First mononuclear and binuclear vanadate esters of mixed aliphatic-aromatic diols

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The title esters \([\text{VO}(\text{gsal})(\text{HL}^1)]\) and \([\text{VO}(\text{gsal})_2(\text{H}_2\text{L}^2)]\) incorporate chelation by ionized 2-hydroxybenzyl alcohol (\(\text{H}_2\text{L}^1\)), its dimer-like derivative (\(\text{H}_2\text{L}^2\)) and the salicylaldehyde of glycine (\(\text{H}_2\text{gsal}\)). The phenolic functions of \(\text{H}_2\text{L}^1\) and \(\text{H}_2\text{L}^2\) are ionized in ester formation. The structure and spectral features of the esters are reported.

Vanadate esters incorporating monoionized aliphatic and aromatic diol chelation as stylized in 1, have been designed in this laboratory\(^\text{1,3}\). Herein we report the first examples of the binding of mixed aliphatic-aromatic diols furnishing mononuclear and dinuclear vanadate esters.

Experimental

UV-vis spectral measurements were carried out with a Shimadzu UVPC 1601 spectrometer and IR spectra were measured with a Nicolet Magna IR 750 Series II spectrometer. Proton NMR and \(^{51}\)V NMR spectra were respectively recorded on a Bruker FT 300 MHz spectrometer and a Varian spectrometer at 78.8 MHz (\(\text{VOCl}_3\) external reference). The atom numbering scheme used for \(^1\)H NMR is the same as that used in crystallography. Spin-spin structures are abbreviated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad. X-ray data were collected by the \(\omega\)-scan technique in the 20 range 3-50\(^\circ\) for 4 and 3-47\(^\circ\) for 5, on a Siemens R3m/V four-circle diffractometer with graphite monochromated Mo K\(\alpha\) (\(\lambda = 0.71073\) \(\text{Å}\)) radiation at 293(2) K. Data were corrected for Lorentz-polarization effects and absorption\(^4\). Structure solution (direct method, anisotropic refinement on \(F^2\)) and refinement were done with the programmes of SHELXTL, Version 5.03\(^5\). Crystal data for 4: \(\text{C}_{16}\text{H}_{14}\text{NO}_7\text{V}, M = 367.22\), monoclinic, \(P2_1/n\), \(a =11.714(5), b = 9.266(3), c = 15.707(7) \text{Å}, \beta = 109.44(3)\), \(V = 1607.8(11) \text{Å}^3, T = 293(2), Z = 4, R_1 = 0.0489 \text{ and } wR_2 = 0.1224\). For 5: \(\text{C}_{36}\text{H}_{22}\text{Cl}_2\text{N}_2\text{O}_7\text{V}, M = 857.42\), triclinic, \(P-1\), \(a =10.846(2), b = 14.494(3), c = 14.615(3) \text{Å}, \alpha = 108.61(3), \beta = 111.49(3), \gamma = 96.28(3)\), \(V = 1958.3(7) \text{Å}^3, T = 293(2), Z = 2, R_1 = 0.1471, wR_2 = 0.3969\). Crystallographic data of 4 have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 219732.

3-[3-(Hydroxymethyl)-5-methylsalicyl]-5-methyl-2-hydroxybenzyl alcohol, \(\text{H}_2\text{L}^2\), was synthesized from \(p\)-cresol and 37% HCHO in 10% NaOH solution modifying the reported procedure.\(^6,7\) To a methanolic solution (15mL) of \([\text{V}^\text{IV}(\text{gsal})(\text{H}_2\text{O})]\) \(^8\) (0.2g, 0.76 mmol) \(\text{H}_2\text{L}^1\) (0.095 g , 0.76 mmol) was added and the mixture was stirred for 10 min in air. A brown dark solution thus obtained was kept undisturbed at room temperature yielding dark crystals of \([\text{VO}(\text{gsal})(\text{HL}^1)]\) after 12 h. These were washed with diethyl ether and then a mixture of diethyl ether : methanol (25 : 1) and dried over fused \(\text{CaCl}_2\) \textit{in vacuo}. Yield of \([\text{VO}(\text{gsal})(\text{HL}^1)]\) is 0.230 g (82%) based on \([\text{V}^\text{IV}(\text{gsal})(\text{H}_2\text{O})]\). \(^1\)H NMR data in \(\text{CDCl}_3\) \([\delta, \text{ppm} \ (J, \text{Hz})]: \ 4.33 \ (d, \text{H}2\text{A}, 13.4), 4.65 \ (d, \text{H}2\text{B}, 12.2), 8.16 \ (s, \text{H}3), 7.52 \ (d, \text{H}5, 7.7), 7.02 \ (m, \text{H}6, \text{H}8, \text{H}15), 7.60 \ (t, \text{H}7, 7.0), 4.43 \ (br, \text{H}10), 6.94 \ (m, \text{H}12, \text{H}13), 7.31 \ (t, \text{H}14, 7.6), 6.25 \ (br, \text{alcoholic OH}). \text{IR (KBr disk): } \nu = 970 \text{ cm}^{-1}, \nu = 3064 \text{ cm}^{-1}. \ [\text{VO}(\text{gsal})_2(\text{H}_2\text{L}^2)]\) was prepared similarly by reacting \([\text{V}^\text{IV}(\text{gsal})(\text{H}_2\text{O})]\) (0.1 g, 0.38 mmol) and \(\text{H}_2\text{L}^2\) (0.055 g, 0.19 mmol) in methanol in air. Crystalization from dichloromethane-hexane mixture afforded single crystals of composition...
Results and discussion

