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NMR, DFT and Luminescence Studies of the Complexation of V(V) Oxoions in Solution with 8-Hydroxyquinoline-5-Sulfonate[ϒ]

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[ϒ] Electronic supplementary information (ESI) available: Deconvolution of the ^{51}V NMR spectrum (region from -555 to -520 ppm).

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Abstract: ^1H, ^{13}C and ^{51}V NMR, DFT calculations, UV/visible absorption and luminescence spectra are used to study complexation of 8-hydroxyquinoline-5-sulfonate (8-HQS) with vanadium(V). A full speciation study over the concentration region studied shows V(V) oxoions form three complexes in the pH range 4-7. Geometries are proposed based on NMR and DFT calculations. Dominant species are 1:2 (metal:ligand) mononuclear six-coordinated isomers with almost octahedral geometry, having the metal centre coordinated to two 8-HQS ligands, and only differing in the arrangement of the donor groups. A minor binuclear complex species was also identified, and possesses two five coordinated metal centres, with a distorted trigonal bipyramidal geometry, bridged by two coordinated 8-HQS molecules. On binding to V(V), marked changes are seen in UV/visible absorption spectra. However, in contrast to other metals (Al(III), Ga(III), Zn(II)), the complexes are only weakly luminescent; this is suggested to be due to quenching of the emission by low-lying ligand-to-metal (LMCT) states close to the emitting ligand-based excited state.

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Introduction

Although vanadium is a trace element, it has considerable chemical and biological relevance. [1,2] Vanadium may be beneficial and possibly essential in humans, but is crucial for some living organisms.[1]

The complex aqueous chemistry of vanadate salts and complexes has attracted a great deal of interest due to their catalytic properties and the ability to induce a large number of biological responses, including insulin-mimetic activity, cardiovascular effects, and their use as diet regulators, antibacterial, antiviral (including anti-HIV), or antineoplastic agents.[1] Additionally, vanadium compounds are promising in the treatment of a number of epidemic tropical diseases, such as leishmaniasis, amebiosis, Chagas' disease and Dengue fever.[2]

Further, vanadium pollution can have an impact in metropolitan and industrialised areas[3] through aerial contamination, mainly in the form of V_2O_5, from mines, industrial enterprises and burning of crude oil,[2-4] and thorugh exposure to vanadium in food and drinking water.[3]

This impact on human health and environment has stimulated interest in the development of novel materials and methods for its detection, quantification and remediation in environmental or physiological samples, or in food products. Optical sensors, either based on changes in fluorescence or absorption spectra in the presence of metals, are particularly attractive because of their ease of use, high sensitivity, possibilities of incorporating in online detection systems for use over a wide range of analyte concentrations, and for real time and space monitoring of these metals.[5,6] Luminescence sensors may emit light of a different wavelength or intensity on binding to a metal from the metal free system. This can be indicative of the type of metal that is bound, providing selectivity.[7,8] Free 8-hydroxyquinoline (8-HQ) is only very weakly luminescent, probably because of fast excited state intramolecular proton transfer leading to a nonfluorescent phototautomer.[9] However, this pathway is normally inhibited on complexation, and the dramatic intensity changes seen in the presence of suitable metal ions can provide the basis for sensitive and selective metal ion sensors.[10] These systems have been extended through rational design to the development of 8-

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hydroxyquinolates linked to fluorene-based conjugated polymers to enhance sensitivity and selectivity.[5,6] Water soluble 8-hydroxyquinoline derivatives, such 8-hydroxy-5-sulfoquinoline (8-HQS), are good candidates for these applications, and allow sensitive, and potentially selective, detection and quantification of metal ions through steady state[11] or time resolved measurements.[12] Nevertheless, their application to a particular metal ion requires an understanding of both the structures and photophysics of complex species formed.

8-HQS finds use as a selective sorbent of toxic metals,[13] it shows relevance in chelation therapy in patients overcharged with metals,[14,15] and its complexes are used as components in optoelectronic devices, including organic light emitting diodes (OLEDs). Metal 8-HQS complexes may be incorporated as water-based components into OLEDs through self-assembly in appropriate matrices, such as layered double hydroxides [16] and liquid crystals.[17]

Recently, we have carried out a detailed structural and spectral study of the interaction of 8-HQS, with the Zn^{2+} cation, and characterised a single 1 : 2 (metal : ligand) complex. This has potential for its fluorescence detection in aqueous medium, such as surface waters and biological fluids,[18] and involves a complex with octahedral geometry having two bidentate 8-HQS ligands and two coordinated water molecules mutually *trans*. With the corresponding 8-HQS complexes of the other group 12 metals Cd^{2+} and Hg^{2+}, again there is a dominant 1 : 2 complex with octahedral coordination. However, in this case the two water molecules show a *cis* geometry.[19] We have also studied the interaction of 8-HQS with the Al^{3+} and Ga^{3+} ions. Three homologous luminescent complexes with 1 : 1, 1 : 2 and 1 : 3 (metal : ligand) stoichiometries were characterized and their geometries determined.[20,21] In all cases, luminescence changes were observed due to metal chelation, which may be used for metal ion detection in an aqueous medium. However, the fluorescence yield was strongly dependent upon the nature of the metal ion.

We are interested in extending these studies to V(V) metal oxoions. Although the complexation of V(V) with 8-HQ and derivatives, such as 8-HQS, has been studied, our knowledge of these systems is far from complete.[11,22-29,30,31,32] In particular, there is limited information on both their structure in

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solution and their photophysical behavior. For sensing, OLEDS, environmental and biomedical applications, structural and spectral characterisation of the oxocomplexes formed between V(V) with 8-HQS is of major importance. This is also relevant to their potential in homogeneous catalysis.

