Pergamon

PII: S0277-5387(96)00173-8

Polyhedron Vol. 16, No. 7, pp. 1247–1253, 1997

0277-5387/97 $17.00+0.00

Synthesis and characterization of oxovanadium(IV) and dichlorovanadium(IV) complexes of biologically active 4-aminoantipyrine derivatives

Ali El-Dissouky,* Aziza K. Shehata and Ghada El-Mahdey

Chemistry Department, Faculties of Science and Education, Alexandria University, Alexandria, Egypt

(Received 18 September 1995; accepted 4 April 1996)

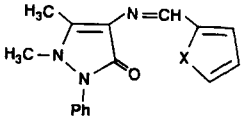
Abstract—A new series of oxovanadyl complexes of the Schiff base ligands 4-(2-pyrrolyl methylideneamino)antipyrine (PyAAP), 4-(2-thienylmethylideneamino)antipyrine (TAAP), 4-furfurylideneaminoantipyrine (FAAP) and 4-(2-hydroxybenzylideneamino)antipyrine (SAAP), have been synthesized and characterized by different physical techniques. The spectral and magnetic data indicate a distorted square pyramidal structure for all complexes. The selective deoxygenation of the oxovanadyl complexes $[(PyAAP\text{-}H)_2(VO)_2SO_4]$ and $[(SAAP\text{-}H)_2VO]$, which gave a good yield of the corresponding dichloro compounds $[L_2VCl_2]$, L = PyAAP-H or SAAP-H, is made by using different deoxygenating agents in different solvents and at various temperatures. The purity and the percentage yield of the products are found to be solvent, temperature and deoxygenating agent dependent. Spectral and magnetic studies are used to elucidate the structure of the dichloro derivatives. The solvent effects upon the electronic spectra of the oxovanadyl complexes and the corresponding dichloro derivatives are ascertained. Copyright © 1997 Elsevier Science Ltd

Keywords: antipyrine; vanadium(IV); spectra; synthesis; magnetism; chlorination.

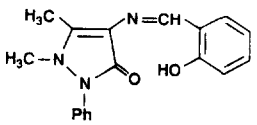
It is becoming increasingly apparent that the chemistry of vanadium is of great importance to a wide variety of biological and industrial systems. Recently, it was found that there is a series of nitrogenase metalloenzymes which have vanadium at the active site [1–8]. In these enzymes vanadium appears to shuttle between V^{2+} and V^{4+} and is possibly bound to an iron–sulfur cluster, as it is difficult for direct linking of iron–sulfur clusters [9] and V^{4+}. Furthermore, the role of vanadium in the biosphere is very important. It has been found that mammals require vanadium at the nano- to pico- molar level, and several lower organisms have a vanadium requirement at a much higher level [3,10].

Vanadium is also important in the fuel industry [9–11]. Vanadium occurs naturally and can be in high concentrations in heavier crude oil. It affects the industry because its necessary removal poisons the heterogeneous catalysis used in processing [12–14]. The intermediate species in the transformation of the naturally occurring VO^{2+} complexes to vanadium sulfide on the upgrading catalyst surface are not well characterized. Some evidence suggests that VO^{2+} is deoxygenated to V(IV) [13,15]. Vanadium compounds have also been used to generate slurry-type catalysts to upgrade heavy oils and assist in coal liquefaction. Clearly the activation of the V=O bond is a critical part in the fuel industry.

Due to the importance of vanadium compounds, we aimed to prepare and characterize some biologically active vanadyl complexes of antipyrine derivatives (I) followed by the deoxygenation of the isolated complexes to form dichloro derivatives.



X = NH, PYAAP
S, TAAP
O, FAAP



SAAP

* Author to whom correspondence should be addressed.

EXPERIMENTAL

Synthesis of the organic ligands

The organic ligands were prepared according to the following method: a solution of the corresponding aldehyde (1.0 or 1.1 g, 0.01 mol of furan-2-aldehyde or thiophene-2-aldehyde, respectively) in EtOH (20 cm^3) was added to a solution of 4-aminoantipyrine (2.1 g, 0.01 mol) in 50 cm^3 of the same solvent. The reaction mixture was refluxed on a water bath for 1–2 h. Upon cooling to room temperature the solid formed in each case was isolated by filtration and recrystallized from EtOH and dried *in vacuo* over P_4O_{10}.

