Water-soluble Schiff-base Complexes of Vanadyl(IV) and Vanadium(III)†

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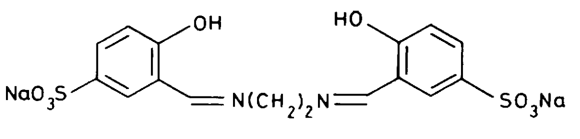
Dicaesium [*NN'*-ethylenebis(salicylideneimine-5'-sulphonato)(4−)]oxovanadate(IV) is obtained from aqueous solution as a red-pink trihydrate. On heating, the blue anhydrous form is obtained. The electronic reflectance spectra indicate that, in the trihydrate, a water molecule is co-ordinated to the vanadium. Aqueous solutions of the complex are thermochromic, being red-pink at 1 and blue at 90 °C. From the electronic absorption spectra, it is concluded that there is an equilibrium between the five-co-ordinate species, and a six-co-ordinate complex formed by axial co-ordination of a water molecule. The corresponding vanadium(III) complex has been characterized in aqueous solution.

Transition-metal complexes of quadridentate Schiff-base ligands formed from salicylaldehyde and 1,2- or 1,3-diamines have been extensively studied.[1] The ligands, and most of the metal complexes, are insoluble in water. By using salicylaldehyde-5-sulphonate in place of salicylaldehyde, water-soluble ligands and complexes can be obtained.[2–4] The complexes can be prepared from the transition-metal ion and either the pre-formed ligand, or a mixture of sals and the diamine. The two methods are, in fact, equivalent, since the water-soluble Schiff-base ligands are extensively hydrolysed in aqueous solution to give sals and the diamine.[4] The present work is concerned with complexes of the ligand Na$_2$(H$_2$salens) [H$_2$salens = *NN'*-ethylenebis(salicylideneimine-5'-sulphonate)] with V^{IV}O and V^{III}. Complexes of the non-sulphonated ligand *NN'*-ethylenebis(salicylideneiminate) (salen) with V^{III},[5,6] V^{IV}O,[5,7] and V^{V} [5] are well characterized.



Na$_2$(H$_2$salens)

Results and Discussion

[V^{IV}O(salens)]$^{2-}$.—*Solid-state studies.* The compound Cs$_2$[V^{IV}O(salens)] crystallizes from aqueous solution as a red-pink trihydrate. On heating at 100 °C *in vacuo* the blue anhydrous form is obtained. Exposure of the anhydrous form to water vapour at atmospheric pressure rapidly regenerates the red-pink colour, with 3 mol of water being taken up in *ca.* 10 min. The reflectance spectrum of the red-pink form shows maxima at 530 and 765 nm, and the blue form at 570 and 725 nm, with a shoulder at *ca.* 450 nm. This suggests that in the trihydrate one of the water molecules is axially co-ordinated to the vanadium to give a six-co-ordinate complex (see below).

The i.r. spectrum of the blue form shows a band at 998 cm^{-1} which is not present for the red-pink form, Na$_2$(H$_2$salens), or Na$_2$[Ni(salens)],[3] and can be attributed to the V=O stretch. In [V^{IV}O(salen)] the corresponding band is at 990 cm^{-1}.[8] Assignment of the V=O stretch in the trihydrate is more difficult. Two possible candidates are bands at 978 and 950 cm^{-1}.

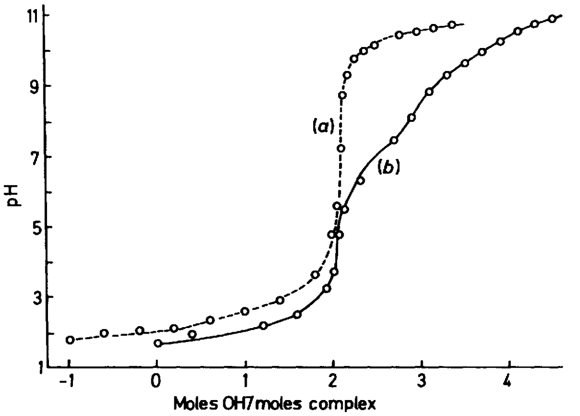


Figure 1. The pH titrations of (*a*) the VO^{2+}, salens system and (*b*) the V^{3+}, salens system at 25 °C. The solutions were 0.01 mol dm^{-3} with respect to metal and ligand

