

## CHEMISTRY OF VO<sup>3+</sup> AND VO<sup>2+</sup> COMPLEXES INCORPORATING N-SALICYLIDENE- $\alpha$ - AMINOACIDATES

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**Abstract**—The complexes [V<sup>IV</sup>O(L)(bpy)] and [V<sup>VO</sup>O(L)(OMe)(OHMe)] (H<sub>2</sub>L = Schiff base condensate of salicylaldehyde and an  $\alpha$ -amino acid and bpy = 2,2'-bipyridine) have been synthesized. The [V<sup>IV</sup>O(L)(OMe)(OHMe)]<sup>-</sup> species have been electrogenerated in solutions. The VO<sup>3+</sup>–VO<sup>2+</sup>  $E_{1/2}$  values of [VO(L)(OMe)(OHMe)] are lower than those of [VO(L)(bpy)] by ~750 mV. Upon exposure to air [VO(L)(OMe)(OHMe)]<sup>-</sup> is spontaneously oxidized to [VO(L)(OMe)(OHMe)]. The [VO(L)(bpy)] and [VO(L)(OMe)(OHMe)]<sup>-</sup> complexes display  $d_{xy}^1$  type axial EPR spectra. The <sup>51</sup>V hyperfine constants follow the order [VO(L)(OMe)(OHMe)]<sup>-</sup> > [VO(L)(bpy)]. The  $d_{xy} \rightarrow d_{xz}, d_{yz}$  transition in these complexes appear in the region 700–720 nm.

This work forms part of our programme on selective stabilization of the VO<sup>2+</sup> and VO<sup>3+</sup> motifs through ligand variation.<sup>1–3</sup> These motifs are of considerable current interest in relation to vanadium biocoordination chemistry.<sup>4–9</sup> The binding of VO<sup>z+</sup> ( $z = 2,3$ ) by salicylaldimines incorporating  $\alpha$ -amino acid residues (H<sub>2</sub>L), **1**, have been documented.<sup>4,10–15</sup>

The present work concerns complexes of type [V<sup>IV</sup>O(L)(bpy)] and [V<sup>VO</sup>O(L)(OMe)(OHMe)]. Reduction potential data provides a rationale for the difference of metal oxidation states in the two groups. The EPR spectra of [VO(L)(bpy)] and electrogenerated [VO(L)(OMe)(OHMe)]<sup>-</sup> are compared.

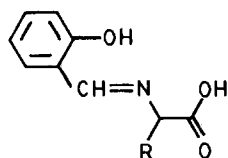
### EXPERIMENTAL

#### Materials

The complexes were synthesized using [VO(L)(H<sub>2</sub>O)]<sup>11</sup> as the starting material. Electrochemical grade tetraethylammonium perchlorate, methanol and dichloromethane were obtained as before.<sup>16</sup> All other chemicals and solvents were of analytical grade and used as obtained.

#### Physical measurements

Electronic spectra were recorded with a Hitachi 330 spectrophotometer, infrared spectra on a Perkin–Elmer 783 spectrometer and EPR spectra in the X-band on a Varian E-109C spectrometer equipped with a quartz Dewar flask for low-temperature (77



- H<sub>2</sub>L<sup>1</sup> R = H  
 H<sub>2</sub>L<sup>2</sup> R = CH<sub>3</sub>  
 H<sub>2</sub>L<sup>3</sup> R = CH(CH<sub>3</sub>)<sub>2</sub>  
 H<sub>2</sub>L<sup>4</sup> R = CH<sub>2</sub> Ph

**1**

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K) measurements. Diphenylpicrylhydrazyl(dpph) ( $g = 2.0037$ ) was used to calibrate the spectra. Magnetic susceptibilities for  $[\text{VO}(\text{L})(\text{bpy})]$  species were measured by using a PAR model 155 vibrating-sample magnetometer fitted with a Walker Scientific L 75 FB AL magnet. Electrochemical measurements were performed on a PAR model 370-4 electrochemistry system as reported earlier.<sup>17</sup> All potentials reported in this work are uncorrected for junction contribution. A Perkin-Elmer 240C elemental analyser was used to collect micro-analytical data (C, H, N).

