

are usually found, while the band at  $1640\text{ cm}^{-1}$  is in the OH asymmetric deformation region. However, the fact that the bands at  $3400\text{--}3600$  and  $1640\text{ cm}^{-1}$  are not affected by deuteration indicates that the bands are not due to lattice water. Furthermore, it is possible to remove the lattice water by heating; the spectra of the dehydrated complexes still contain the bands at  $3400\text{--}3600$  and  $1640\text{ cm}^{-1}$  proving that they do not arise from lattice water vibrations.

The bands could possibly be due to  $\text{NH}_2$  stretching and deformation modes even though  $\text{NH}_2$  bands are normally found at lower frequencies than these. However, the deuterium-exchange experiments throw considerable doubt on this possibility.

An alternative hypothesis is that the bands arise

from  $\text{CH}_2$  vibrations. The bands are much higher in frequency than would be expected for normal  $\text{CH}_2$  groups, which necessitates that the methylene groups be in a very unusual environment. If the bands arise from vibrations of the methylene in the glycine residue, then, as a result of the bulkiness of the ester group, the complex might exist in a conformation in the crystal lattice whereby the methylene hydrogens are forced into a very crowded environment about the metal. Such a condition might increase the stretching and deformation frequencies significantly.

**Acknowledgment.**—Partial support of these investigations by the National Science Foundation is gratefully acknowledged.

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## Normal and Mixed-Ligand Chelates of Vanadyl(IV) with Schiff Bases

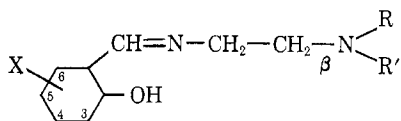
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Received September 27, 1965

Vanadyl(IV) chloride reacts with ring-substituted salicylaldehydes and N-substituted ethylenediamines to form two series of compounds, normal or mixed-ligand chelates, according to the nature of substituents at the nitrogen ethylenediamine atom. Visible spectra suggest a five-coordinate structure for normal complexes, resulting from coordination of two Schiff bases acting bidentately around a vanadyl unit, and a hexacoordinate structure for mixed-ligand complexes, resulting from coordination of a salicylaldehyde group and a Schiff base acting tridentately around a vanadyl unit.

### Introduction

Previous papers from this laboratory have dealt with the complexing ability of Schiff bases of the general formula



formed from ring-substituted salicylaldehydes and N-substituted ethylenediamines, toward the bivalent metals of the first transition series.<sup>1</sup> With nickel(II) and cobalt(II), ligands of this type behave in a bi- or tridentate manner, according to the nature of substituents R, R', X and the chelated atom, forming planar, octahedral, tetrahedral, or pentacoordinate complexes.

In the present paper we intend to study the behavior of these ligands and of the parent salicylaldehydes with the vanadyl(IV) ion. It has been found that according to the nature of the substituents R and R' two different types of complexes are obtained: (1) complexes with the general formula  $[\text{X-SALen-N(R)R'}]_2\text{VO}$ , in which the vanadium is linked to two Schiff bases; (2) com-

plexes with the formula  $[(\text{X-SAL})(\text{X-SALen-N(R)-R}')\text{VO}]$ , in which the vanadium is linked to only one Schiff base and to a salicylaldehyde group. Seventeen compounds of these two series have been prepared and characterized. Their electronic spectra and magnetic susceptibilities have been measured and the results are discussed in order to obtain information on the stereochemistry of the compounds, in the solid state as well as in solution.

### Experimental Section

**Preparation of the Compounds. Compounds with N- or N,N-Substituted Salicylideneethylenediamines.**—These were prepared by the following general method: a syrupy aqueous solution of  $\text{VOCl}_2$  (3.6 ml, ca. 0.01 mole) was added to a solution of 0.02 mole of X-salicylaldehyde and 0.02 mole of N- or N,N-substituted ethylenediamine. Sodium acetate (0.02 mole) was then added and the solution was heated under reflux on a water bath for 10 min to 1 hr, depending on the compound. In some cases a product separated immediately from the solution; in other cases, however, a few milliliters of water was added to start the precipitation. The compounds of type 1 can generally be recrystallized without taking particular precaution against oxidation.

