

## The Electronic Structure of VO(5-X-salen), X = H, OMe, OH, Cl, Br and NO<sub>2</sub>

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### Abstract

The vanadyl complexes of the derivatives of salicylaldimine, VO(5-X-salen), where X = H, OMe, OH, Cl, Br and NO<sub>2</sub>, are prepared and their electronic spectra measured. A fairly good relation can be drawn between the LMCT band energies and the Hammett parameters. The solvent effects upon the electronic and EPR spectra are also ascertained.

### Introduction

The electronic properties of a metal complex can be finely tuned by changing the coordination environment of the metal ion. For a square complex of a quadridentate ligand, such as Co(salen) (salen: salicylaldimine) which exhibits reversible oxygen carrier properties [1], there are two ways to modify the electronic structure. One is making substitution on the quadridentate ligand with an electron donating or withdrawing group. The other is by making further coordination to the vacant site. To probe the similarity and difference of these two approaches, we selected to study the electronic structure of the simple d<sup>1</sup> complex VO(salen) and its derivatives.

The electronic structure of oxovanadium(IV) coordinated by two bidentate ligands, such as acetylacetonate [2–5] and perfluoropinasolate [6], to

form a nearly square pyramidal complex, is well understood. The effect of ligand coordination to the sixth coordination site can easily be examined by UV–Vis absorption spectroscopy and ESR. In VO(acacen) (acacen: *N,N'*-ethylenebisacetylacetonimine) which is analogous to VO(salen), coordination by the solvent has been suggested to be absent [5]. It is based on the reasoning that coordination to the vacant site will bring the VO group closer to the N<sub>2</sub>O<sub>2</sub> ligand plane, and the rigidity of the quadridentate ligand prevents the vanadium from approaching any closer. On the other hand, if coordination by the exogeneous ligand to the vacant site is energetically favorable, there is no reason to prevent such a coordination from happening.

The electronic spectra and EPR of VO(salen) and its derivatives have been studied by several groups [7–10]. The influence of salen modification as well as ligand coordination on the electronic structure has not been systematically investigated. Here, we report the electronic and EPR spectra of VO(5-X-salen) (X = H, OMe, OH, Cl, Br, NO<sub>2</sub>) and VO(salen) in various solvents.

### Experimental

VO(5-X-salen) (X = H, OMe, OH, Cl, Br, NO<sub>2</sub>) were prepared by standard methods [9]. The results of elemental analysis of these complexes are listed in Table 1.

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TABLE 1. Elemental analysis data for VO(5-X-salen)

	C (%)		H (%)		N (%)		Cl (%)	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
VO(salen)	56.12	(57.66)	4.31	(4.20)	8.70	(8.41)		
VO(5-Br-salen)	38.16	(39.10)	2.56	(2.44)	5.66	(5.70)		
VO(5-Cl-salen)	45.12	(47.76)	2.98	(2.99)	6.71	(6.97)	17.44	(17.66)
VO(5-OH-salen) <sup>a</sup>	44.73	(44.76)	4.34	(5.13)	7.96	(6.53)		
VO(5-OCH <sub>3</sub> -salen)	52.15	(52.03)	4.52	(4.88)	6.88	(7.59)		
VO(5-NO <sub>2</sub> -salen) <sup>a</sup>	40.92	(39.43)	3.51	(4.11)	12.08	(11.50)		

<sup>a</sup>These compounds are with two solvated methanol.

Spectral grade solvents were obtained from E. Merck Chemical Co. and dried over Merck 4A molecular sieves. Since traces of oxygen had an appreciable effect upon the EPR linewidth, the EPR solution samples were carefully degassed by repetitive melt–freeze–pump technique. The concentration of VO(5-X-salen) solutions were about  $10^{-3}$  M, well below the critical concentration. EPR spectra were recorded at room temperature and 77 K on a Bruker ER 200 D 10/12 SRC spectrometer using diphenylpicrylhydrazide as a  $g$  value marker. The EPR spectrometer is interfaced with a PC-AT micro-computer for data processing. Optical spectra were recorded on a Perkin-Elmer Lambda-5 spectrophotometer. The absorption spectra were analyzed using a resolver based on Gaussian lineshape.

## Results and Discussion

The electronic spectra of VO(5-X-salen) (X = H, OMe, OH, Cl, Br, NO<sub>2</sub>) in THF consist of four absorption bands in the ranges of 15, 16, 24–28 and 31–35 kK. The highest energy band has a molar extinction coefficient of about 20 000, which can be assigned to the ligand band. They are not examined any further and are omitted in the subsequent discussion. A typical spectrum is shown in Fig. 1 together with a Gaussian spectral fitting to the low intensity bands to determine the absorption maxima and molar extinction coefficients accurately. The relevant spectral data are included in Table 2.