Aqueous solution studies. Figure 1 shows the pH titration of the V^{IV}O^{2+}, Na$_2$(H$_2$salens) system with aqueous KOH. The [V^{IV}O(salens)]$^{2-}$ complex is stable over the approximate pH range 6—10. This was confirmed from measurements of the electronic absorption spectra at various values of pH. The solutions are thermochromic, being red-pink at 1 and blue at 90 °C. Figure 2 presents the electronic absorption spectra at a number of different temperatures. At 1 °C two maxima appear at 526 (ε 152) and *ca.* 810 nm (ε 43 dm^3 mol^{-1} cm^{-1}), while at 90 °C there is a maximum at 549 (ε 120 dm^3 mol^{-1} cm^{-1}) and a shoulder at *ca.* 650 nm. The addition of ethanol at room temperature produces effects very similar to those caused by a rise in temperature of the aqueous solution. The electronic spectra of vanadyl(IV) complexes have been quite extensively studied both experimentally and theoretically.[9] Most five-co-ordinate species are blue or green, whilst many six-co-ordinate complexes are orange or red. Farmer and Urbach[10] have concluded that axial co-ordination of a ligand to a five-co-ordinate complex will cause a blue shift of the lowest-energy transition ($^2B_2 \rightarrow {}^2E$ in C_{4v} symmetry), and a red shift of the next transition ($^2B_2 \rightarrow {}^2B_1$). It therefore seems that the thermochromism of aqueous solutions of [V^{IV}O(salens)]$^{2-}$ arises from an equilibrium between the five-co-ordinate species and a six-co-

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† *Non-S.I. units employed:* B.M. ≈ 9.27 × 10^{-24} J T^{-1}, G = 10^{-4} T.

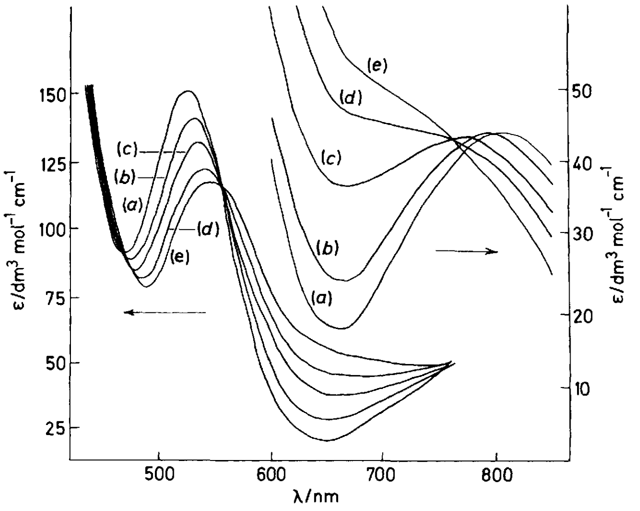

Figure 2. The electronic absorption spectra of $[VO(salens)]^{2-}$ in aqueous solution as a function of temperature: (*a*) 1, (*b*) 24, (*c*) 50, (*d*) 70, and (*e*) 90 °C at pH 7.7 (0.2 mol dm^{-3} *N'*-2-hydroxyethylpiperazine-*N*-ethanesulphonic acid buffer)

ordinate complex formed by axial co-ordination of one water molecule. It is not possible to determine the equilibrium quantitatively, but it seems that at 1 °C the aquated form predominates, whilst at 90 °C the six-co-ordinate species is mainly present.

At room temperature the addition of the strongly co-ordinating solvents pyridine (up to 65% v/v), dimethyl sulphoxide (90% v/v), hexamethylphosphoramide (90% v/v), and tetramethylene sulphoxide (90% v/v) gave blue-green solutions whose electronic spectra resembled that of the five-co-ordinate species. This apparent reluctance to complex may be due to steric effects. The electronic spectra of the non-sulphonated species $[V^{IV}O(salen)]$ in co-ordinating solvents show no evidence for complex formation.[8]

The magnetic moment of $[VO(salens)]^{2-}$ in aqueous solution is 1.76 B.M. (pH 8.4). The e.s.r. spectrum showed the characteristic eight-line pattern due to hyperfine splitting by ^{51}V (99.8% abundant, $I = \frac{7}{2}$). At room temperature g_0 was 1.971 ± 0.001 and A_0 was 92.4 ± 0.5 G. For a solution in acetonitrile–water (67% v/v CH_3CN), where the electronic spectrum showed that the five-co-ordinate species was mainly present, g_0 was 1.972 ± 0.001 and A_0 was 96.7 ± 0.5 G. Axial co-ordination of water thus causes a reduction in A_0. A similar reduction has been observed for other vanadyl(IV) complexes such as $[V^{IV}O(acac)_2]$ [11] (acac = acetylacetonate) in going from non-co-ordinating to co-ordinating solvents. However, changes in hydrogen bonding to the V=O group may also play some part.[12]