In the preparation of complexes with R, R' alkyl groups, except in the cases in which X = 5,6-benzo, it was necessary to filter the solution of the reagents in order to eliminate a green precipitate which was formed immediately, and then evaporate the filtered solution at moderate temperatures under vacuum. For the compound with X = H,  $-\text{N(R)R}' = -\text{N}(\text{CH}_2)_3$  (piper-

(1) (a) L. Sacconi, P. Nannelli, and U. Campigli, *Inorg. Chem.*, **4**, 818 (1965); (b) L. Sacconi, P. Nannelli, N. Nardi, and U. Campigli, *ibid.*, **4**, 943 (1965); (c) L. Sacconi, M. Ciampolini, and G. P. Speroni, *ibid.*, **4**, 1116 (1965).

TABLE I  
SUMMARY OF PHYSICAL AND ANALYTICAL DATA FOR VANADYL COMPLEXES<sup>a</sup>  
Compounds of the Series [X-SALen-N(R)R']<sub>2</sub>VO.

X	-N(R)R'	Crystallization	Formula	Mp, °C	% N		% V	
					Calcd	Found	Calcd	Found
H	-N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	CHCl <sub>3</sub>	C <sub>26</sub> H <sub>38</sub> N <sub>2</sub> O <sub>3</sub> V	105	11.05	11.00	10.08	9.66 <sup>b</sup>
5,6-Benzo		C <sub>2</sub> H <sub>5</sub> OH	C <sub>34</sub> H <sub>42</sub> N <sub>2</sub> O <sub>3</sub> V	168-169	9.24	9.06	8.41	8.60
H	-N(H)C <sub>6</sub> H <sub>5</sub>	CHCl <sub>3</sub> + C <sub>2</sub> H <sub>5</sub> OH	C <sub>30</sub> H <sub>30</sub> N <sub>2</sub> O <sub>3</sub> V	185-186	10.27	10.10	9.34	9.27 <sup>c</sup>
H	-N(H)- <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	CHCl <sub>3</sub> + C <sub>2</sub> H <sub>5</sub> OH	C <sub>32</sub> H <sub>34</sub> N <sub>2</sub> O <sub>3</sub> V	180-181	9.77	9.77	8.88	9.02
H	-N(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub>	CHCl <sub>3</sub> + C <sub>2</sub> H <sub>5</sub> OH	C <sub>32</sub> H <sub>34</sub> N <sub>2</sub> O <sub>3</sub> V	150-151	9.77	9.74	8.88	8.91
H	-N(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	CHCl <sub>3</sub> + C <sub>2</sub> H <sub>5</sub> OH	C <sub>42</sub> H <sub>38</sub> N <sub>2</sub> O <sub>3</sub> V	191-193	8.03	8.06	7.28	7.44

## Compounds of the Series [(X-SAL)(X-SALen-N)(R)R']VO

X	-N(R)R'	Crystallization	Formula	Mp, °C	% N		% V	
					Calcd	Found	Calcd	Found
H	-N(CH <sub>3</sub> ) <sub>2</sub>	...	C <sub>18</sub> H <sub>20</sub> N <sub>2</sub> O <sub>4</sub> V	>340	7.39	7.61	13.40	13.50
H	-N(H)C <sub>6</sub> H <sub>5</sub>	...	C <sub>18</sub> H <sub>20</sub> N <sub>2</sub> O <sub>4</sub> V	>340	7.39	7.51	13.40	13.18
H	-N(H)- <i>m</i> -C <sub>3</sub> H <sub>7</sub>	...	C <sub>19</sub> H <sub>22</sub> N <sub>2</sub> O <sub>4</sub> V	>340	7.11	7.22	12.95	13.20
5,6-Benzo		CHCl <sub>3</sub> + C <sub>2</sub> H <sub>5</sub> OH	C <sub>27</sub> H <sub>28</sub> N <sub>2</sub> O <sub>4</sub> V	>340	5.68	5.94	10.32	10.39
H	-N(H)CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	Acetone	C <sub>23</sub> H <sub>22</sub> N <sub>2</sub> O <sub>4</sub> V	>340	6.35	6.71	11.54	11.68 <sup>d</sup>
5,6-Benzo		CHCl <sub>3</sub>	C <sub>31</sub> H <sub>26</sub> N <sub>2</sub> O <sub>4</sub> V	>340	5.17	5.30	9.41	9.12
H	-N(CH <sub>2</sub> ) <sub>4</sub>	CHCl <sub>3</sub> + C <sub>2</sub> H <sub>5</sub> OH	C <sub>20</sub> H <sub>22</sub> N <sub>2</sub> O <sub>4</sub> V	>340	6.91	6.70	12.36	12.01 <sup>e</sup>
5-Cl		CHCl <sub>3</sub> + C <sub>2</sub> H <sub>5</sub> OH	C <sub>20</sub> H <sub>20</sub> N <sub>2</sub> O <sub>4</sub> Cl <sub>2</sub> V	>340	5.91	6.10	10.74	10.61
5,6-Benzo		CHCl <sub>3</sub> + C <sub>2</sub> H <sub>5</sub> OAc	C <sub>28</sub> H <sub>26</sub> N <sub>2</sub> O <sub>4</sub> V	>340	5.54	5.54	10.08	10.27 <sup>f</sup>
H	-N(CH <sub>2</sub> ) <sub>5</sub>	...	C <sub>21</sub> H <sub>24</sub> N <sub>2</sub> O <sub>4</sub> V	>340	6.68	6.77	12.15	11.93
5,6-Benzo		CHCl <sub>3</sub> + acetone	C <sub>29</sub> H <sub>28</sub> N <sub>2</sub> O <sub>4</sub> V	>340	5.39	5.38	9.81	9.74