From the small molar extinction coefficients of the two low energy bands, they can be assigned to d–d transitions. After extensive studies, the electronic energy level ordering [2, 11] of bisacetylacetonatooxovanadium(IV) is generally accepted to be  $b_2(d_{x^2-y^2}) < e\pi^*(d_{xz}, d_{yz}) < b_1^*(d_{z^2}) < a_1^*(d_{xy})$ . Since  $e\pi^*$  is doubly degenerate, one expects  $b_2 \rightarrow e\pi^*$  to be more intense than  $b_2 \rightarrow b_1^*$ . However, the data in Table 2 contradict with our expectation, which indicate that the energy level ordering in

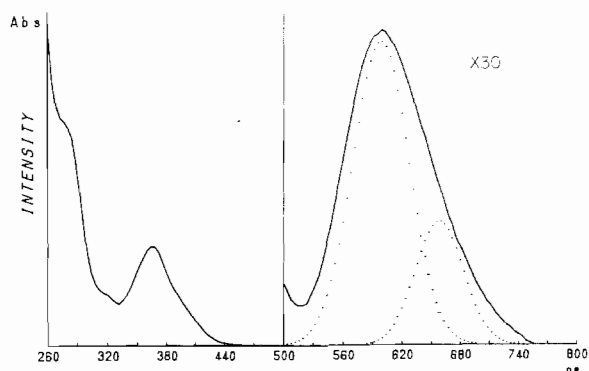


Fig. 1. The absorption spectrum of VO(5-X-salen). The absorption  $>500$  nm is  $\times 30$ .

TABLE 2. UV–Vis absorption data for VO(5-X-salen) in THF

Complex	$\lambda_{\max} (\epsilon)^a$			
	I	II	III	IV
VO(5-OH-salen)	32.26	24.49 (8400)	16.47 (220)	15.39 (130)
VO(5-OCH <sub>3</sub> -salen)	32.34	24.97 (5000)	16.65 (100)	15.28 (65)
VO(salen)	39.31	27.35 (13000)	16.76 (190)	15.16 (105)
VO(5-Br-salen)	31.25	28.31 (13000)	16.72 (190)	15.43 (120)
VO(5-Cl-salen)	31.35	27.17 (8900)	16.80 (160)	15.60 (95)
VO(5-NO <sub>2</sub> -salen)		28.72	16.85	15.68

<sup>a</sup>Maxima are given as kK (1 kiloKaysar = 1000  $\text{cm}^{-1}$ ); molar extinction coefficient given as  $\text{M}^{-1} \text{cm}^{-1}$ .

VO(5-X-salen) could be  $b_2 < b_1^* < e\pi^* < a_1^*$ . The  $b_2 \rightarrow a_1^*$  transition is buried under the high intensity bands. An extended Hückel MO calculation of VO(salen) [12] reveals that the vanadium 3d orbital populations are  $d_{x^2-y^2} > d_{xz} \approx d_{yz} > d_{z^2} > d_{xy}$ . This ordering is consistent with the assignment that the lowest energy band is  $b_2 \rightarrow b_1^*$ . Furthermore, Patal and coworkers [8] have also assigned the lowest energy band in VO(3-OMe-salen) to be  $b_2 \rightarrow b_1^*$ , based on the observation that the  $b_2 \rightarrow e\pi^*$  is split into two closely spaced bands. Thus, the 3d energy level ordering of oxovanadium(IV) in the salen type of complex is different from that of the bisdiketonate complex. The high intensity band can be assigned as charge transfer. As shown in Fig. 2, the band position is dependent on the Hammett parameter  $\sigma_p$  of the substituent, the higher the  $\sigma_p$  the higher the band energy. It clearly indicates that this is a ligand to metal charge transfer band (LMCT). It is noteworthy that  $b_2 \rightarrow b_1^*$  and  $b_2 \rightarrow e\pi^*$  band positions also depend linearly on  $\sigma_p$  with a spectral range smaller

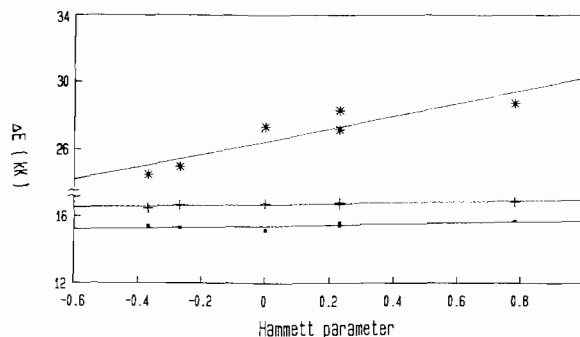


Fig. 2. Relation between the Hammett parameter and the LMCT energy of VO(5-X-salen).