### Synthesis of the complexes

The complexes reported in this work were prepared by the same general method. Details are given for two representative cases only.

(*Methoxo*) (*methanol*) (*N-salicylidene-L-valinato*) *oxovanadium(IV)*,  $[\text{VO}(\text{L}^3)(\text{OMe})(\text{OHMe})]$ . A solution of  $[\text{VO}(\text{L}^3)(\text{H}_2\text{O})]$  (100 mg, 0.29 mmol) in methanol (10 cm<sup>3</sup>) was allowed to stand in air. After slow evaporation of the solvent at room temperature for 2 days dark crystals were collected. Yield: 91%.

(2, 2' - *Bipyridine*) (*N-salicylidene-L-valinato*) *oxovanadium(IV)*,  $[\text{VO}(\text{L}^3)(\text{bpy})]$ . To a solution of  $[\text{VO}(\text{L}^3)(\text{H}_2\text{O})]$  (100 mg, 0.29 mmol) in methanol (10 cm<sup>3</sup>) was added 2,2'-bipyridine (44.5 mg, 0.29 mmol). The resulting solution upon stirring for 15 min yielded a snuff coloured crystalline solid. It was filtered off, washed thoroughly with methanol and dried *in vacuo* over  $\text{P}_4\text{O}_{10}$ . Yield: 87%.

### Electrogeneration of $[\text{VO}(\text{L})(\text{OMe})(\text{OHMe})]^-$ species

The representative example of  $[\text{VO}(\text{L}^3)(\text{OMe})(\text{OHMe})]^-$  is described. A solution of 18 mg (0.05 mmol) of  $[\text{VO}(\text{L}^3)(\text{OMe})(\text{OHMe})]$  in 15 cm<sup>3</sup> of dry methanol (0.1 mol dm<sup>-3</sup>  $[\text{NEt}_4][\text{ClO}_4]$ ) was reduced at  $-0.25$  V vs SCE in a nitrogen atmosphere. Electrolysis stopped when 4.82 C had passed. The calculated one-electron coulomb count was 4.98. The reduced solution was used for spectral and electrochemical measurements.

## RESULTS AND DISCUSSION

### Synthesis, characterization and structure

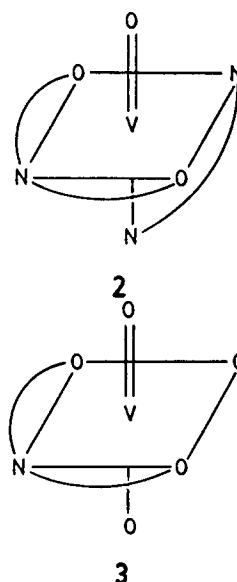
Four salicylaldimine ligands  $\text{H}_2\text{L}^1$ – $\text{H}_2\text{L}^4$  (general abbreviation  $\text{H}_2\text{L}$ ) have been used in the present work. The complexes  $[\text{VO}(\text{L})(\text{bpy})]$  ( $\text{L} = \text{L}^2$ )<sup>15</sup> and  $[\text{VO}(\text{L})(\text{OMe})(\text{OHMe})]$  ( $\text{L} = \text{L}^1, \text{L}^2$ )<sup>12,13</sup> are known. Upon standing in methanolic solution in

air  $[\text{V}^{\text{IV}}\text{O}(\text{L})(\text{H}_2\text{O})]$  is spontaneously converted to  $[\text{V}^{\text{V}}\text{O}(\text{L})(\text{OMe})(\text{OHMe})]$  via aerial oxidation. If bpy is present in solution, it binds to the vanadium centre and blocks oxidation. These findings are consistent with the reduction potential data presented later in this paper.

