

Electronic supplementary Information

Polystyrene bound oxidovanadium(IV) and dioxidovanadium(V) complexes of histamine derived ligand for the oxidation of methyl phenyl sulfide, diphenyl sulfide and benzoin

Mannar R. Maurya, Aarti Arya, Amit Kumar and João Costa Pessoa

Electronic spectral study

The electronic spectral studies of Hsal–his and $[V^{IV}O(\text{sal–his})(\text{acac})]$ have been described earlier in detail.²¹ The electronic spectra of anchored and neat complexes are reproduced in Figs. S1 and S2, respectively. The electronic spectral patterns exhibited by the polymer-bound ligand and metal complexes are similar (Table S1) to those obtained for the corresponding non-polymer bound analogues, except for the low intensity of bands. The lower energy (less intense) bands appearing at 532 and 776 nm due to d – d transitions in $[V^{IV}O(\text{sal–his})(\text{acac})]$ could not be located in the polymer-bound complex due to its poor loading in the polymer matrix. A band appearing at 394 nm in $[V^VO_2(\text{sal–his})]$ is assigned to a ligand-to-metal charge transfer (lmct) transition. Only a weak shoulder band could be observed in the polymer-bound dioxidovanadium(V) complex in this region.

Table S1 Electronic spectral data of ligands and complexes

Compounds	Solvent	λ_{max} / nm
Hsal–his I	Methanol	214, 254, 314, 402
$[V^{IV}O(\text{acac})(\text{sal–his})]$ 3	Methanol	215, 257, 277, 319, 384, 532, 776
$[V^VO_2(\text{sal–his})]$ 4	Methanol	213, 253, 279, 322, 394
PS-Hsal–his II	Nujol	211, 229, 286, 330, 414
PS- $[V^{IV}O(\text{acac})(\text{sal–his})]$ 1	Nujol	209, 280, 329, 416
PS- $[V^VO_2(\text{sal–his})]$ 2	Nujol	206, 276, 340, 390

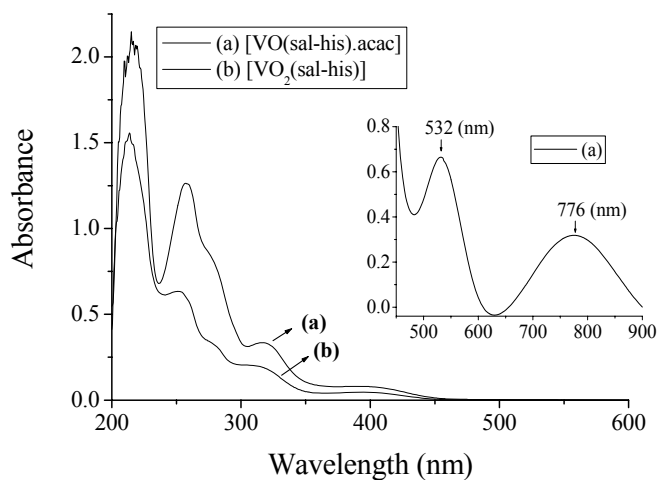


Fig. S1 Electronic spectra of neat metal complexes **3** and **4** in MeOH solution (ca. 10^{-4} M). The insert shows the spectrum of **1** in the visible range, recorded with a higher concentration of complex (ca. 10^{-3} M).

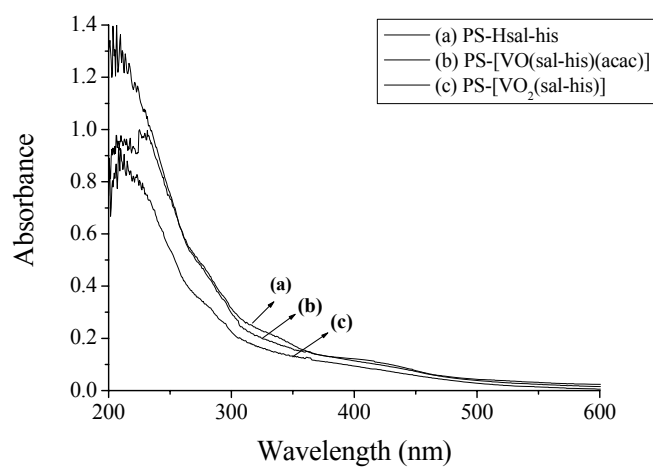


Fig. S2 Electronic spectra of polymer-anchored ligand and metal complexes dispersed in nujol mulls.

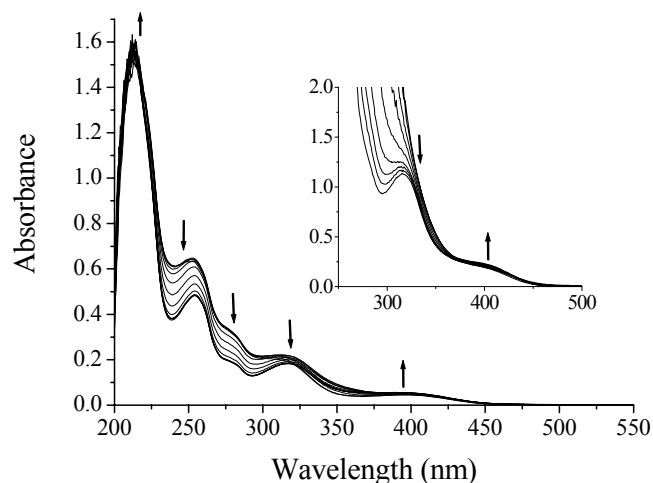


Fig. S3 Spectral changes observed during titration of $[\text{V}^{\text{V}}\text{O}_2(\text{sal-his})]$ **4** with H_2O_2 . The spectra were recorded after successive additions of one drop portions of H_2O_2 (6.6×10^{-4} mmol of 30% H_2O_2 dissolved in 10 mL of methanol) to 50 mL of ca. 10^{-4} M solution of **4** in methanol. The inset shows the equivalent titration, but with higher concentration of $[\text{V}^{\text{V}}\text{O}_2(\text{sal-his})]$ (ca. 10^{-3} M) with one drop portions of H_2O_2 (2 mmol of 30% H_2O_2 dissolved in 5 mL of methanol).