TABLE 3. Magnetic parameters for VO(5-X-salen) in THF<sup>a</sup>

Complex	$g_{\parallel}$	$g_{\perp}$	$g_0$	$A_{\parallel}$	$A_{\perp}$	$A_0$
VO(5-OH-salen)	1.9522	1.9929	1.9781	177.39	57.30	99.29
VO(5-OCH <sub>3</sub> -salen)	1.9515	1.9922	1.9766	178.39	57.56	99.57
VO(salen)	1.9509	1.9913	1.9780	178.26	59.56	100.07
VO(5-Br-salen)	1.9530	1.9918	1.9782	177.45	56.98	100.12
VO(5-Cl-salen)	1.9536	1.9933	1.9781	178.83	58.56	100.12
VO(5-NO <sub>2</sub> -salen)	1.9531	1.9938	1.9782	177.48	57.40	100.04

<sup>a</sup>Isotropic hyperfine splitting constants are given as gauss.

than that of LMCT band (0.52 and 0.38 kK versus 3.63 kK). Varying the substituent in 5-X-salen has a large effect on the LMCT band, but only a small effect on the d-d bands.

The EPR parameters of VO(5-X-salen) in frozen THF solution at 77 K and at room temperature are also collected in Table 3. The  $g_{\parallel}$ ,  $g_{\perp}$  and isotropic  $g_0$  values, which agree well with the values calculated from  $g_{\parallel}$  and  $g_{\perp}$ , are practically independent of the nature of substituent X. The vanadium hyperfine coupling constants,  $A_v$ , measured at room temperature are slightly larger than those deduced from  $A_{\parallel}$  and  $A_{\perp}$ . Though  $A_v$  varies over a small range ( $\approx 1$  G), a general trend that  $A_v$  increases as  $\sigma_p$  increases can be found. It has been established that in VO(acac)<sub>2</sub> [2],  $A_v$  is due to spin polarization which is also expected to be the case in VO(5-X-salen). A better in-plane  $\sigma$  and  $\pi$  interaction leads to a reduction in  $A_v$ . Hence, for a good electron donating substituent X in VO(5-X-salen), a small  $A_v$  is observed, indicating a better in-plane interaction as expected. However, the range of  $A_v$  is rather limited ( $\approx 1$  G). It further supports the fact that substituent X has only a small effect on the in-plane interactions as observed in the electronic spectra.

The electronic spectral data and EPR parameters of VO(salen) in a number of solvents are collected in Tables 4 and 5. The solvent effects on electronic

TABLE 4. UV-Vis absorption data for VO(salen) in various solvents

Solvent	$\lambda_{\max}$ ( $\epsilon$ ) <sup>a</sup>			
	I	II	III	IV
Benzene	35.36	26.98	16.64	15.06
	(20000)	(10000)	(190)	(80)
Dioxane	35.66	27.29	16.75	15.15
	(22000)	(10000)	(190)	(110)
THF	39.31	27.35	16.76	15.16
	(17000)	(13000)	(190)	(105)
CHCl <sub>3</sub>	35.29	27.03	16.81	14.93
	(27000)	(10000)	(185)	(80)
Pyridine		27.35	16.90	15.24
		(10000)	(160)	(90)
CH <sub>2</sub> Cl <sub>2</sub>	35.87	27.25	16.94	15.37
	(37000)	(10000)	(220)	(130)
Acetone		27.64	16.89	15.34
		(8000)	(150)	(100)
DMF	37.74	27.64	17.02	15.43
	(28000)	(8000)	(155)	(100)
DMSO	38.52	27.62	17.30	15.61
	(10000)	(8000)	(140)	(90)
CH <sub>3</sub> OH	36.28	27.81	17.56	16.13
	(18000)	(6000)	(110)	(60)

<sup>a</sup>Maxima are given as kK (1 kiloKaysers = 1000 cm<sup>-1</sup>); molar extinction coefficient given as M<sup>-1</sup> cm<sup>-1</sup>.

