Solution Properties of [*NN'*-Bis(salicylidene)-*S*-(+)-butane-1,3-diamino]oxovanadium(IV)

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Summary The results of i.r. electronic, c.d., and e.s.r. solution spectra indicate that [*NN'*-bis(salicylidene)-*S*-(+)-butane-1,3-diamino]oxovanadium(IV), [VO(sal)$_2$-(+)tnMe], is five-co-ordinate in chloroform, but becomes six-co-ordinate in solvents such as pyridine, dimethylformamide, and methanol.

OXOVANADIUM(IV) complexes with tetradentate Schiff base ligands generally exhibit little tendency to form six-co-ordinate adducts with additional donors.[1] A notable exception to this behaviour is found in the recently reported crystal structure of the orange compound, [*NN'*-bis(salicylidene)-propane-1,3-diamino]oxovanadium(IV), VO(sal)$_2$-tn,[2] in which the individual molecules are joined by an infinite chain of V–O–V bonds. We report here the properties of the related complex, VO(sal)$_2$(+)tnMe, in non-donor and donor solvents.

The i.r. mull spectra of both VO(sal)$_2$tn[2] and VO(sal)$_2$-(+)tnMe have an unusually low VO stretching frequency of *ca.* 855 cm^{-1}, indicating that VO(sal)$_2$(+)tnMe also contains bridging vanadyl groups in the solid state. VO(sal)$_2$(+)-tnMe exhibits the following VO stretching frequencies in different solvents: chloroform, 991 cm^{-1}; pyridine or dimethylformamide, *ca.* 960 cm^{-1}. These results indicate that ν_{VO} is relatively unperturbed in a non-donor solvent but is lowered significantly upon axial co-ordination of a donor solvent molecule. Similar shifts in ν_{VO} have been observed for VO(acac)$_2$[3] and were attributed to solvent interaction.

The electronic spectrum of VO(sal)$_2$(+)tnMe in chloroform is similar to that of previously reported five-co-ordinate salicylaldimine-oxovanadium(IV) complexes which show no solvent dependency and are presumably square-pyramidal.[1,4] The *d–d* spectral region of VO(sal)$_2$(+)tnMe in chloroform consists of a single peak at 17,540 cm^{-1} (ϵ 67), with shoulders at 13,900 cm^{-1} (ϵ 27) and 21,400 cm^{-1} (ϵ 95). In co-ordinating solvents, the *d–d* region exhibits two well defined maxima at *ca.* 13,300 cm^{-1} (ϵ *ca.* 30) and *ca.* 19,000 cm^{-1} (ϵ 80), with an additional shoulder at *ca.* 21,800 cm^{-1} (ϵ 90). The electronic mull spectrum of VO(sal)$_2$(+)tnMe shows a peak at 11,800 cm^{-1} and a shoulder at 20,000 cm^{-1}. These shifts, similar to the changes observed in the electronic spectra of VO(acac)$_2$ upon axial co-ordination,[5] suggest, that VO(sal)$_2$(+)tnMe is five-co-ordinate in chloroform and six-co-ordinate in pyridine, dimethylformamide, and methanol.

Improved band resolution occurs in the c.d. spectra (*cf.* Table) of VO(sal)$_2$(+)tnMe compared to the electronic spectra, and three bands are observed in the *d–d* region in both chloroform and pyridine. Unlike five-co-ordinate optically active salicylaldimine-oxovanadium(IV) complexes, whose $\Delta\epsilon$ values remain fairly constant in going from chloroform to donor solvents,[4] the $\Delta\epsilon$ values of VO(sal)$_2$(+)tnMe are significantly less in donor solvents compared to chloroform. These changes can be interpreted in terms of a more planar arrangement of the tetradentate ligand upon co-ordination of a solvent molecule in position 6.

Finally, an attempt was made to correlate shifts in the A_0 values obtained from e.s.r. spectra to axial co-ordination in donor solvents. Slight shifts were observed, but were not large enough (A_0 = 98·36 in chloroform compared to A_0 = 93·76 in methanol) to be assigned entirely to co-ordination effects. The g_0 values also remained constant within the solvent series; ranging from 1·974 in methanol to 1·976 in dimethylformamide. Both the A_0 and g_0 values are in good agreement with those published for other salicylaldimine-oxovanadium(IV) complexes.[1]

Circular dichroism spectra of VO(sal)$_2$(+)tnMe

Solvent	ν, cm^{-1} ($\Delta\epsilon$)
CHCl$_3$	13,160[a](−0·26) (I);[b] 17,390(−0·451) (II); 21,280(−1·18) (III); 24,690(−7·66); 27,320 (+1·43); 34,480(−8·5)
C$_5$H$_5$N	13,300[a](−0·10) (I); 17,700(−0·236) (II); 20,830 (−0·393) (III); 25,320 (−4·1)
MeOH	13,300[a] (−0·15) (I); 18,870 (−0·276) (II); 21,280sh (−0·19) (III); 27,030 (−2.3)
HCONMe$_2$	13,300[a] (−0·18) (I); 18,180 (−0·561) (II); 20,830sh (−0·38) (III); 25,640 (−3·54)

[a] Band lies too close to long wavelength limit of instrument to be fully resolved.

[b] Refers to the numbering of the low energy bands.

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