Selected characterization data of the complexes are listed in Table 1. The  $[\text{VO}(\text{L})(\text{OMe})(\text{OHMe})]$  species are diamagnetic while the magnetic moment of the  $[\text{VO}(\text{L})(\text{bpy})]$  species correspond to one unpaired electron ( $S = 1/2$ ). The electronic spectral data of the complexes are listed in Table 2 and representative spectra are displayed in Fig. 1. The expected ligand field transition ( $d_{xy} \rightarrow d_{xz}, d_{yz}$ )<sup>18</sup> for the neutral  $[\text{VO}(\text{L})(\text{bpy})]$  and electrogenerated  $[\text{VO}(\text{L})(\text{OMe})(\text{OHMe})]^-$  species appear in the region 700–720 nm.

The  $[\text{VO}(\text{L})(\text{bpy})]$  and  $[\text{VO}(\text{L})(\text{OMe})(\text{OHMe})]$  complexes display a strong  $\text{V}=\text{O}$  stretch in the region 950–990 cm<sup>-1</sup> which is suggestive of hexacoordination.<sup>2,4,19</sup> The complexes have a well-defined band near 1620 cm<sup>-1</sup> (Table 1) assigned to asymmetric carboxyl stretch corresponding to monodentate carboxyl binding.<sup>20</sup> The symmetric stretch could be expected near 1350 cm<sup>-1</sup> but presence of other bands vitiated its identification.

The X-ray structures of  $[\text{V}^{\text{IV}}\text{O}(\text{L}^2)(\text{bpy})]$ <sup>15</sup> and  $[\text{V}^{\text{V}}\text{O}(\text{L}^2)(\text{OMe})(\text{OHMe})]$ <sup>13</sup> have been reported and the coordination spheres are of type 2 and 3.



recently showed that the structural type 2 also occurs in (2,2'-bipyridine)(2-hydroxy-2'-carboxy-5-methylazobenzenato)oxovanadium(IV).<sup>2</sup>

### EPR spectra

The  $[\text{VO}(\text{L})(\text{bpy})]$  and electrogenerated  $[\text{VO}(\text{L})(\text{OMe})(\text{OHMe})]^-$  species ( $S = 1/2$ ) display axial

Table 1. Characterization data

Compound	Analysis (%) <sup>a</sup>			IR data <sup>b</sup> (cm <sup>-1</sup> )	$\mu_{\text{eff}}^c$ ( $\mu_{\text{B}}$ )
	C	H	N		
[VO(L <sup>1</sup> )(bpy)]	56.8 (57.0)	3.9 (3.8)	10.4 (10.5)	955, 1620	1.78
[VO(L <sup>2</sup> )(bpy)]	57.7 (58.0)	4.0 (4.1)	10.0 (10.1)	960, 1620	1.72
[VO(L <sup>3</sup> )(bpy)]	59.5 (59.7)	4.7 (4.8)	9.7 (9.5)	965, 1615	1.76
[VO(L <sup>4</sup> )(bpy)]	63.4 (63.7)	4.4 (4.3)	8.5 (8.6)	970, 1625	1.71
[VO(L <sup>1</sup> )(OMe)(OHMe)]	43.2 (43.0)	4.7 (4.6)	4.8 (4.6)	980, 1620	<sup>d</sup>
[VO(L <sup>2</sup> )(OMe)(OHMe)]	44.7 (44.9)	5.1 (5.0)	4.2 (4.4)	985, 1615	<sup>d</sup>
[VO(L <sup>3</sup> )(OMe)(OHMe)]	48.4 (48.1)	5.8 (5.7)	3.8 (4.0)	990, 1620	<sup>d</sup>
[VO(L <sup>4</sup> )(OMe)(OHMe)]	54.2 (54.4)	4.9 (5.0)	3.2 (3.5)	980, 1625	<sup>d</sup>

<sup>a</sup> Calculated values in parentheses.<sup>b</sup> In KBr discs.<sup>c</sup> At 298 K.<sup>d</sup> Diamagnetic.Table 2. Spectral and electrochemical<sup>a</sup> data at 298 K