TABLE 5. Magnetic parameters for VO(salen) in various solvents<sup>a</sup>

Solvent	$g_{\parallel}$	$g_{\perp}$	$g_0$	$A_{\parallel}$	$A_{\perp}$	$A_0$
Benzene	1.9543	1.9896	1.9783	173.51	52.60	100.18
Dioxane	1.9556	1.9859	1.9797	172.47	54.43	99.19
THF	1.9509	1.9913	1.9780	178.26	59.56	100.07
CHCl <sub>3</sub>	1.9603	1.9913	1.9797	168.60	59.81	98.62
Pyridine	1.9551	1.9866	1.9796	173.23	56.13	98.43
CH <sub>2</sub> Cl <sub>2</sub>	1.9457	1.9927	1.9803	175.18	59.21	98.96
Acetone	1.9543	1.9918	1.9796	176.57	57.72	99.58
DMF	1.9539	1.9937	1.9753	176.46	57.85	98.81
DMSO	1.9543	1.9851	1.9773	172.93	55.61	96.96
CH <sub>3</sub> OH	1.9636	1.9942	1.9789	175.04	57.70	96.83

<sup>a</sup>Isotropic hyperfine splitting constants are given as gauss.

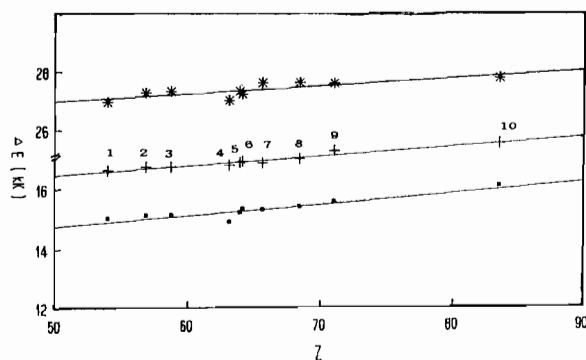


Fig. 3. Relation between the solvent parameter  $Z$  and the absorption bands for VO(salen) in various solvents: 1, benzene, 2, dioxane; 3, THF; 4,  $\text{CHCl}_3$ ; 5 pyridine; 6,  $\text{CH}_2\text{Cl}_2$ ; 7, acetone; 8, DMF; 9, DMSO; 10, methanol.

band positions can be divided into three categories. Firstly, the solvent molecules organize around VO(salen) to interact with the dipole of the complex, whereas in the excited Frank-Condon state, the solvent molecules do not have enough time to rearrange in response to the dipole change in excited VO(salen). Secondly, the energy level may be shifted due to the coordination of the solvent molecule to the sixth coordination site. Thirdly, there is hydrogen bonding between the oxovanadyl group and active hydrogen in methanol or chloroform. The dependence of the LMCT band position on the solvent can largely be attributed to the first effect [13], and a linear correlation between LMCT band positions and solvent  $E_T$  or  $Z$  parameters is expected. This is confirmed experimentally as shown in Fig. 3. In the absence of solvent coordination, the d-d band positions are generally understood [13] to be insensitive to the solvent. Thus, the  $\lambda_{\text{max}}$  dependence of  $b_2 \rightarrow b_1^*$  and  $b_2 \rightarrow e\pi^*$  on the solvent is indicative of solvent coordination to the sixth coordination site of VO(salen). Interestingly, the  $\lambda_{\text{max}}$  values of  $b_2 \rightarrow b_1^*$  and  $b_2 \rightarrow e\pi^*$  are also linearly dependent on the  $E_T$  or  $Z$  solvent parameter.

As indicated in Table 5, the isotropic  $A_v$  dependence on the solvent furnishes further support to the coordination of the solvent molecule to vanadium. When the donor number of the solvent increases,  $A_v$  decreases, the only exception being THF. This correlation can be explained based on solvent coordination. When the solvent molecule is coordinated to the sixth coordination site, vanadium, which is 0.606 Å above the  $\text{N}_2\text{O}_2$  plane of salen [14], should move toward the ligand plane to optimize the coordination bond strength. This movement was clearly demonstrated by the observation that VO is 0.13–0.14

Å [15] greater above the four atom coordination plane in VO(salen) than in the VO complex of ethyl-enebis(*o*-hydroxyphenylglycine), which has six-coordinated vanadium. The approach of the oxovanadyl group to the  $\text{N}_2\text{O}_2$  plane should lead to a better in-plane interaction. This interaction can be gauged by  $A_v$  which varies from 100 gauss to 97 gauss.

Comparing the range of  $\lambda_{\text{max}}$  values in Tables 2 and 4, it becomes obvious that the substituent X in VO(5-X-salen) has a larger effect on LMCT band energy than on d-d band energies. On the other hand, the solvent has about the same effect on both LMCT and d-d band energies. Consistent with the electronic spectral variation,  $A_v$ s also indicate that X has a much smaller effect than the solvent on in-plane interaction. Thus, variation of X in VO(5-X-salen) can offer a wide range of  $\lambda_{\text{max}}$  of the LMCT band, while solvent variation will have a large influence on the in-plane interaction.

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