Synthesis of oxovanadyl complexes

All vanadyl complexes of the 4-aminoantipyrine Schiff bases were prepared by the general method; namely, the salt $VOSO_4 \cdot 2H_2O$ (2.0 g, 0.01 mol) was dissolved in water (15 cm^3) and the solution was added to a warm, stirred solution of the corresponding organic compound (6.2, 6.5, 6.3 or 6.8 g; 0.022 mol of PyAAP, TAAP, FAAP or SAAP, respectively) in ethanol (50 cm^3). An aqueous solution (15–20 cm^3) of NaOAc (0.3 M solution) was added and the suspension was stirred for 2 h. The corresponding crystalline product was filtered off, washed with water, EtOH, diethyl ether and dried *in vacuo* over P_4O_{10}.

Synthesis of dichlorovanadium complexes, $[(PyAAP\text{-}H)_2VCl_2]$ *and* $[(SAAP\text{-}H)_2VCl_2]$

The synthesis was carried out under dry, purified dinitrogen gas. Different deoxygenating agents such as $SOCl_2$, PCl_5 or CH_3COCl and different solvents were used. The following procedure was applied, $[(PyAAP\text{-}H)_2(VO)_2SO_4]$ (2.0 g, 0.025 mol) or $[(SAAP\text{-}H)_2VO]$, (1.8 g, 0.0025 mol) was dissolved in 50 cm^3 of the appropriate solvent (toluene, CH_2Cl_2, bezene or dioxene). In all cases a dark green or dark brown solution was obtained. The solution was degassed and the deoxygenating agent (1.0, 1.8 or 0.6 g of $SOCl_2$, PCl_5 or CH_3COCl, respectively; 0.80 mol) was added while stirring at room temperature. In some cases a boiling condition was utilized. The reaction mixture was stirred at room temperature overnight and then layered with the appropriate solvent and placed in a freezer. The crystalline product in each case was filtered off and dried. Recrystallization from CH_2Cl_2 or $C_2H_4Cl_2$/hexane mixture lead to pure materials as determined from their physical measurements.

Elemental analysis

Carbon, hydrogen and nitrogen contents in each sample were estimated at the Microanalysis Unit, Cairo University. Vanadium content was determined by igniting a suitable accurate weight in silica crucible to a constant weight. The product was VO_2, in which the vanadium content was determined. Chlorine and sulfur contents were determined argentometrically and gravimetrically, respectively [16].

Physical measurements

Molecular weight for each sample was determined by the method of depression of freezing point. The other physical measurements and the elemental analyses were carried out as previously reported [16].

RESULTS AND DISCUSSION

The oxovanadyl complexes were found to be air stable, soluble in most common organic solvents, but insoluble in water. The formulation of the complexes was based on the elemental analysis, molecular weight determination and the molar conductivity values (Table 1).

The selective deoxygenation of the two complexes $[(PyAAP\text{-}H)_2(VO)_2SO_4]$ and $[(SAAP\text{-}H)_2VO]$ which gave pure and high percentage yields of the corresponding dichloro complex $[(L_2VCl_2]$, L = PyAAP-H or SAAP-H, was made by using $SOCl_2$, PCl_5 and CH_3COCl. It was found that both oxo-complexes react to a different extent with the three different deoxygenating agents. Furthermore, the purity of the reaction product and percentage yield were found to be solvent and temperature dependent (Table 2).