Compound	UV-vis		$E_{1/2},^c$ V( $\Delta E_p,^f$ mV)
	$\lambda_{\text{max}}$ , nm	( $\epsilon$ , dm <sup>3</sup> mol <sup>-1</sup> cm <sup>-1</sup> )	
[VO(L <sup>1</sup> )(bpy)] <sup>b</sup>	720(46),	350(3330)	0.87(140)
[VO(L <sup>2</sup> )(bpy)] <sup>b</sup>	705(36),	390(4410)	0.84(120)
[VO(L <sup>3</sup> )(bpy)] <sup>b</sup>	700(25),	390(3200)	0.78(200)
[VO(L <sup>4</sup> )(bpy)] <sup>b</sup>	710(32),	360(3500)	0.75(140)
[VO(L <sup>1</sup> )(OMe)(OHMe)] <sup>c</sup>	510(450),	350(6610)	0.08(140)
[VO(L <sup>2</sup> )(OMe)(OHMe)] <sup>c</sup>	480(390),	345(5210)	0.08(160)
[VO(L <sup>3</sup> )(OMe)(OHMe)] <sup>c</sup>	475(510),	340(6080)	0.07(150)
[VO(L <sup>4</sup> )(OMe)(OHMe)] <sup>c</sup>	490(430),	360(6140)	0.05(170)
[VO(L <sup>3</sup> )(OMe)(OHMe)] <sup>-d</sup>	710(26),	365(4000)	—
[VO(L <sup>4</sup> )(OMe)(OHMe)] <sup>-d</sup>	700(27),	380(4820)	—

<sup>a</sup> Supporting electrolyte [NEt<sub>4</sub>][ClO<sub>4</sub>] (0.1 mol dm<sup>-3</sup>), platinum electrode, SCE reference electrode, solute concentration  $\sim 10^{-3}$  mol dm<sup>-3</sup>.<sup>b</sup> In dichloromethane.<sup>c</sup> In methanol.<sup>d</sup> Electro-generated in methanol solution by exhaustive coulometry at  $-0.25$  V [ratio of observed and calculated (for one-electron) coulomb counts in the range 0.94–0.98].<sup>e</sup> Calculated as the average of anodic ( $E_{\text{pa}}$ ) and cathodic ( $E_{\text{pc}}$ ) peak potentials.<sup>f</sup>  $E_{\text{pa}} - E_{\text{pc}}$ .

EPR spectra in frozen dichloromethane and 1:1 methanol-toluene solution respectively (77 K) with well-resolved <sup>51</sup>V ( $I = 7/2$ ) hyperfine lines. Spectral parameters of the complexes are listed in Table 3 and representative spectra are displayed in Fig. 2. The characteristic  $g_{\parallel} < g_{\perp}$  and  $A_{\parallel} \gg A_{\perp}$  relation-

ships corresponding to an axially compressed  $d_{xy}^1$  configuration are present.<sup>21–23</sup> The hyperfine constants in the [VO(L)(bpy)] complexes incorporating VO<sub>4</sub>N<sub>2</sub> coordination are significantly lower than those in [VO(L)(OMe)(OHMe)]<sup>-</sup> involving VO<sub>5</sub>N coordination. This is attributed