We report a detailed study of the complexation of V(V) metal oxoions with 8-hydroxy-5-sulfoquinoline (8-HQS) using multinuclear NMR spectroscopy (^{1}H, ^{13}C, ^{51}V), DFT calculations in parallel with UV/visible absorption and luminescence techniques. A full speciation study has been carried out, and the results will be compared with those previously reported. There are marked changes in the UV/visible absorption spectra of 8-HQS on binding to the metal, while, in contrast with other 8-HQS complexes, the 8-HQS fluorescence decreases on complexation with V(V). We suggest that this is due to the presence of low-lying ligand-to-metal charge transfer (LMCT) states. The combination of all these methods has allowed a full structural characterization of the systems, which is valuable for remediation of water containing high levels of vanadium, and for the development of optical sensors for V(V) ions. In addition, the redox characterisitics of VO_2^{2+} in these complexes may be relevant for applications as electron injection or hole blocking materials in optoelectronic systems.

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Experimental Section

Materials and solution preparation

Analytical grade ammonium vanadate and commercially available 8-hydroxyquinoline-5-sulfonic acid hydrate were used as received. For NMR experiments, the pH was adjusted by addition of DCl and NaOD; the pH* values quoted are the direct pH-meter readings (room temperature) after standardization with aqueous (H_2O) buffers.

NMR experiments

The ^1H, ^{13}C and ^{51}V spectra were obtained on a Varian Unity-500 NMR spectrometer (at 499.843, 125.695 and 130.285 MHz, respectively). The ^{13}C spectra were recorded using proton decoupling techniques (Waltz-16) taking advantage of the nuclear Overhauser effect. As a consequence, signal intensities for ^{13}C spectra are not quantitative. The methyl signal of *tert*-butyl alcohol was used as internal reference for ^1H (δ 1.3) and ^{13}C (δ 31.2) relative to TMS. ^{51}V NMR spectra were obtained using $VOCl_3$ ($\delta = 0$) as external reference and typically, spectral widths of 80000 Hz, acquisition times of 0.5 s, pulse delays of 0.01 s and about 5000 pulses.

Computational Details

The molecular structures of the $[VO_2(HQS)_2]^{3-}$ and $[V_2O_4(HQS)_2]^{2-}$ complexes were optimized at the DFT level using the GAMESS code [33] employing the B3LYP (Becke three parameter Lee–Yang–Parr) [34,35] exchange correlation functional. The LANL2TZ(f)[36-38] valence and effective core potential (ECP) functions were used for the metals and the 6–311G(d) basis sets were used for the expansion of the Kohn–Sham orbitals of the sulfur, oxygen, nitrogen, carbon and hydrogen atoms. Structures II, III and V were built imposing C_2 symmetry. All structures were optimized considering the bulk solvent (water) effects through the polarizable continuum model (PCM) of Tomasi and co-workers.[39,40] Default van der Waals radii were used for all atoms except vanadium, for which 2.64 Å was used. The Hessian was calculated for the resultant stationary points, and all were characterized as true minima (i.e., no imaginary frequencies). In all cases, the gradient threshold for

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geometry optimization was taken as 10^{-5} hartree $bohr^{-1}$. The relative energies of isomers presented in the discussion include zero-point vibrational energy corrections.

Photophysical studies

UV/visible absorption and fluorescence spectra were recorded on Shimadzu UV-2100 and Jobin-Ivon SPEX Fluorolog 3-22 spectrometers, respectively. Fluorescence spectra were registered with excitation at 330 nm and were corrected for the wavelength response of the system. However, the detector sensitivity decreases dramatically at wavelengths longer than 650 nm and correction factors are unreliable with the week fluorescence observed in these systems. When not being used for measurements, all samples were kept in the absence of light.

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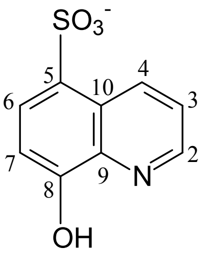
Results and discussion

Multinuclear NMR studies

Scheme I shows the structure of the water soluble 8-hydroxyquinoline-5-sulfonate (8-HQS).



I

The proton and carbon chemical shifts, as well as the proton-proton coupling constants of 8-HQS have been measured in aqueous solution over the whole pH range, and fully assigned in a previous study.[18] The ^1H and ^{13}C NMR chemical shifts were found to change with pH, indicating differences in the degree of protonation/deprotonation of the two acidic functions present in the molecule (the OH group and quinoline nitrogen), whilst the proton-proton coupling constants show no significant changes. This indicates that there are no significant conformational changes, such as would be expected for any keto-enol tautomerism.

Proton and carbon chemical shifts are known to provide a good indication of the chelation sites of the ligand upon complexation with metal ions. Broadening or coordination induced shifts of the ^1H and ^{13}C signals of the ligand in the presence of the metal ions, when compared with those of the free ligand, can provide clear indications of the ligand to metal coordination sites. In addition, with aromatic ligands, inductive effects at specific positions in the aromatic rings allow the identification of the electronic environment of the coordination site.[41] This was recently illustrated in the studies of the complexation of 8-HQS with Zn^{2+}, Cd^{2+}, Hg^{2+}, Al^{3+} and Ga^{3+} ions.[18-21] The combination of proton, carbon-13 and metal ion NMR can provide valuable structural information, including the type of metal centre present in the complexes, as widely exemplified in our previous work on the complexation of metal ions, such as aluminium, gallium and metal oxoions of vanadate, molybdate and tungstate with relevant ligands.[20,21,42-51]

In the present case, ^{51}V spectra can provide further structural insights, including the type of metal centre present in these complexes, through their characteristic chemical shift ranges. In particular,