Under refluxing conditions, $SOCl_2$ reacts with the oxo-vanadyl complexes in dry benzene producing a pure and good yield of $[L_2VCl_2]$. This reaction may proceed according to eq. (1).

$$[L_2VO] + SOCl_2 \xrightarrow{\text{dry benzene}} [L_2VCl \cdot SO_2Cl] \rightarrow [L_2VCl_2] + SO_2 \quad (1)$$

In 1,4-dioxan, PCl_5 gives the best dichloro complexes at room temperature according to eq. (2).

$$2PCl_5 \rightleftharpoons PCl_4 \cdot PCl_6 + [L_2VO] \xrightarrow{\text{1,4 dioxan}} [LVCl \cdot ClPOCl_3] \rightarrow [LVCl_2] + POCl_3 \quad (2)$$

Acetyl chloride was found to be the best deoxygenating agent in toluene at room temperature, since it leads to the formation, in high yield, of dichloro derivatives. The reaction mechanism may proceed by electrophilic attack of the CH_3COCl on vanadyl oxygen, as shown in eq. (3).

$$[L_2VO] + 3CH_3COCl \xrightarrow{\text{toluene}} [L_2VCl_2] + (CH_3COO)_2O + CH_3{-}C_6H_4{-}COCH_3 \quad (3)$$

In all cases, 50% of the deoxygenating agent has been employed to minimize the extent of hydrolysis of $SOCl_2$, PCl_5 or CH_3COCl. This is in addition to the use of dry solvents. The above reactions would suggest

Table 1. Analytical data for the vanadyl complexes and some physical properties

Compound[a]	Colour	Λ_M^b	μ_{eff}^c	M.W. Found (Calc.)	% Found (% Calc.) C	H	N	V	X
$[L_2^1(VO)_2SO_4]$	pale green	1.30	1.61	796 (788)	48.5 (48.7)	4.0 (3.8)	14.0 (14.2)	13.1 (12.9)	4.3 (4.1)
$[L_2^1VCl_2]$	blue green	2.90	1.76	680 (680)	56.6 (56.5)	4.6 (4.4)	16.5 (16.5)	7.8 (7.5)	16.6 (10.4)
$[L_2^2VO]SO_4$	yellowish green	96.40	1.76	760 (757)	50.4 (50.7)	3.9 (4.0)	11.1 (11.1)	6.8 (6.7)	12.5 (12.7)
$[L_2^3VO]SO_4$	pale yellow	87.55	1.78	720 (725)	52.7 (53.0)	3.9 (4.1)	11.6 (11.6)	7.3 (7.0)	4.5 (4.4)
$[L_2^4VO]$	green	1.90	1.73	681 (679)	63.4 (63.6)	4.7 (4.7)	12.4 (12.4)	7.8 (7.5)	
$[L_2^4VCl_2]$	blue	2.05	1.75	736 (734)	58.8 (58.9)	4.5 (4.4)	11.3 (11.4)	7.2 (6.9)	10.0 (9.7)

[a] L^1 = PyAAP-H, L^2 = SAAP-H, L^3 = TAAP, L^4 = FAAP.
[b] Molar conductivity values of 10^{-3} M solutions at 25 ± 1 °C.
[c] Effective magnetic moment (B.M.) at room temperature.

Table 2. Products from the reaction of vanadyl complexes with the different deoxygenating agents as shown from the spectroscopic studies

Starting complex	Deoxygenating agent	Solvent	Temperature	Purified yield%[a] (1)	(2)
	$SOCl_2$	CH_2Cl_2	R.T.	28	22
		toluene	boiling	31	38
		benzene	boiling	38	36
		1,4-dioxane	R.T.	30	28
$[L_2^1(VO)_2SO_4]$	PCl_5	toluene	boiling	25	34
or		CH_2Cl_2	R.T.	34	40
$[L_2^4VO]$		1,4-dioxane	R.T.	36	42
	CH_3COCl	1,4-dioxane	R.T.	41	48
		CH_2Cl_2	R.T.	48	48
		benzene	boiling	52	46
		toluene	R.T.	63	70
		toluene	boiling	56	49

[a] (1) L^1 = PyAAP-H. (2) L^4 = SAAP-H.

the formation of a *cis* isomer as previously reported [17]. It was found that *cis/trans* isomerization is rapid, allowing for the formulation of the observed *trans* isomer [17]. Table 2 summarizes the products from the reaction of the vanadyl complexes with the different deoxygenating agents, as shown from the spectroscopic studies.