The diols used in the present work are 2-hydroxybenzyl alcohol (H₂L₁, 2) and its dimer-like derivative H₄L², 3. A few transition metal complexes of 2 have been reported. However, to the best of our knowledge there is no instance of the binding of either ligand to vanadium. The two esters described in the present work are

\[ [\text{VO(gsal)}(\text{HL₁})], 4 \text{ and } [\text{VO(gsal)}]_2(\text{H₂L₂})], 5 \text{ where gsal}^{2-} \text{ is the tridentate diionized salicylaldimine of glycine.} \]

These were prepared by the stoichiometric reaction of [\text{VO(gsal)(H₂O)}]³⁺ with H₂L₁ and H₄L².

The visible region bands of 4 and 5 are assigned to phenoxide --π → dₓᵧ LMCT excitation. Its shift to lower energy in going from 4 (526 nm) to 5 (612 nm) is consistent with the presence of electron donating substituents (-Me, -CH₃) in 5. Further the shift of \(^{51}\text{V}\) NMR lines from -529 ppm (in 4) to -461 ppm (5) matches the LMCT energy trend. In the crystal structure of 5 the two halves of the dimer are not related by any crystallographic symmetry elements (see below) but in mobile solution they become equivalent as revealed by the single \(^{51}\text{V}\) resonance as well as by the equivalence of the \(^{1}H\) NMR lines of the two halves.

The structure of 4 is shown in Fig. 1. All hydrogen atoms were located in difference Fourier maps. In ester formation the H₂L₁ ligand has undergone dissociation of the more acidic phenolic proton, the alcoholic function (-CH₂OH) remaining undisassociated. In the distorted octahedral VO₅N coordination sphere the metal atom is displaced towards the oxo oxygen atom from the equatorial plane of O₂, O₃, O₅ and N by 0.30Å. The five V-O bond lengths span the range 1.59-2.35 Å (Fig. 1). Of the two V-O (phenoxidic) distances that in the V(HL₁) fragment is shorter by ~ 0.05 Å. The weakly bonded alcohol group lies trans to the strongly coordinated oxo oxygen atom. The alcoholic function is hydrogen bonded to the uncoordinated carboxylate oxygen atom of a symmetry related neighbouring molecule generating an infinite chain [O₄ ... O₆, 2.611(5) Å].

The structure of 5 has also been determined. Due to the presence of highly disordered solvent of
crystallization (CH₂Cl₂) in the lattice a high degree of refinement has not been achieved so far. However, the gross connectivity and bond parametric values are not in any doubt. The structure is shown in Fig. 2. The two halves of the molecule though not related by any formal crystallographic symmetry element, are closely similar. The geometry and bond parameter within each half are in turn similar to those in 4. The V···V distance is 5.785(3) Å and the alignment of the two V=O groups is approximately anti, the dihedral angle between the V1, V2, O1 and V1, V2, O2 planes being 124.9° (idealized values: syn, 0° and anti, 180°).

In conclusion, the first vanadate esters of mixed aliphatic-aromatic diols have been isolated and characterized in the form of 4 and 5. The diols bind with only the phenolic proton dissociated. Unlike the reported² catecholate esters, 4 and 5 are unreactive to molecular oxygen in solution

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References