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^{51}V chemical shifts in vanadium complexes are sensitive to the coordination number and to the nature of the ligands.[52,53] Additional structural information can be gathered from the linewidth of the ^{51}V signals, which can be related to the symmetry around the metal centre. ^{51}V (100%, I=7/2) has a moderately large quadrupole moment (Q=-4.8 fm^2),[53] which normally leads to broad signals arising from a dominant quadrupolar relaxation mechanism.[53-55] However, quadrupolar nuclei (spin $I \geq 1$), rather than being undesirable, can give considerable structural information, since their relaxation is mainly due to the interaction of the quadrupole moment with electrical field gradients present at the nucleus. This depends on the arrangement and nature of the ligands around the central atom. Complexes with cubic symmetry have, in principle, a zero field gradient (q=0), and give rise to sharp signals, while asymmetry in the ligand field produces an increase in the NMR linewidth.[53-55]

For a complete structural characterization of the interaction of V(V) metal oxoions with 8-HQS in aqueous solution, we have obtained ^{51}V, ^{1}H and ^{13}C NMR spectra for total concentrations of metal and 8-HQS ranging from 10 mmol dm^{-3} to 20 mmol dm^{-3}, metal:ligand molar ratios from 1:1 to 1:3, and pH* values ranging from 4 to 7.

Figure 1 shows the ^{51}V NMR spectrum for the system V(V)/8-HQS, while Figures 2 and 3 show a series of ^{1}H and ^{13}C NMR spectra of 8-HQS alone and in the presence of ammonium metavanadate. The complete ^{51}V, ^{1}H and ^{13}C NMR spectral parameters are shown in Tables 1-4, respectively. In addition to the characteristic signals of a mixture of the oligomeric forms of vanadate, decavanadate, $V_{10}O_{28}^{6-}$, monovanadate, $H_2VO_4^{-}$, divanadate, $H_2V_2O_7^{2-}$ and tetravanadate, $V_4O_{12}^{4-}$,[54]Figure 1 shows two broad signals (-538.7 and at -527.5 ppm), which can be ascribed to the complexes formed between V(V) and 8-HQS (Figure 1 and Table 1). The broad signal centred at -538.7 ppm can be assigned to two six-coordinated complexes (CN-6), as it has been deconvoluted into two major signals (Table 1 and Supplementary Information, Figure S1) which can be assigned to two complexes having hexa-coordinated metal centres. In addition to the effect of quadrupole relaxation, the broadening of the signals can be affected by the dynamic behaviour of the system through the intermolecular exchange processes, provided the exchange is sufficiently fast to supress the detection of the specific forms taking part in the equilibrium. [54]

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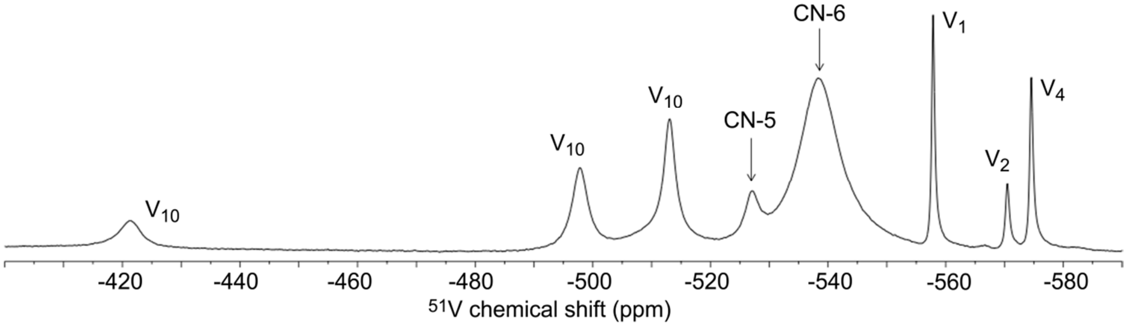

Figure 1. ^{51}V MR spectra (130.285 MHz) of a D_2O solution of V(V)/8-HQS 5:10 mmol dm^{-3}, pH* 6.2, temp. 298 K; (V_{10}-the three different vanadium sites in decavanadate, $V_{10}O_{28}^{6-}$, V_1-monovanadate, $H_2VO_4^-$, V_2-divanadate, $H_2V_2O_7^{2-}$ and V_4-tetravanadate, $V_4O_{12}^{4-}$ from ref.54; CN-6 and CN-5, complexes containing hexa-coordinated and penta-coordinated vanadium metal centres, respectively).