Vibrational spectra

Table 3 lists the most important and characteristic bands of the IR spectra of oxovanadyl and the dichloro derivatives. The absence of bands at 968 and 986 cm^{-1} characteristic of V=O in $[(PyAAP\text{-}H)_2(VO)_2SO_4]$ and $[(SAAP\text{-}H)_2VO]$, respectively, indicates the conversion to the dichloro complexes. This observation is taken as a good parameter for the completeness of the deoxygenation process. The low value of $\nu(V{=}O)$ for $[(PyAAP\text{-}H)_2(VO)_2SO_4]$ may be taken as evidence for the polymeric nature of this complex as shown from its IR spectrum. Its deoxygenation may proceed according to eq. (4)

$$[(PyAAP\text{-}H)_2(VO)_2SO_4) \rightleftharpoons [(PyAAP\text{-}H)_2VO] + VOSO_4$$

$$[(PyAAP\text{-}H)_2VO] + \begin{matrix}SOCl\\ \text{or } PCl_5\\ \text{or } Ch_3COCl\end{matrix} \rightarrow [(PyAAP\text{-}H)_2VCl_2] + \begin{matrix}SO_2\\ \text{or } POCl_3\\ \text{or } (CH_3CO_2)O\end{matrix} \quad (4)$$

Table 3. Infrared spectral data (ν cm^{-1}) for the vanadyl complexes

Compound[a]	ν(C=O)	ν(C=N)	ν(V=O)	ν(V—N)	ν(V=O)	ν(V—Cl)
HL^1	1659s	1600				
L^2	1942	1596				
L^3	1637	1603				
HL^4	1650	1592				
$[L^1_2(VO)_2SO_4]$	1639s	1589m	968vs	463m	360	
				334m		
$[L^1_2VCl_2]$	1660s	1579m	—	458m	—	364
				436m		
		1572m				
$[L^4_2VO]$	1649s		986s	448m	338m	
		1566s				
$[L^4_2VCl_2]$	1652s	1570m	—	432m	342	356
		1575s				
$[L^3_2VO]SO_4$	1621m		976s	449m	346m	
		1560s				
		1590m				
$[L^2_2VO]SO_4$	1616m		988s	468m	356m	
		1582s				

[a] L^1 = PyAAP-H, L^2 = FAAP, L^3 = TAAP, L^4 = SAAP-H.

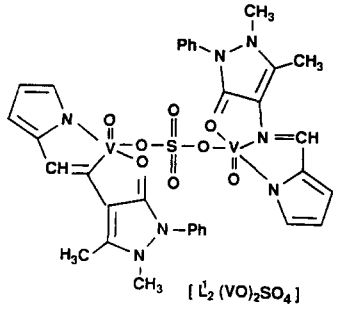
The ν(C=O) mode in the parent Schiff base, except SAAP, shifts to lower wavenumbers by *ca* 20 cm^{-1} in the case of their oxovanadyl complexes, indicating the bond of the amide oxygen to vanadium, but not in the case of complex [(SAAP-H)$_2$VO]. The band in the range 1613–1590 cm^{-1} in the free organic compounds due to ν(C=N) is shifted to 1590–1572 cm^{-1} upon complexation. This observation suggests that the C=N bond is weakened due to coordination of the azomethine-N to vanadium. The splitting of this band in the investigated complexes, except [(PyAAP-H)$_2$(VO)$_2$SO$_4$], suggests that the two azomethine groups are distorted below and above the horizontal plane. The broad band at 3434 cm^{-1} with a band width of 1660 cm^{-1} in the spectrum of SAAP, is assigned to hydrogen bonded OH. Furthermore, the existence of a broad weak band at 1915 cm^{-1} can be taken as evidence for the presence of intramolecular hydrogen bonding of the type O—H···N. This was also supported by the appearance of the ν(C—O) phenolic band at 1267 cm^{-1}. Upon complexation, the bands at 3434 and 1915 cm^{-1} disappeared and that at 1267 cm^{-1} was shifted to 1305 cm^{-1}, indicating the bonding of the ionized phenolic oxygen to vanadium.