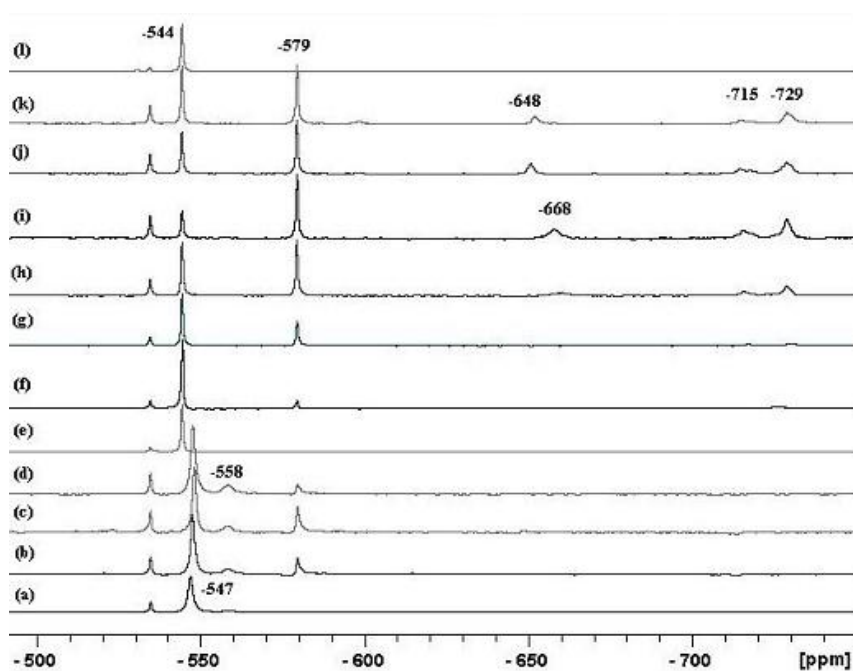


Fig. S4 ^{51}V NMR spectra for $[\text{V}^{\text{V}}\text{O}_2(\text{sal-his})]$ **4**: (a) in MeOH; (b) 0.5 eq. H_2O_2 ; (c) 1.0 eq. H_2O_2 ; (d) 1.5 eq. H_2O_2 ; (e) after 20 hr; (f) 0.5 eq. H_2O_2 ; (g) 1.0 eq. H_2O_2 ; (h) 1.5 eq. H_2O_2 ; (i) 2.0 eq. H_2O_2 ; (j) 1.0 eq. methyl phenyl sulfide; (k) 2.0 eq. methyl phenyl sulfide; (l) 2.0 eq. methyl phenyl sulfide (after 24 hr). All spectra were recorded including an external reference of aqueous vanadate at pH ~12 (peak at ca. -536 ppm).

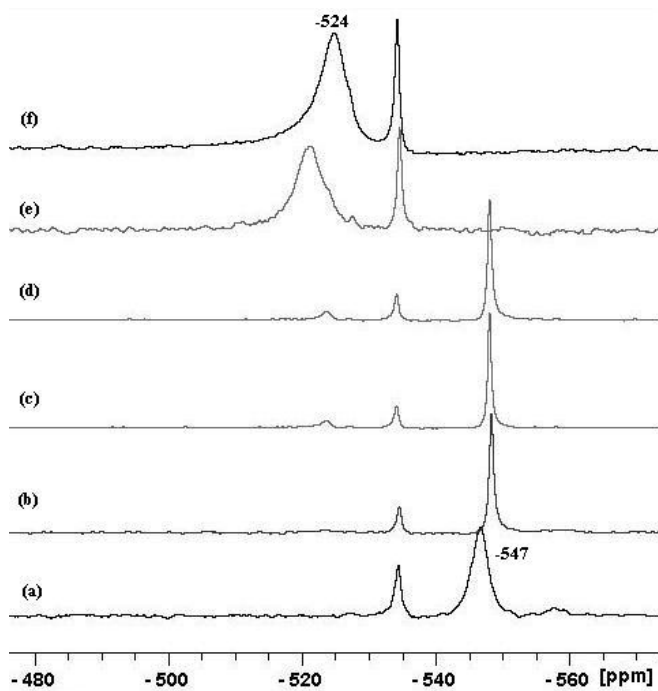


Fig. S5 ^{51}V NMR spectra for $[\text{V}^{\text{V}}\text{O}_2(\text{sal-his})]$: (a) in MeOH, (b) 0.5 equiv HCl; (c) 1.0 equiv HCl; (d) 1.5 equiv HCl; (e) 2.0 equiv HCl; (f) 2.5 equiv HCl. All spectra were recorded including an external reference of aqueous vanadate at pH ~12 (peak at ca. -536 ppm).