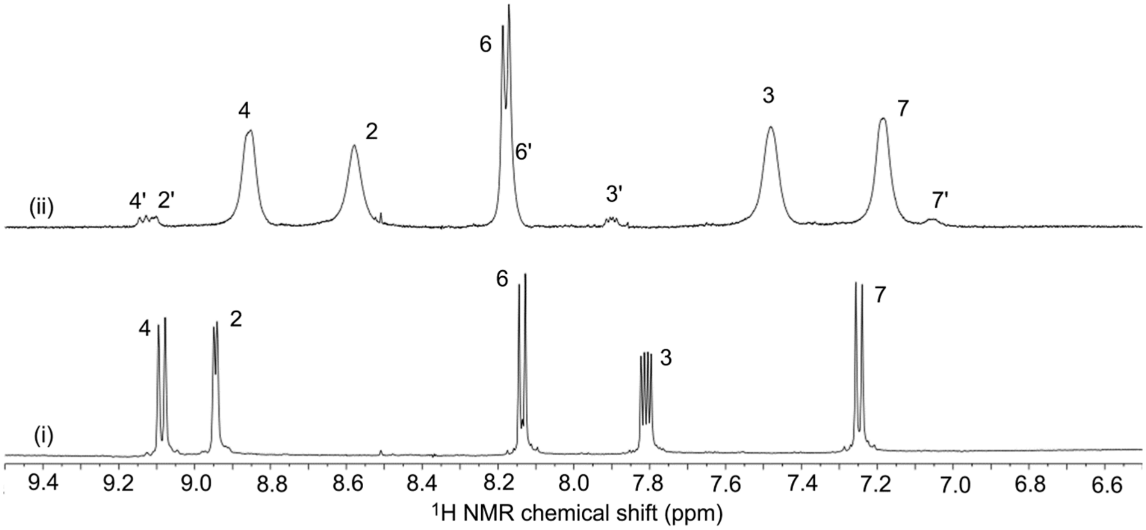

Figure 2. ^{1}H NMR spectra (499.824 MHz) of D_2O solutions of (i) 8-HQS 10 mmol dm^{-3}, pH* 6.5, (ii) V(V)/8-HQS 10:10 mmol dm^{-3}, pH* 6.1, temp 298 K.

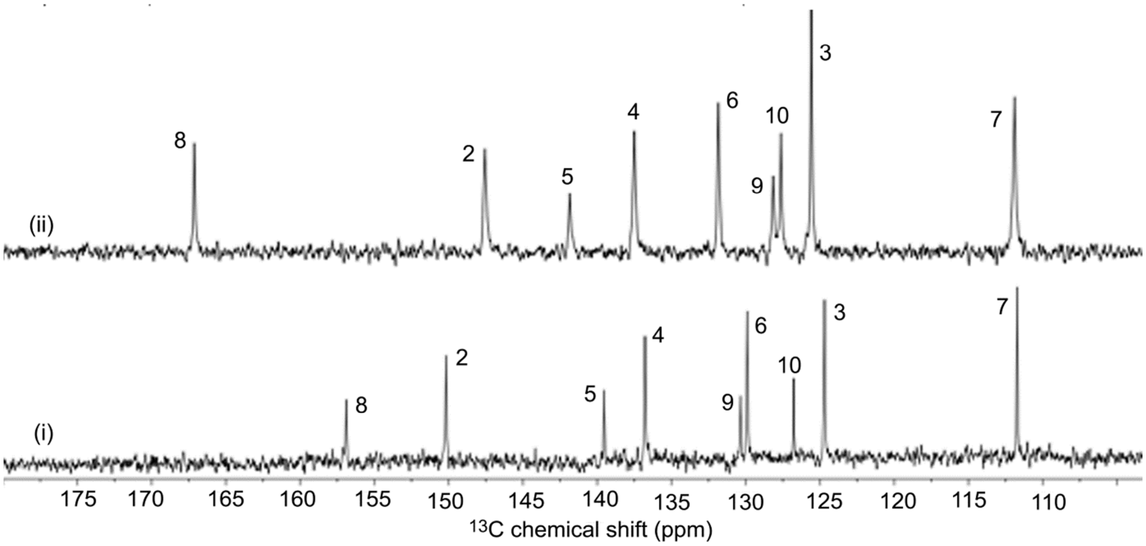

Figure 3. ^{13}C NMR spectra (125.695 MHz) of D_2O solutions of (i) 8-HQS 10 mmol dm^{-3}, pH* 6.5, (ii) V(V)/8-HQS 5:10 mmol dm^{-3}, pH* 6.2, temp. 298 K

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Table 1. ^{51}V NMR parameters ^{a} for the V(V)/8-HQS complexes (298 K)

	δ ^{51}V	Δ$\nu_{1/2}$ /Hz
V(VI)/8-HQS		
CN-6 complexes ^{b} (pH* 6.2)	-537.4 ^{c} -539.5	978 852
CN-5 complex ^{b} (pH* 6.2)	-527.0	382

^{a} δ values, in ppm, relative to external reference $VOCl_3$; Δ$\nu_{1/2}$ values in Hz.

^{b} 5:10 mmol dm^{-3} V(V)–8-HQS solution.

^{c} more intense signal.

Table 2. ^{1}H NMR parameters ^{a} for 8-HQS and its complexes with V(V) (298 K)

	H-2	H-3	H-4	H-6	H-7	$J_{2,3}$	$J_{3,4}$	$J_{2,4}$	$J_{6,7}$
8-HQS^{b}									
pH*=3.0	9.14	8.21	9.65	8.33	7.49	5.0	8.6	1.2	8.3
pH*=4.0	9.00	7.98	9.32	8.21	7.33	5.4	8.8	1.2	8.2
pH*=5.0	8.96	7.85	9.15	8.16	7.27	4.4	8.8	1.2	8.2
pH*=6.5	8.95	7.81	9.09	8.14	7.25	4.2	8.7	1.0	8.2
pH*=7.0	8.95	7.81	9.08	8.13	7.24	4.2	8.7	1.0	8.2
V(V)/8-HQS									
CN-6 Complexes^{c} (pH* 6.2)									
δ	8.58	7.48	8.86	8.18	7.19				
Δδ	-0.37	-0.33	-0.23	0.04	-0.06				
CN-5 complex^{d} (pH* 6.2)									
δ	9.11	7.90	9.14	8.18	7.06	4.6	8.1	-^{e}	-^{e}
Δδ	0.16	0.09	0.05	0.04	-0.19				

^{a} δ values, in ppm, relative to Me_4Si, using *tert*-butyl alcohol (δ_H=1.3) as internal reference; *J* values in Hz.

^{b} 10 mmol dm^{-3} 8-HQS solution.

^{c} 5:10 mmol dm^{-3} V(V)–8-HQS solution.

^{d} 10:10 mmol dm^{-3} V(V)–8-HQS solution.

^{e} not observed due to the broadness of the signals.