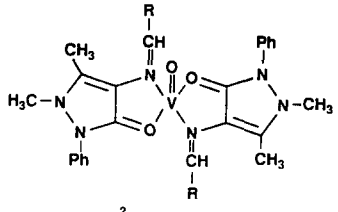
The spectrum of (PyAAP) shows a broad band at 2964–3156 cm^{-1} due to the different vibrational modes of –NH– of the pyrrole ring, and is absent in [(PyAAP-H)$_2$(VO)$_2$SO$_4$] indicating its deprotonation upon complexation. The spectra of FAAP and SAAP display bands at 1505 and 1332 cm^{-1} due to C—O—C and C—S—C, respectively. These bands were found to be largely unaffected upon complexation, indicating the non-bonding nature of the oxygen and sulphur in the heterocyclic rings.

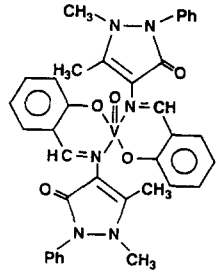
The far-IR spectra for all complexes except [(PyAAP-H)$_2$VCl$_2$] display a band at 338–360 cm^{-1} due to ν(V—O). The spectrum of [(PyAAP-H)$_2$VCl$_2$] exhibits a band at 1660 cm^{-1} due to ν(C=O) indicating that the amide oxygen is not bonded to vanadium. The band in the range 468–432 cm^{-1} is assigned to ν(V—N) of the azomethine group. In addition, the spectra of [(PyAAP-H)$_2$(VO)$_2$SO$_4$] and [(PyAAP-H)$_2$VCl$_2$] exhibit another band at 443 and 436 cm^{-1} assignable to ν(V—N)$_{pyrrole}$. The dichloro complexes exhibit bands at 303 and 309 cm^{-1} due to ν(V—Cl) in [(PyAAP-H)$_2$VCl$_2$] and [(SAAP-H)$_2$VCl$_2$], respectively.

The diagnostic IR band frequencies of the sulphate anions indicate its ionic nature in [(FAAP)$_2$VO]SO$_4$ and [(TAAP)$_2$VO]SO$_4$ and act as a bridging group in the case of [(PyAAP-H)$_2$(VO)$_2$SO$_4$] [18].

It appears, therefore, that PyAAP behaves as a monobasic tridentate ligand in [(PyAAP-H)$_2$(VO)$_2$SO$_4$] and as a monobasic bidentate ligand in [(PyAAP-H)$_2$VCl$_2$]. In the first complex the vanadyl group is coordinated to PyAAP *via* ketoamide oxygen, azomethine and pyrrole nitrogen atoms. In the second it is coordinated via the azomethine and pyrrole nitrogen atoms. The previously mentioned IR data indicate the bidentate nature of SAAP, through the azomethine nitrogen and the phenolate oxygen atoms. The other and ligands (FAAP and TAAP) appear to be neutral bidentate ligands coordinated to VO *via* the azomethine-N and ketoamide oxygen atoms. Accordingly, the following structures could be assumed.







One can observe that the ν(C=N) for the dichloro complexes appears at a lower wavenumber than that for the starting oxovanadyl complexes. This is consistent with the observations reported for *trans*-dihalo complexes of V(IV) [19–21], and can be rationalized by considering the metal complex symmetry and the nature of the ligands. ESR studies of several V(IV) dihalide complexes [22] revealed that on going from the vanadyl structure (where the metal is somewhat out of the plane of the equatorial ligands) to the *trans* structure (where the metal is in the plane of the ligands) stabilizes both the σ-bonding d_{xy} orbital, slightly, and the π-bonding $d_{x^2-y^2}$ orbital, greatly, due to increased orbital overlap. This, in turn, increases delocalization and effectively reduces the charge on the ligand. This results in a decrease in frequency of the diagnostic ligand bands. Contrary to the *trans* structure, the orbital overlap of the *cis* structure is reduced, because the deviation from the ligand plane is increased. This localizes the charge on the ligand, and results in increasing the frequencies of the diagnostic ligand bands. Furthermore, the geometry of $VCl_2(t\text{-}C_4H_9COCHCO)\text{-}t\text{-}C_4H_9)_2$ is determined by examining the V—Cl bands in the far IR [23]. The reported assignment of 362 cm^{-1} for the *trans* geometry matches ours of 364 and 356 cm^{-1} for $[(PyAAP\text{-}H)_2VCl_2]$ and $[(SAAP\text{-}H)_2VCl_2]$, respectively. The previously mentioned evidence indicates that $[(PyAAP\text{-}H)_2VCl_2]$ and $[(SAAP)_2VCl_2]$ also have a *trans* geometry.

