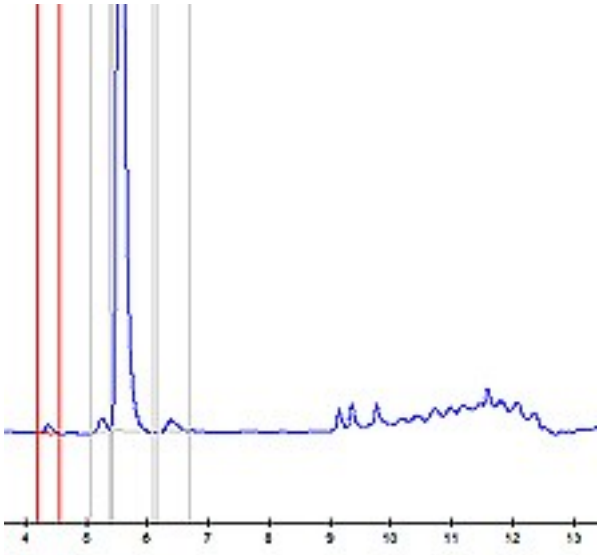
Entry	System	$k_2[CH_3CN]/k_1$ (M)	k_2/k_1
1	H_2O_2/O_2/**1**/PCA (this work)	0.14	0.008
2	$H_2O_2/O_2/(n\text{-}Bu_4N)VO_3$/PCA	0.14	0.008
3	H_2O_2/O_2/"**Cu_4**"/CF_3COOH	0.20	0.012
4	H_2O_2/O_2/"**Cu_4**"/HCl	0.10	0.006
5	$H_2O_2/O_2/[Co_4Fe_2OSae_8]/HNO_3$	0.14	0.008
6	$H_2O_2/O_2/Cp^*_2Os$/py	0.09÷0.19	0.0055÷0.011
7	H_2O_2/O_2/ Cp_2Fe/Py/PCA	0.19	0.011
8	H_2O_2/O_2/"Fe_2(TACN)"/PCA	0.19	0.011
9	H_2O_2/O_2/**2**/carboxylic acid	4	0.24

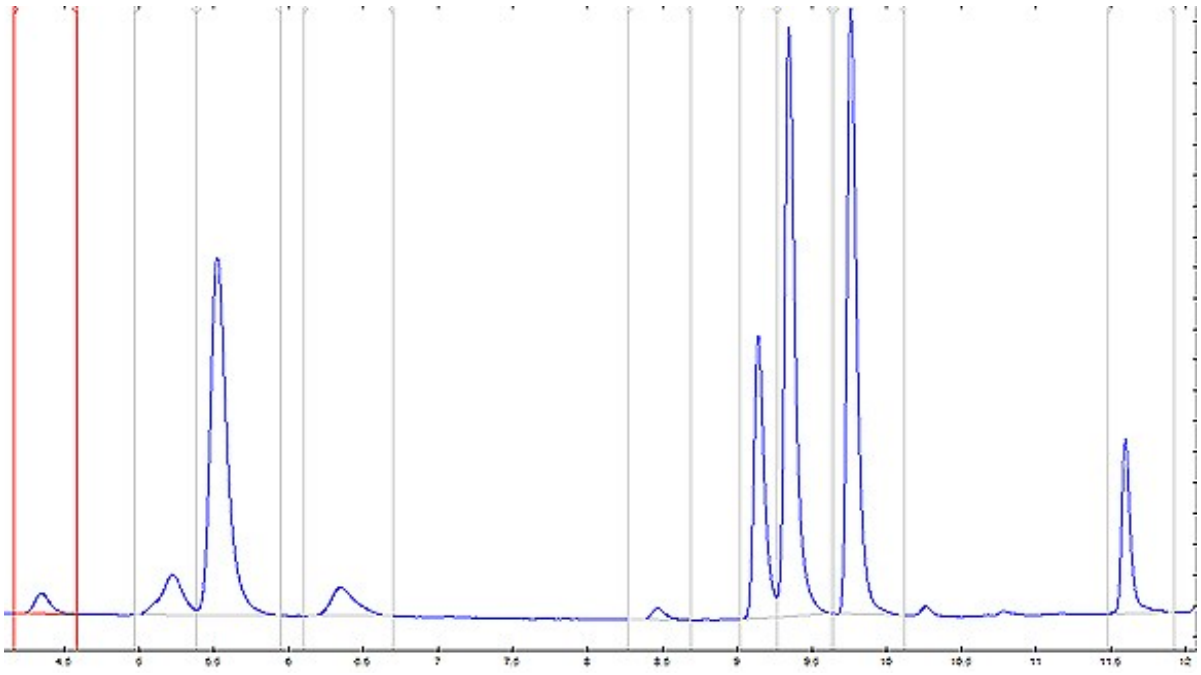
[a] Concentration $[CH_3CN]_0$ was assumed to be 17 M. Abbreviations: PCA is pyrazine-2-carboxylic acid. "**Cu_4**" is tetracopper(II) triethanolaminate complex $[O\subset Cu_4\{N(CH_2CH_2O)_3\}_4(BOH)_4][BF_4]_2$. Complex $[Co_4Fe_2OSae_8]\cdot 4DMF\cdot H_2O$, where H_2Sae = salicylidene-2-ethanolamine. Cp^*_2Os is decamethylosmocene. Cp_2Fe is ferrocene. "Fe_2(TACN)" is an iron(III) complex with 1,4,7-triazacyclononane.