Table 3. ^{13}C NMR parameters ^{a} for 8-HQS and its complexes with V(V) (298 K)

	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10
8-HQS^{b}									
pH*=3.1	146.23	124.82	143.63	133.59	131.68	114.64	153.26	131.29	127.48
pH*=4.0	148.09	124.75	140.34	136.33	130.81	113.22	154.91	130.91	127.07
pH*=5.0	149.59	124.71	137.78	138.60	130.16	112.14	156.29	130.49	126.84
pH*=6.5	150.19	124.71	136.79	139.54	129.81	111.73	156.91	130.35	126.78
pH*=7.0	150.12	124.67	136.69	139.59	129.91	111.72	157.14	130.04	126.75
V(V)/8-HQS									
CN-5 complex^{c} (pH* 6.2)									
δ	147.53	125.50	137.44	141.78	131.76	111.77	167.10	128.09	127.53
Δδ	-2.66	0.79	0.65	2.24	1.95	0.04	10.19	-2.26	0.75

^{a} δ Values, in ppm, relative to Me_4Si, using *tert*-butyl alcohol (δ_C 31.2) as internal reference; *J* values in Hz.

^{b} 10 mmol dm^{-3} 8-HQS solution.

^{c} 5:10 mmol dm^{-3}V(V)–8-HQS solution.

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From the ^{51}V NMR spectrum, a conditional equilibrium constant log K_2 = 4.63 at pH 4.78 can be estimated.

On the basis of molecular models, three six-coordinated structures (CN-6) with a near octahedral geometry are possible. Two of them are symmetrical (approximately C_2 symmetry) (Structures II and III), while a third asymmetrical species (Structure IV) cannot be ruled out *a priori* due to the observation of a broad signal. However, as we will see shortly, DFT calculations help clarify this assignment. In addition, the remaining signal which appears at -527.5 ppm is assigned to a minor complex characterised by penta-coordinated (CN-5) metal centres (Structure V).[49-51]

Hexa-coordinated complexes give rise to only one set of ^{1}H and ^{13}C signals, which are broader than those of the free ligand (Figures 2 and 3), suggesting an intermolecular exchange on the NMR time scale of the complexed and free ligand. Only traces of the penta-coordinated complex are detected in the ^{13}C NMR spectra**,** due to its low concentration, although it is detected in the ^{1}H NMR spectra (H-2', H-3', H-4', H-6' and H-7' signals).

In the set of signals assigned to hexa-coordinated complexes, C-2, C-5, C-6, C-8 and C-9 nuclei lead to ^{13}C NMR signals which undergo significant changes in their chemical shifts on complexation, whereas the other carbon atoms, C-3, C-4, C-7 and C-10, show much smaller shifts relative to free ligand under the same conditions (Table 3). The coordination induced shifts observed for the C-2 and C-8 nuclei support the involvement of deprotonated quinoline (N) and hydroxyl (O) groups in the complexation, as discussed previously for related complexes.[18,20,21] It is known that the induced shift for a carbon nuclei which bears a coordinated function results from several contributions to σ_p[55,56]including changes in the electronic density related with the coordination and with the ionization which occurs upon complexation. Comparing the changes in C-2 and C-8 chemical shift as a function of pH observed for free 8-HQS with those induced upon metal ion complexation, it can be seen that the chemical shifts of these nuclei parallel the reduced deshielding or shielding observed for C-2 and the large deshielding observed for C-8 upon complexation.[18] C-2 and C-8 nuclei are those most strongly affected by the protonation/deprotonation of the $N\text{-}H^+$ (pKa=4.09) and C-OH (pKa=8.66) [57,58]groups, respectively. Chemical shifts of both C-2 and C-8 nuclei in free 8-HQS increase with pH until around pH 7, and for pH > 7, C-2 chemical shifts decrease as a result of the decreasing positive charge of quinoline (N), while C-8 chemical shifts increase with the increasing negative charge of the oxygen atom of

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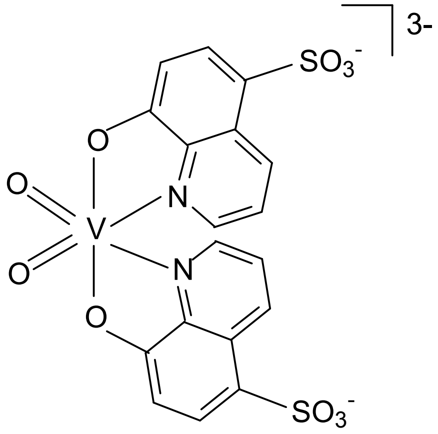
the OH group, as discussed in previous studies.[18] The trends observed in the other carbon shifts are in agreement with the effects of deprotonation of the ligand upon complex formation.[18-21] In particular, the large deshielding observed for C-5 is in accordance with what occurs with this nucleus in the free ligand upon increasing pH, and consequent deprotonation of NH^+ and OH.[18,57,58] The proton signals are also shielded or deshielded as a consequence of the deprotonation on complexation, as was observed in previous studies with 8-HQS, 8-HQ and has been addressed in calculations for pyridine.[41,59] In the hexa-coordinated complexes, the observed ^{51}V chemical shifts (Figure 1 and Table 1) suggest that two molecules of 8-HQS coordinate one octahedral VO_2^+ centre, with the two terminal oxo groups in a *cis* arrangement.[52,60] Additionally, hexa-coordinated species give rise to a single set of ^1H and ^{13}C signals, suggesting an intermolecular exchange of the free and coordinated ligand on the NMR time scale of the near octahedral 1:2 (metal:ligand) complexes.