$[V^{III}(salens)]^-$.—This complex ion was studied only in aqueous solution. Figure 1 presents the pH titration of the V^{3+}–$Na_2(H_2salens)$ system with aqueous KOH, and shows the formation of the $[V^{III}(salens)]^-$ complex. At higher pH, further protons are lost, presumably from axial water molecules. The magnetic moment μ of the $[V^{III}(salens)]^-$ ion (2.80 B.M.) is close to the spin-only value of 2.83 B.M. The electronic absorption spectrum shows a maximum at 323 nm (ε 8 100 dm^3 mol^{-1} cm^{-1}). This band increases in intensity at higher pH values, and shifts to 353 nm. The non-sulphonated complex (as the disulphato anion) gives a peak at 352 nm (ε 9 800 dm^3 mol^{-1} cm^{-1}) in CH_3OH solution.[5] In all cases, the expected *d–d* transitions are observed by the tails of the charge-transfer absorptions.

Experimental

Sodium salicylaldehyde-5-sulphonate (sals) was prepared as described previously.[3]

$Na_2(H_2salens)$.—The salt sals (0.51 g, 0.0021 mol) was added to ethanol (75 cm^3) and heated to 60 °C. Water was added dropwise until the solid just dissolved, followed by ethylenediamine (74 μl, 0.0011 mol) in ethanol (2 cm^3).The mixture was stirred at 60 °C for 1 h and then cooled to 0 °C. The solid was filtered off, washed with ethanol and diethyl ether, and air dried. Yield 0.15 g (30%) (Found: C, 40.55; H, 3.05; N, 6.00. $C_{16}H_{14}N_2Na_2O_8S_2$ requires C, 40.7; H, 3.00; N, 5.95%).

$Cs_2[V^{IV}O(salens)]\cdot 3H_2O$.—To a stirred solution of sals (0.48 g, 0.002 mol) in water (4 cm^3) was added vandyl sulphate (0.23 g, 0.001 mol), followed by ethylenediamine (67 μl, 0.001 mol). Aqueous 1 mol dm^{-3} NaOH was added to bring the pH to 8—9, followed by a saturated aqueous solution of CsCl (*ca.* 5 cm^3). The solid was washed with 25% CsCl solution, methanol, ethanol, and diethyl ether, and air dried. Yield 0.6 g (73%) (Found: C, 23.85; H, 1.95; N, 3.40. $C_{16}H_8Cs_2N_2O_{12}S_2V$ requires C, 23.7; H, 2.25; N, 3.45%).

$Cs_2[V^{IV}O(salpns)]\cdot 3H_2O$.—This was prepared similarly, using 1,2-diaminopropane in place of ethylenediamine. Yield 0.3 g (36%) (Found: C, 24.3; H, 2.05; N, 3.30. $C_{17}H_{20}Cs_2N_2O_{12}S_2V$ requires C, 24.75; H, 2.45; N, 3.40%). Its properties were very similar to those of $Cs_2[V^{IV}O(salens)]\cdot 3H_2O$.

In both cases, the presence of three molecules of water was confirmed by the loss of weight on heating.

Hydrated vanadyl sulphate (B.D.H. Ltd.) was analysed by titration in 2N H_2SO_4 with 0.1N $KMnO_4$. The formula corresponded to $VO(SO_4)(H_2O)_{3.55}$. Vanadium trichloride (B.D.H. Ltd.) was analysed by addition of the solid to an excess of $[NH_4][Fe(SO_4)_2]$ in 1N H_2SO_4. and subsequent titration with 0.1N $KMnO_4$. The purity was 97—98% (based on V^{III}).

For physical measurements, solutions containing V^{III} or $V^{IV}O$ were normally handled in an argon atmosphere. Electronic spectra were measured on Perkin-Elmer 551 and Pye-Unicam 108 spectrometers. Variable-temperature measurements were made as described previously.[4] The e.s.r. spectra were measured on a Varian E12 spectrometer operating at *ca.* 9.2 GHz using a 'flat' quartz cell and 0.001 mol dm^{-3} solutions. Magnetic susceptibility determinations were made using an n.m.r. method [13] on a Perkin-Elmer R32 spectrometer.

At pH *ca.* 5, an aqueous solution of $[V^{III}(salens)]^-$ was quantitatively oxidized by I_3^- to $[V^{IV}O(salens)]^{2-}$ over *ca.* 20 min, as shown by the electronic absorption spectra. At the same pH, dioxygen also caused quantitative oxidation to $[V^{IV}O(salens)]^{2-}$ in *ca.* 4 h (24 h with air). An aqueous solution of $[V^{IV}O(salens)]^{2-}$ was quantitatively reduced to $[V^{III}(salens)]^-$ by H_2 in the presence of Pd on asbestos.

Acknowledgements

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