Salicylaldimino Complexes [SAL-NR]<sub>2</sub>VO

R	Crystallization	Formula	Mp, °C	% N		% V	
				Calcd	Found	Calcd	Found
CH <sub>3</sub>	...	C <sub>16</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub> V	209-211	8.36	8.34	15.15	14.95
C <sub>6</sub> H <sub>5</sub>	...	C <sub>26</sub> H <sub>20</sub> N <sub>2</sub> O <sub>3</sub> V	238-239	6.09	6.05	11.09	11.20

<sup>a</sup> Calcd for bis(5-chlorosalicylaldehyde)oxovanadium(IV): V, 13.48. Found: V, 13.70. <sup>b</sup> Calcd: C, 61.77; H, 7.57. Found: C, 61.56; H, 7.72. <sup>c</sup> Calcd: C, 66.10; H, 5.55. Found: C, 65.03; H, 5.50. <sup>d</sup> Calcd: C, 62.58; H, 5.02. Found: C, 62.30; H, 5.20.

<sup>e</sup> Calcd: C, 59.30; H, 5.47. Found: C, 59.27; H, 5.50. <sup>f</sup> Calcd: C, 66.53; H, 5.19. Found: C, 66.58; H, 5.23.

idino), it was necessary to keep the solution cold for 2 days in order to obtain a crystalline precipitate.

It should be noted that the compounds of type 2 are also formed starting from Schiff bases and vanadyl chloride after prolonged heating of the solution under reflux.

**Bis(N-methylsalicylaldimino)oxovanadium(IV).**—Syrupy VOCl<sub>2</sub> (3.6 ml, *ca.* 0.01 mole) and sodium acetate (0.02 mole) were added to a hot solution of 0.02 mole of salicylaldehyde and 0.025 mole of methylamine in 50 ml of ethyl alcohol. After heating the solution on a water bath for a few minutes, sparkling brown crystals began to separate. When the crystallization was complete, the crystals were collected on a filter, washed with petroleum ether, and dried under vacuum.

**Bis(N-phenylsalicylaldimino)oxovanadium(IV)** was prepared by an analogous method.

**Bis(5-chlorosalicylaldehyde)oxovanadium(IV).**—This compound was obtained by mixing 3.6 ml of syrupy VOCl<sub>2</sub> with 0.02 mole of sodium acetate and 0.02 mole of 5-chlorosalicylaldehyde in hot ethanol. The resulting solution was refluxed on a water bath for a few minutes and some water was added to start the precipitation of the crystalline product.

The physical and analytical data of the compounds studied are summarized in Table I.