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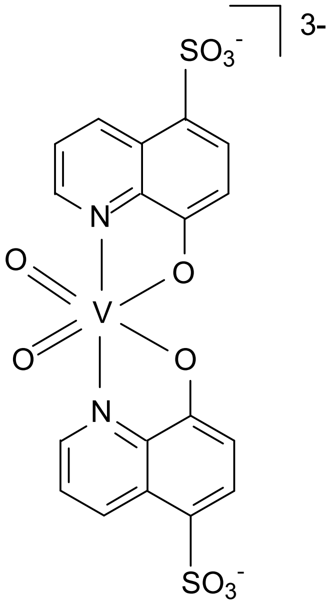

III

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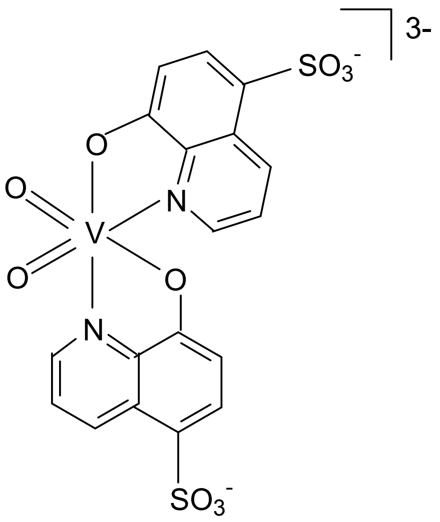

IV

DFT calculations on the complexes

To gain information on the relative stabilities of structures II, III and IV, their geometries were optimized at the DFT level considering the bulk solvent (water) effects through the polarizable continuum model (PCM) of Tomasi and co-workers.[39,40] The application of DFT calculations has proven to be very useful in providing detailed insights into structures and isomer stabilities of metal complexes in solution.[18-21,47,61,62] In both structures II and III, the arrangement of the ligands is symmetrical, with C_2 point group symmetry. The third possible isomer is asymmetrical and has a *cis* arrangement of both the V-N and V-O bonds (structure IV). The optimized geometries and selected structural parameters are presented in Figure 4 and Table 4, respectively. Structure II was found to be the most stable of the three isomers considered. This finding is in agreement with the X-ray structures presented for the crystals obtained from solutions of V(V)/8-HQ.[30-32] Structure IV is the second most stable, lying 6.56 kJ mol^{-1} above structure II and structure III is the least stable (22.24 kJ mol^{-1} above structure II), and for that reason is not present in solution.

Accordingly with the geometrical parameters (Table 4) structures II, III and IV are near octahedral. The structural *trans* influence of the oxo ligands can be observed in the fact that the longest V-O bonds are found whenever these bonds are *trans* to the oxo ligands (structures III and IV, Table 4).

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In a similar fashion, the longest V-N bonds are found whenever these bonds are *trans* to the oxo ligands (structures II and IV, Table 4).

Theoretical calculations support the assignment of the broad signal centred at -538.7 ppm to two major (structures II and IV) six-coordinated complexes, excluding the presence of the other six-coordinated complex (III)). In addition, accordingly with NMR results, the free and bound ligands in complexes II and IV are involved in an intermolecular exchange process, on the NMR time scale. The geometry of the most stable complex, structure II, parallels the geometry obtained by X-ray for the complex previously isolated from solutions V(V)/8-HQ,[30-32] while in the solid state, complexes with a similar geometry to structure IV were not obtained,, as they are less stable than II.

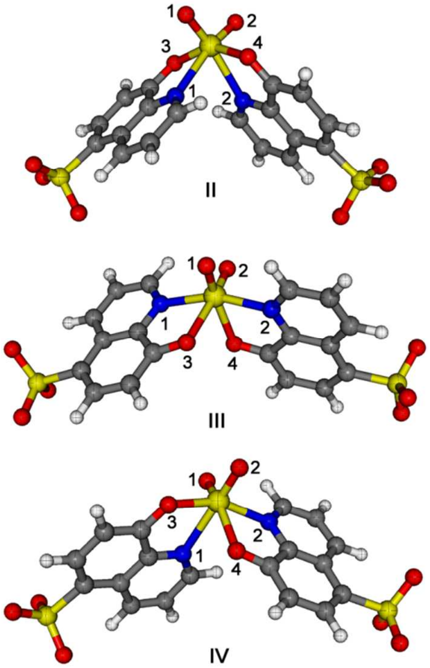

Figure 4. B3LYP/LANL2TZ(f) optimized geometries of three possible $[VO_2(8\text{-HQS})_2]^{3-}$ isomers.

Considering the ^{51}V chemical spectrum, the minor species detected is assigned to a dinuclear complex, characterised by penta-coordinated metal centres (CN-5) $[V_2O_4(8\text{-HQS})_2]^{2-}$ (Structure V).[52,63] The ^1H coordination induced shifts observed for this species (Table 2) support the involvement of deprotonated quinoline (N) and hydroxyl (O) groups in the complexation, as discussed previously for related complexes.[18,20,21]

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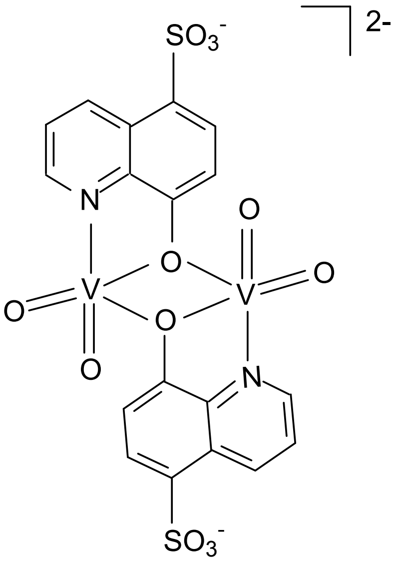
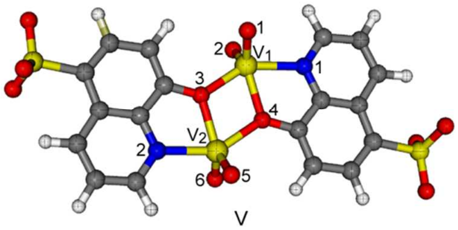


V

The $[V_2O_4(8\text{-HQS})_2]^{2-}$ structure was also optimized at the DFT level and the equilibrium geometry is shown in Figure 5. Selected geometrical parameters for this complex are also presented in Table 4, and accordingly, the five-coordinated centres of the binuclear complex species ($V_2O_4^{2+}$ centre) present a distorted bipyramidal trigonal geometry.