Magnetic and electronic spectral data

The positive spin–orbit coupling [24] (λ) for oxovanadium(IV) complexes exhibits a room temperature magnetic moment very close to the spin only value (1.73 B.M.) [25]. The complexes under investigation, except $[(PyAAP\text{-}H)_2(VO)_2SO_4]$, also exhibit room temperature magnetic moments in the range 1.73–1.78 B.M. corresponding to one unpaired spin. The value for $[(PyAAP\text{-}H)_2(VO)_2SO_4]$ of 1.61 B.M. indicates the possibility of a magnetic exchange interaction between the vanadyl centres through the bridging sulphate group, or possibly some V(V) impurity.

The electronic spectral data of the oxovanadium complexes and the dichloro derivatives, either as solid or solution, are summarized in Table 4. No bands are found at lower energies, and splitting of the low energy band is found, as in the case of $[VO(N\text{-}CH_3)_3]Cl_2$ [26]. The large extinction coefficients for $[(SAAP\text{-}H)_2VO]$, $[(FAAP)_2VO]SO_4$ and $[(TAAP)_2VO]SO_4$ compared with $[(PyAAP\text{-}H)_2(VO)_2SO_4]$ may arise from a greater metal–ligand bond covalency and/or a larger distortion from the C_{2v} symmetry assumed for this type of complex. The bands with smaller molar extinction coefficients can be assigned to *d–d* transitions. The spectrum of $[(PyAAP\text{-}H)_2(VO)_2SO_4]$ exhibits two intense *d–d* transition at about 15,800 and 12,820 cm^{-1}, and a third one of lower intensity at 21,300 cm^{-1}, all of which are on the tail of a charge transfer band. In $CHCl_3$, three well-defined bands are observed, with no great change in position, indicating that no geometrical change in $CHCl_3$ took place. The increase in the intensities of these bands may be attributed to the disproportionation of the polymeric complex $[(PyAAP\text{-}H)_2(VO)_2SO_4]$ [eq. (5)], followed by the interaction of the solvent molecules, organized around $[(PyAAP\text{-}H)_2VO]$, with the dipole of the complex.

$$[(PyAAP\text{-}H)_2(VO)_2SO_4] \rightleftharpoons [(PyAAP\text{-}H)_2VO] + VOSO_4 \quad (5)$$

In the excited Frank–Condon state, the solvent molecules do not have enough time to rearrange in response to the dipole in the excited complex $[(PyAAP\text{-}H)_2VO]$. There is a possible hydrogen bonding formation between the oxovanadyl group and the active hydrogen in $CHCl_3$. This is confirmed from the red shift of the charge transfer band as given in Table 4. The effects of $CHCl_3$ on the band positions in the case of the other oxovanadium complexes (Table 4) are similar to those for $[(PyAAP\text{-}H)_2(VO)_2SO_4]$. The spectral features are consistent with those reported for square pyramidal oxovanadium complexes [27–29].