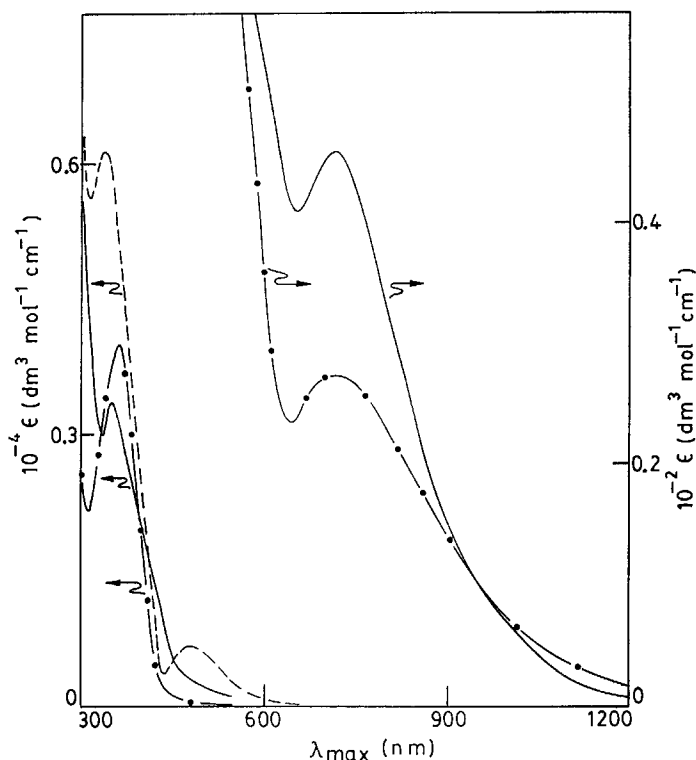


Fig. 1. Electronic spectra of  $[\text{VO}(\text{L}^1)(\text{bpy})]$  (—),  $[\text{VO}(\text{L}^3)(\text{OMe})(\text{OHMe})]$  (---) and  $[\text{VO}(\text{L}^3)(\text{OMe})(\text{OHMe})]^-$  (—●—●—) in dichloromethane, methanol and methanol respectively at 298 K.

Table 3. EPR data at 77 K

Compound	$g_{\parallel}(A_{\parallel}/G)$	$g_{\perp}(A_{\perp}/G)$	$g_{\text{av}}(A_{\text{av}}^d/G)$
$[\text{VO}(\text{L}^1)(\text{bpy})]^a$	1.951 (177.2)	1.985 (60.7)	1.974 (99.5)
$[\text{VO}(\text{L}^2)(\text{bpy})]^a$	1.952 (177.6)	1.985 (61.7)	1.974 (100.3)
$[\text{VO}(\text{L}^3)(\text{bpy})]^a$	1.954 (177.9)	1.985 (61.4)	1.975 (100.2)
$[\text{VO}(\text{L}^4)(\text{bpy})]^a$	1.953 (177.8)	1.985 (61.4)	1.975 (100.2)
$[\text{VO}(\text{L}^3)(\text{OMe})(\text{OHMe})]^{-b}$	1.947 (188.6)	1.988 (68.6)	1.974 (108.3)
$[\text{VO}(\text{L}^4)(\text{OMe})(\text{OHMe})]^{-b}$	1.947 (188.1)	1.989 (68.6)	1.975 (108.1)

<sup>a</sup> In dichloromethane.

<sup>b</sup> In 1 : 1 methanol–toluene.

<sup>c</sup>  $g_{\text{av}} = 1/3[2g_{\perp} + g_{\parallel}]$ .

<sup>d</sup>  $A_{\text{av}} = 1/3[2A_{\perp} + A_{\parallel}]$ .

to the difference in nucleophilicity of the coordinating atoms: nitrogen(bpy) > oxygen(OMe<sup>-</sup>, OHMe).<sup>1-3,21,24</sup>

#### Redox behaviour

All the complexes are found to display a quasi-reversible cyclic voltammetric response in solution due to the  $\text{VO}^{3+}-\text{VO}^{2+}$  couple. The redox potentials are listed in Table 2 and representative voltammograms are shown in Fig. 3. The  $E_{1/2}$  values of the  $[\text{VO}(\text{L})(\text{OMe})(\text{OHMe})]$  species are found to

be lower by 700–800 mV than the corresponding  $[\text{VO}(\text{L})(\text{bpy})]$  species. This is qualitatively consistent with charge types of ligands: monoanionic (OMe)(OHMe)<sup>-</sup> vs neutral bpy.