V

Figure 5. B3LYP/LANL2TZ(f) optimized geometry of the $[V_2O_4(8\text{-HQS})_2]^{2-}$ complex.

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Table 4. Selected bond lengths (Å) and angles (degrees) calculated at the B3LYP/LANL2TZ(f) level using the polarizable continuum model (PCM) to simulate the solvent bulk effects.

	II	III	IV	V
V1−O1	1.628 (1.626)[a]	1.631 (1.625)	1.632	1.609 (1.609)
V1−O2	[a]	[a]	1.623	1.607 (1.605)
V1−O3	1.994 (1.988)	2.152 (2.184)	1.970	2.007 (2.007)
V1−O4	[a]	[a]	2.148	2.067 (2.072)
V1−N1	2.411 (2.414)	2.164 (2.170)	2.464	2.130
V1-N2	[a]	[a]	2.179	-
V2−N2	-	-	-	2.127
O1−V1−O2	106.83	104.51	105.80	109.10
O3−V1−O4	149.38	78.73	85.65	71.30
O1−V1−O3	101.32 (101.88)	91.55 (88.98)	105.04	102.36
O1−V1−O4	97.50 (95.55)	161.52 (159.18)	152.68	127.08
O2−V1−O3	[a]	[a]	98.3	103.04
O2−V1−O4	[a]	[a]	97.19	123.66
N1−V1−N2	76.09	160.43	89.90	-
N1−V1−O1	89.21 (88.98)	100.00 (103.68)	83.56	96.72
N1−V1−O2	162.1 (163.2)	89.66 (90.57)	168.94	96.32
N2−V1−O1	[a]	[a]	89.08	-
N2−V1−O2	[a]	[a]	96.04	-

[a] As a consequence of point group symmetry being switched off internally in GAMESS during calculations using the polazible continuum model (PCM), minor differences in the bond lengths and angles were found for symmetry-equivalent ligands in the optimized geometries. The symmetry equivalent parameters are given in brackets.

Figure 6 shows the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals for the two major $[VO_2(8\text{-}HQS)_2]^{3-}$ complexes and the $V_2O_4(8\text{-}HQS)_2{}^{2-}$ complex (structures II, IV and V). The HOMO orbitals are localized exclusively in the ligands, mainly on 8-HQS, but having a small fraction in the terminal oxo ligands. In contrast, the LUMO orbitals have high charge density on the metals and throughout the whole molecule, except for the sulfonate groups.

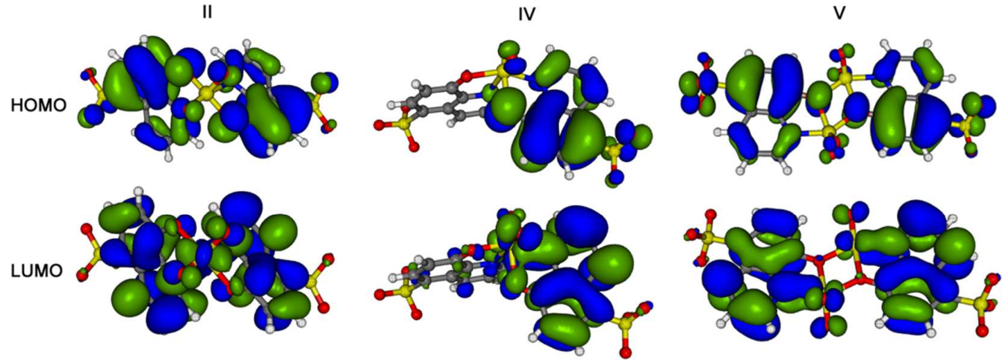

Figure 6. HOMO and LUMO orbitals of the major $[VO_2(8\text{-}HQS)_2]^{3-}$ complexes and the $V_2O_4(8\text{-}HQS)_2{}^{2-}$ complex calculated at the B3LYP/LANL2TZ(f) level.

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UV-Vis absorption and fluorescence spectra

The complexation between 8-HQS and V(V) has also been investigated using UV-Vis absorption and fluorescence spectroscopy under conditions corresponding to formation of the 1:2 (metal:ligand) complexes. Figure 7 shows the absorption and fluorescence spectra of 8-HQS alone and with increasing concentrations of V(V) at pH 5 and 7. As the V(V) concentration increases and complexation between 8-HQS and the metal occurs, there is a decrease in the absorption band around 310 nm, and a new band is observed with a maximum around 365 nm. An isosbestic point can clearly be seen showing that, under these conditions, there is a single equilibrium between free and coordinated 8-HQS, which we attribute to formation of complexes **II** and **IV,** through the overall reaction:

$$VO_2^{+} + 2\ 8\text{-HQS}^{-} \leftrightarrows [VO_2(8\text{-HQS})_2]^{3-}$$

In the UV-Vis absorption spectrum, the long wavelength band is more pronounced and stronger with V(V) than what was observed with the metals (Al(III), Ga(III), Zn(II)).[18,20,21] In addition, and in contrast to what has been observed with these other metals, the complex between V(V) and 8-HQS is only weakly luminescent. We believe this is due to the presence of LMCT states close to the emitting ligand-based level. This is in agreement with the changes in charge distribution in the HOMO and LUMO, and will quench the normal ligand-based emission through an alternative nonradiative pathway, thus decreasing the fluorescence yield. In support of this, LMCT bands have been observed in a variety of catechol and hydroxamate complexes of vanadium(V) oxoions, and generally fall in the 500-900 nm region, with the wavelength being strongly dependent on the coordinating ligand, the nature of the vanadium(V) oxocentre, and is related to the ^{51}V chemical shift.[64,65]