The spectral bands of all complexes in DMSO exhibit a drastic change in the positions and intensities of the *d–d* transitions as well as the charge transfer bands,

Table 4. Electronic spectral data for the vanadyl(IV) complexes

Compound[a]	Medium	ν(cm^{-1})(ε mol^{-1} l cm^{-1})			
		d–d transitions			C.T.
$[L^1_2(VO)_2SO_4]$	Nujol mull	21,300	15,800	12,800	29,400
	$CHCl_3$	21,500(32)	15,600(52)	12,700(54)	27,900(8200)
	DMSO		17,300(19)	14,200(10)	28,900(10300)
$[L^4_2VO]$	Nujol mull	21,600	16,500		28,400
	$CHCl_3$	20,800(44)	16,300(68)	13,200	27,300(7480)
	DMSO		17,200(18)	12,800(52)	
				13,900(11)	
$[L^3_2VO]SO_4$	Nujol mull	22,400	16,300		27,900
	$CHCl_3$	23,100(26)	16,000(68)	13,300	27,300(7620)
	DMSO		17,000(21)	13,200(36)	36,900(9700)
				14,000(12)	
$[L^2_2VO]SO_4$	Nujol mull	22,300	16,300		28,000
	$CHCl_3$	22,500(40)	16,100(98)	13,200	28,400(8050)
	DMSO		16,900(28)	12,900(60)	27,500(12300)
				13,800(16)	
$[L^1VCl_2]$	Nujol mull		16,400		27,000
	EtOH		16,200(16)	13,200	26,400(4760)
				13,000(45)	
$[L^4VCl_2]$	Nujol mull		17,000		27,100
	EtOH		17,100(19)	13,400	27,000(7000)
				13,100(42)	

[a] L^1 = PyAAP-H, L^2 = FAAP, L^3 = TAAP, L^4 = SAAP-H.

indicating solvent coordination to the sixth coordination site of the oxovanadyl complexes. These spectral features are consistent with those reported for similar compounds [27,28].

The energy level and MO calculations on square pyramidal oxovanadium complexes [28–31] revealed that the vanadium 3*d* orbital populations are $d_{x^2-y^2}$ (b_2) < d_{xz}, d_{yz} (e^*_π) < d_{z^2}(b^*_1) < d_{xy} (a^*_1). This ordering is consistent with the assignment of the $b_2(d_{xy}, d_{xz}) \rightarrow b_1(d_{z^2})$ transition for the lowest energy band (12,660–13,300 cm^{-1}). The band at 15,600–16,350 cm^{-1} is due to the $b_2 \rightarrow e^*_\pi$ transition, while that at 20,600–22,500 cm^{-1} is assigned to the $b_2 \rightarrow a^*_1$ transition. In DMSO, three *d–d* transitions in the range of 13,800–14,200, 16,800–17,480 and 22,030–24,000 cm^{-1} are assigned to $b_2 \rightarrow b^*_1$, $b_2 \rightarrow e^*_\pi$ and $b_2 \rightarrow a_1$ transitions, respectively, characteristic for a distorted octahedral oxovanadium complex [30,31]. On the basis of the data available, it appears that these complexes have a tetragonally distorted structure. The transition due to $b_2 \rightarrow b_1$ (16,800–17,480 cm^{-1}) is taken as 10 Dq. Therefore the ligands could be ordered according to their strengths as: SAAP > PyAAP > FAAP > TAAP. This ordering may be attributed to the effect of the moiety bonded to the azomethine group [C_4H_4O (FAAP); C_4H_5N (PyAAP); C_6H_4O (SAAP); C_4H_4S (TAAP)].

The spectra of $[(PyAAP\text{-}H)_2VCl_2]$ and $[(SAAP\text{-}H)_2VCl_2]$ as Nujol mulls and as $CH_2Cl_2/SOCl_2$ (19 : 1 V/V) solutions are identical and similar to those reported for various dichlorovanadium(IV) complexes in an octrahedral ligand field [32]. The Nujol mull spectra exhibit only two *d–d* transitional bands at 13,200, 13,400 and 16,100, 16,350 cm^{-1} for $[(PyAAP\text{-}H)_2VCl_2]$ and $[(SAAP\text{-}H)_2VCl_2]$, respectively. The third band may be buried under the intense absorption originating at 20,000 cm^{-1}. The two bands could be assigned to $b_2 \rightarrow b^*_1$ and $b_2 \rightarrow e^*_\pi$ transitions, respectively.