Table S2. Selectivity parameters obtained in the oxidation of linear and branched alkanes in acetonitrile with H_2O_2 catalyzed by complex **1** and (for comparison) some other systems.[a]

Entry	System	C(1):C(2):C(3):C(4)	1º:2º:3º	*trans*:*cis*	
		n-Heptane	MCH	*c*-1,2-DMCH	*t*-1,2-DMCH
1	**1**/H_2O_2 (this work)	1.0:5.6:5.8:5.5	1.0:5.1:10.8	0.9	
2	**1**/PCA/H_2O_2 (this work)	1.0: 6.25:6.75:6.25	1.0;5.0:12.6	0.8	
3	(*n*-Bu_4N)[VO_3]/PCA/H_2O_2	1:9:7:7	1:6:18	0.75	0.80
4	hν/H_2O_2	1:7:6:7		0.90	
5	$FeSO_4$/H_2O_2	1:5:5:4.5	1:3:6	1.3	1.2
6	[Cp_2Fe]/PCA/H_2O_2	1:7:7:6	1:10:33	0.80	0.80
7	[$Os_3(CO)_{12}$]/py/H_2O_2	1:4:4:4	1:5:11		0.85
8	$Al(NO_3)_3$/H_2O_2	1:5:5:5	1:6:23	0.8	0.8
9	$[Mn_2L_2O_3]^{2+}$/$MeCO_2H$/H_2O_2	1:42:37:34	1:26:200	0.34	4.1
9	**2**/oxalic acid/H_2O_2	1:91:99:68		0.31	13
10	$[Mn_2L_2O_3]^{2+}$/oxalic acid/Oxone	1:30:28:30	1:12:150	0.5	0.2