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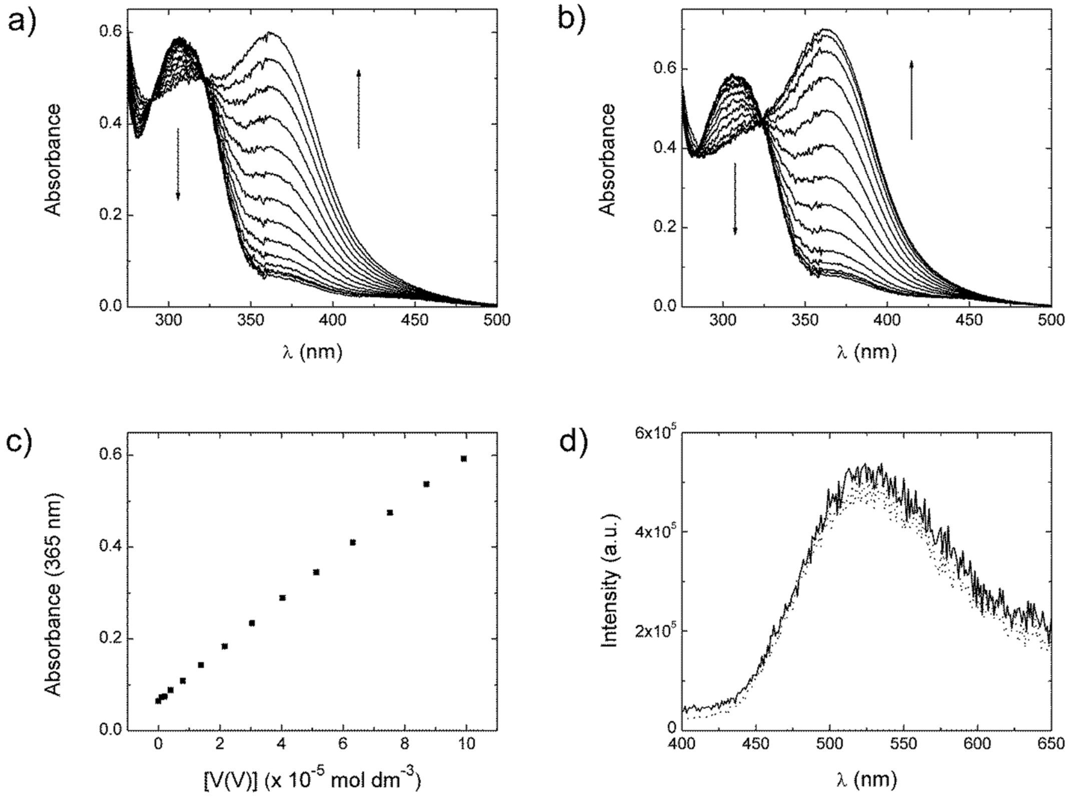

Figure 7. Absorption spectra of 8-HQS (1.0×10^{-4} mol dm^{-3}) alone and in the presence of increasing concentrations of V(V) (1.0×10^{-6} – 9.9×10^{-5} mol dm^{-3}) for pH 5 (a) and pH 7 (b); (c) Absorbance at 365 nm as a function of V(V) concentration for pH 5; (d) Fluorescence spectra of 8-HQS (1.0×10^{-4} mol dm^{-3}) alone (solid line) and in the presence of 9.9×10^{-5} mol dm^{-3} V(V) (dotted line) for pH 7 (similar fluorescence spectra were obtained for pH 5 and are not shown).

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Conclusion

This paper addresses the detailed structural characterisation, and its relation to the spectral and photophysical behaviour, following the interaction of V(V) with the ligand 8-HQS in aqueous solutions. We have carried out complete speciation studies of the system using multinuclear magnetic resonance spectroscopy. This data, coupled with theoretical techniques, in particular DFT, has allowed the structural characterization, while UV/visible and luminescence spectra have provided information on electronic structure.

We identify two dominant 1:2 isomers and one 2:2 (metal:ligand) complex, using ^{1}H, ^{13}C and ^{51}V NMR, UV/visible absorption and fluorescence spectroscopy. In the 1:2 complexes, two molecules of 8-HQS coordinate one near octahedral VO_2^+ centre through the deprotonated quinoline (N) and the hydroxyl (O^-) groups. DFT calculations show that the isomer having the M-N bonds *trans* to the terminal M=O bonds (Structure II) is the most stable. The second most stable isomer (Structure IV), is asymmetrical and has a *cis* arrangement of both the V-N and V-O bonds The energy difference for the isomers (Structures II and IV) was found to be 6.56 kJ mol^{-1}. A minor binuclear complex species ($V_2O_4^{2+}$ centre) was also identified (Structure V), with two five-coordinated metal centres with a distorted bipyramidal trigonal geometry, bridged by two coordinated 8-HQS molecules.

The complexation of V(V) metal ion with 8-HQS is accompanied by marked changes in the UV/visible absorption spectra of 8-HQS, but, unlike the cases of Zn(II),[18] Ga(III) or Al(III)[20,21] , there is no significant fluorescence increase upon complexation. Consideration of literature data[64,65] suggests that there is a low energy LMCT excited state close to the lowest ligand based excited state, which provides a route for nonradiative decay, thus decreasing the fluorescence yield.

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