REFERENCES

1. R. L. Robson, R. R. Eady, T. H. Richardson, R. W. Miller, M. Hawkins and J. R. Postgate, *Nature* 1986, **322,** 388.
2. J. M. Arber, B. R. Dobson, R. R. Eady, P. Stephens, S. S. Hasanin, C. D. Garner and B. E. Smith, *Nature* 1987, **325,** 372.
3. C. N. Dennis (Ed.), *Vanadium in Biological Systems*, Kluwer Academic Publishers, Dordrecht, The Netherlands (1990).
4. A. Butler and C. J. Carrano, *Coord. Chem. Rev.* 1991, **61,** 109.
5. D. Rehdre, *Angew. Chem., Int. Ed. Engl.* 1991, **30,** 148.
6. J. Dai, S. Akiyama, M. Munakata and M. Mikuriya, *Polyhedron* 1994, **13,** 2495.
7. E. Alberico, G. Micera, D. Sanna and A. Dessi, *Polyhedron* 1994, **13,** 1763.
8. N. Azuma and T. Ozawa, *Inorg. Chim. Acta* 1994, **71,** 227.
9. E. L. Jones, J. G. Reynolds, J. C. Huffman and G. Christou, *Polyhedron* 1991, **10,** 1817.

10. C. A. Root, J. D. Hoeschele, C. R. Cornman, J. W. Kampf and V. L. Pecorare, *Inorg. Chem.* 1993, **32,** 3855.
11. H. S. Soedjak and A. Butler, *Biochemistry* 1990, **29,** 7974.
12. J. F. Branthaver, *ACS Symp. Ser.* 1987, **344,** 188.
13. J. G. Speight, *The Chemistry and Technology of Petroleum Chemical Industries*, Vol. 3, Marcel Dekker, New York (1983).
14. P. W. Tamm, H. F. Harnsberger and A. G. Bridge, *Ind. Eng. Chem. Proc. Res. Dev.* 1981, **20,** 262.
15. P. C. H. Mitchell and J. A. Valers, *Inorg. Chim. Acta* 1983, **71,** 179; *React. Kinet. Catal. Lett.* 1982, **20,** 219.
16. A. El-Dissouky and G. B. Mohammad, *Inorg. Chim. Acta* 1989, **162,** 263.
17. J. G. Reynolds, E. L. Jones, J. C. Huffmann and G. Christou, *Polyhedron* 1993, **12,** 407.
18. K. Nakamoto, *Infrared Spectra of Inorganic Coordination Compounds*, p. 156, John Wiley, New York (1963).
19. T. W. Hambley, C. J. Hawkins and T. A. Kabanos, *Inorg. Chem.* 1987, **26,** 3740.
20. K. Bahzadi and A. J. Thompson, *J. Less Comm. Met.* 1987, **128,** 281.
21. C. J. Hawkins and T. A. Kabanos, *Inorg. Chem.* 1989, **28,** 1084.
22. A. Jezierski and J. B. Raynor, *J. Chem. Soc., Dalton Trans.* 1981, 1.
23. R. B. Von Dreele and R. C. Fay, *J. Am. Chem. Soc.* 1972, **94,** 7935.
24. A. Syamal, *Coord. Chem. Rev.* 1975, **16,** 309.
25. B. N. Figgis, *Introduction to Ligand Fields*, p. 226. Wiley, New York (1966).
26. J. E. Drake, J. Vekris and J. S. Wood, *J. Chem. Soc. (A)* 1968, 1000.
27. S. H. Cheng, S. R. Sheen, C. P. Cheng and C. T. Chang, *Inorg. Chim. Acta* 1990, **21,** 171.
28. H. J. Stoklosa, J. R. Wasson and B. J. McCormick, *Inorg. Chem.* 1974, **13,** 592.
29. C. J. Ballhausen and H. B. Gray, *Inorg. Chem.* 1962, **1,** 111.
30. J. Selbin, *Chem. Rev.* 1965, **65,** 153; *Coord. Chem. Rev.* 1966, **1,** 293. J. Selbin and L. Morpurgo, *J. Inorg. Nucl. Chem.* 1965, **27,** 673.
31. R. Hoffmann, *J. Chem. Phys.* 1962, **39,** 1397.
32. W. E. Farrar, *Am. J. Med.* 1963, **34,** 134.