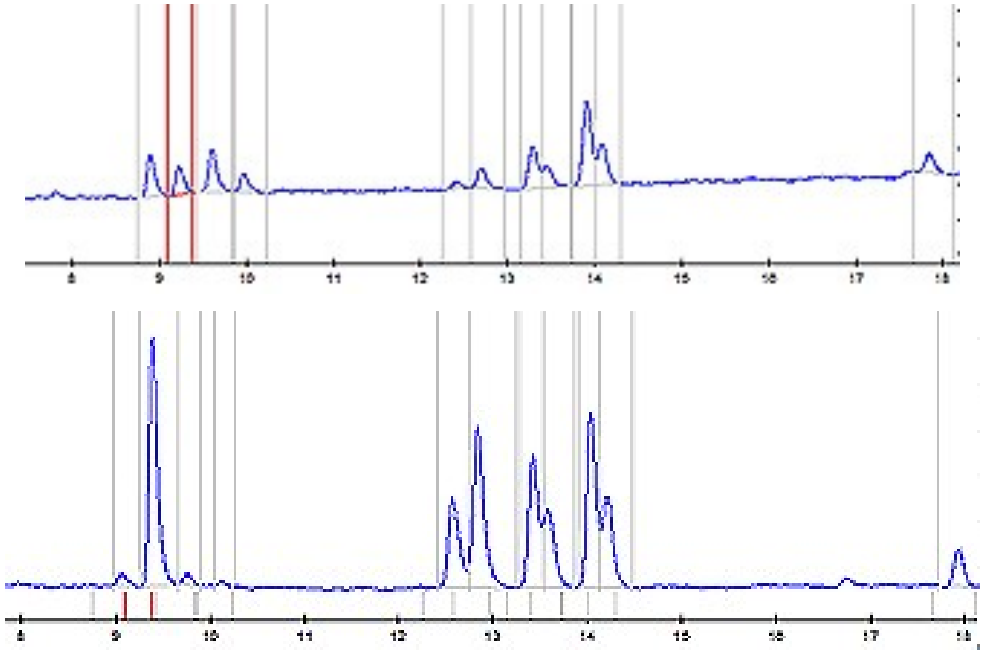
[a] All parameters were measured after reduction of the reaction mixtures with triphenylphosphine before GC analysis and calculated based on the ratios of isomeric alcohols. Parameter C(1):C(2):C(3):C(4) is the relative normalized (taking into account the number of hydrogen atoms at each carbon) reactivities of hydrogen atoms at carbons 1, 2, 3 and 4 of the chain of *n*-heptane. Parameter 1º:2º:3º is the relative normalized reactivities of hydrogen atoms at primary, secondary and tertiary carbons of methylcyclohexane (MCH). Parameter *trans*/*cis* is the ratio of isomers of *tert*-alcohols with mutual *trans*- and *cis*-orientation of ***the methyl groups*** formed in the oxidation of *cis*- and *trans*-1,2-dimethylcyclohexane (DMCH). Term hν means UV irradiation. [Cp_2Fe] is ferrocene. Complex $[Mn_2L_2O_3]^{2+}$ is the binuclear manganese derivative $[LMn(\mu\text{-}O)_3MnL]^{2+}$, where L = 1,4,7-trimethyl-1,4,7-triazacyclononane (TMTACN). Complex **2** is $[Mn_2(R\text{-}L^{Me2R})_2(\mu\text{-}O)_2]^{3+}$ where R-L^{Me2R} = (*R*)-1-(2-hydroxypropyl)-4,7-dimethyl-1,4,7-triazacyclononane. The data are taken from Ref[2–20]. Examples of chromatograms obtained in the oxidation of *n*-heptane and methylcyclohexane (MCH) are presented in Figs. S2 and S3, respectively.





Time (min) →

Fig. S2. Chromatograms obtained in the *n*-heptane before treating (top picture) and after treating (bottom picture) with PPh_3



Time (min) →

Fig. S3. Chromatograms obtained in the methylcyclohexane oxidation before treating (top picture) and after treating (bottom picture) with PPh_3