The yellow coloured electrogenerated  $[\text{VO}(\text{L})(\text{OMe})(\text{OHMe})]^-$  species have the same voltammogram (initial scan anodic) as the parent  $[\text{VO}(\text{L})(\text{OMe})(\text{OHMe})]$  solution (initial scan cathodic). The parent complex is quantitatively regenerated upon coulometric oxidation of  $[\text{VO}(\text{L})(\text{OMe})(\text{OHMe})]^-$ . The same happens when  $[\text{VO}(\text{L})(\text{OMe})(\text{OHMe})]^-$  is left in air or oxygen and this

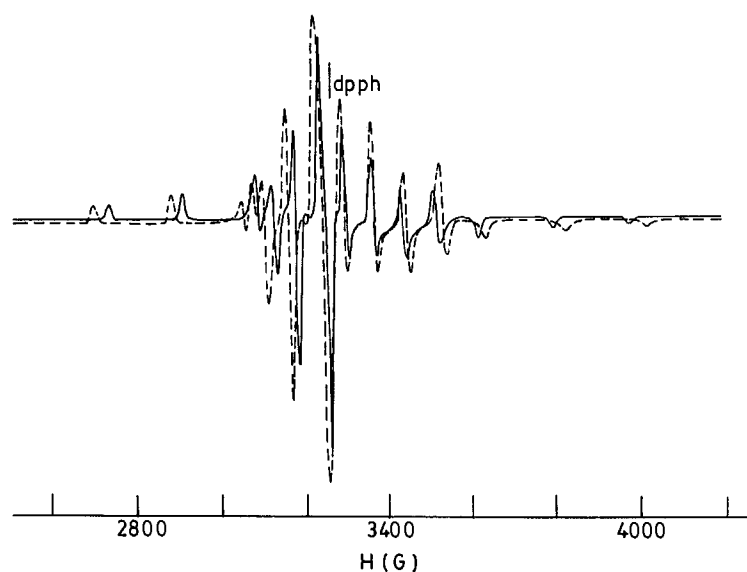


Fig. 2. X-band EPR spectra of [VO(L<sup>4</sup>)(bpy)] (—) in dichloromethane glass (77 K) and [VO(L<sup>3</sup>)(OMe)(OHMe)]<sup>-</sup> in 1:1 methanol-toluene glass at 77 K.

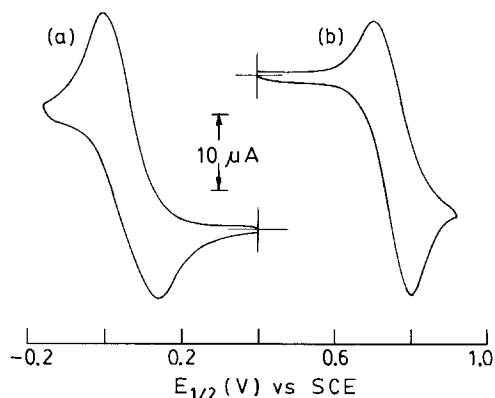


Fig. 3. Cyclic voltammograms (platinum electrode, 298 K) of (a) [VO(L<sup>3</sup>)(OMe)(OHMe)] in methanol and (b) [VO(L<sup>4</sup>)(bpy)] in dichloromethane (10<sup>-3</sup> mol dm<sup>-3</sup>, 0.1 mol dm<sup>-3</sup> [NEt<sub>4</sub>][ClO<sub>4</sub>]).

explains the formation of [V<sup>V</sup>O(L)(OMe)(OHMe)] from [V<sup>IV</sup>O(L)(H<sub>2</sub>O)] and methanol in air. Attempted bulk generation of [V<sup>V</sup>O(L)(bpy)]<sup>+</sup> in solution via coulometry has not been successful due to inherent instability of the oxidized complex.

### CONCLUSIONS

In air the VO<sup>3+</sup> ion is stabilized in complexes of type [VO(L)(OMe)(OHMe)]. On the other hand bpy coordination stabilizes the VO<sup>2+</sup> moiety as in [VO(L)(bpy)]. The stability difference is reflected in the large difference (700–800 mV) between the VO<sup>3+</sup>–VO<sup>2+</sup> E<sub>1/2</sub> values of the two groups. In the EPR spectra of [VO(L)(bpy)] and electrogenerated

[VO(L)(OMe)(OHMe)]<sup>-</sup> the metal hyperfine coupling constant is significantly lower in the former due to nucleophilicity difference of bpy nitrogen and methanolic oxygen.

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