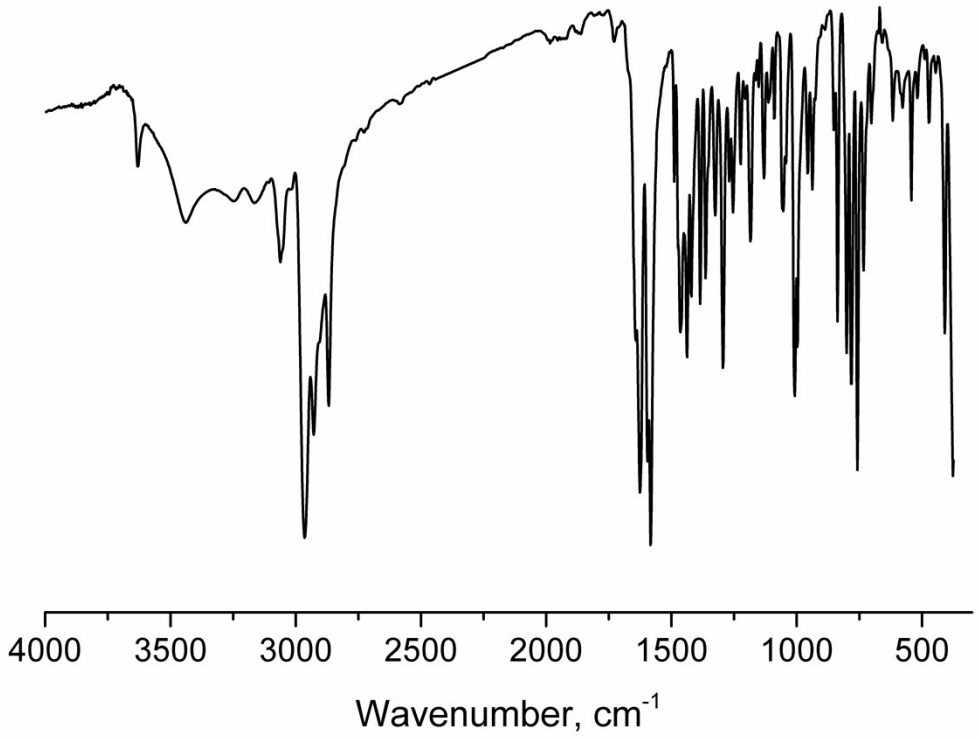


Fig. S4. IR spectrum of [$VOCl_2$(dpp-bian)] (**1**)

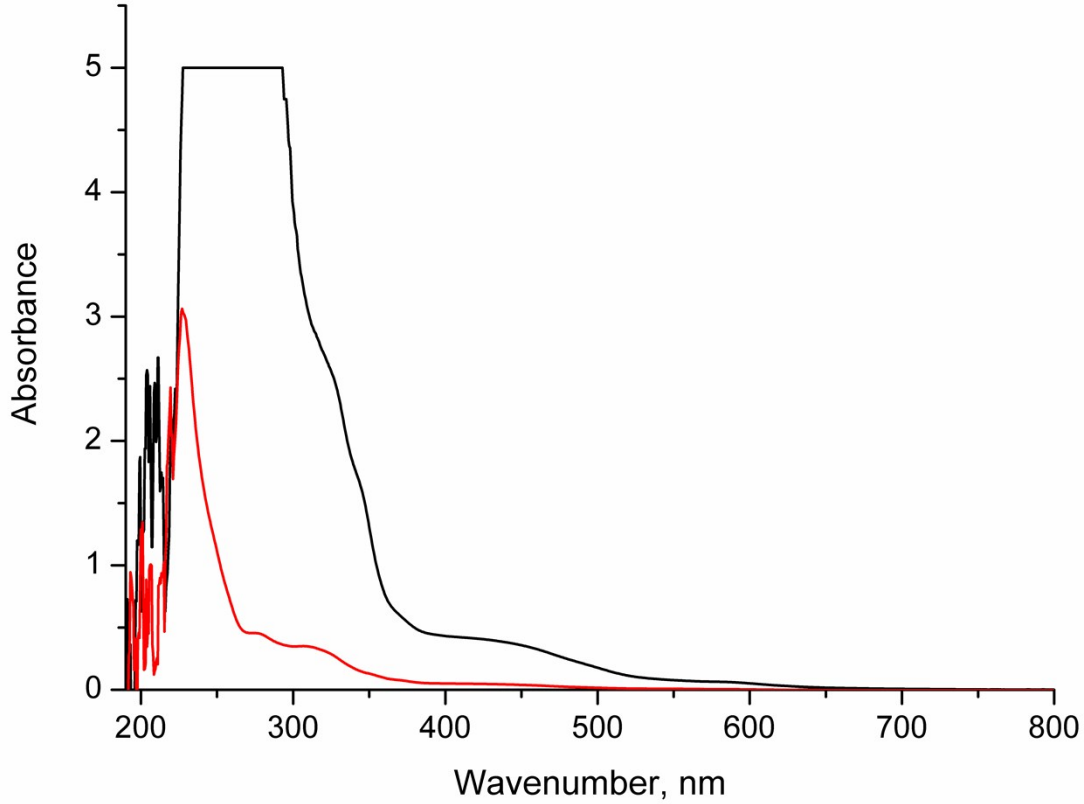


Fig. S5. UV-vis specrum of [$VOCl_2$(dpp-bian)] (**1**): C = $3.3 \cdot 10^{-4}$ M (black line), $3.3 \cdot 10^{-5}$ M (red line)

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