**Spectra.**—Absorption spectra were recorded in the range 5000–25,000 cm<sup>-1</sup> at room temperature with a Beckman DK-2 spectrophotometer and 1-cm silica cells. Solvents were of reagent grade quality. Chloroform was washed six times with water, dried for 24 hr over phosphorus pentoxide, and distilled from potassium carbonate under nitrogen. The diffuse reflectance spectra were measured using the standard Beckman reflectance attachment and magnesium oxide as the reference. The infrared spectra were recorded on Nujol mulls using a Perkin-Elmer Model 337 spectrophotometer.

**Magnetic Measurements.**—The magnetic measurements were performed by the Gouy method with the apparatus and experimental technique described previously.<sup>2</sup> The sample tube was calibrated with Hg[Co(NCS)<sub>4</sub>] and freshly distilled water.<sup>3</sup>

**Molecular Weight Measurements.**—Molecular weights were determined in chloroform at 37° with a Mechrolab Model 301A vapor pressure osmometer calibrated with benzil. Scale readings were made 2 min after the drop of the solution was placed on the thermistor. Concentrations of the solutions were in the range 10<sup>-2</sup>–10<sup>-3</sup> M.

## Results

(1) **Complexes with the Same Ligands [X-SALen-N(R)R']<sub>2</sub>VO.**—These are formed when one or both substituents R and R' are aryl groups and when R and R' are both ethyl groups. The compounds are green in color and paramagnetic, with magnetic moments in the range 1.7–1.9 BM. Two typical compounds with X = H, R = R' = C<sub>2</sub>H<sub>5</sub> have been found to be monomers in chloroform solution. In the infrared absorption spectra of compounds of this series a strong band, characteristic of the V=O group,<sup>4</sup> appears at 950–1000 cm<sup>-1</sup>.

The reflectance spectra show three characteristic bands in the crystal field region, the first at 11,500–12,000 cm<sup>-1</sup> ( $\nu_1$ ) and the other two at 16,650–16,950 ( $\nu_2$ ) (often as a shoulder) and 18,200–19,050 cm<sup>-1</sup> ( $\nu_3$ ). The spectra of the chloroform solutions show bands which are practically at the same frequencies as in the reflectance spectra, with  $\epsilon_1 \approx 15$ –20,  $\epsilon_2 \approx 30$ ,  $\epsilon_3 \approx 50$ –60.

(2) L. Sacconi, R. Cini, M. Ciampolini, and F. Maggio, *J. Am. Chem. Soc.*, **82**, 3487 (1960).

(3) B. N. Figgis and L. Lewis, "Modern Coordination Chemistry," J. Lewis and L. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p 415.

(4) (a) C. G. Barraclough, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 3552 (1959); (b) J. Selbin, L. H. Holmes, Jr., and S. P. McGlynn, *J. Inorg. Nucl. Chem.*, **25**, 1359 (1963).

TABLE II  
SPECTRAL DATA FOR VANADYL COMPLEXES  
Compounds of the Series  $[X-SALen-N(R)R']_2VO$

X	$-N(R)R'$	State	Absorption max, $cm^{-1}$ ( $\epsilon_{molar}$ for soln)
H	$-N(C_2H_5)_2$	Solid	12,050, 16,650, 18,200
		$CHCl_3$	11,900 (15), 16,650 ( $\approx 45$ ), 18,350 (54)
		Py	13,350 (21), 16,400 ( $\approx 35$ ), 18,350 (50)
5,6-Benzo		Solid	11,900, 16,400, 17,250
		$CHCl_3$	12,350 (25), 16,400 sh, 18,200 (95)
		Py	13,350 (55), 16,400 sh, 18,500 (90)
H	$-N(H)C_6H_5$	Solid	12,050, 16,650, 18,200
		$CHCl_3$	11,750 (15), 16,650 (50), 18,500 (60)
		Py	13,800 (25), 16,650 ( $\approx 35$ ), 18,600 (50)
H	$-N(H)-p-CH_3C_6H_4$	Solid	11,500, 16,650 sh, 18,200
		$CHCl_3$	11,750 (20), 16,650 ( $\approx 50$ ), 18,350 (65)
		Py	13,800 (25), 16,650 ( $\approx 50$ ), 18,850 (50)
H	$-N(CH_3)C_6H_5$	Solid	11,900, 16,950, 18,200
		$CHCl_3$	11,900 (15), 16,650 ( $\approx 45$ ), 18,500 (55)
		Py	13,700 (30), 16,400 ( $\approx 25$ ), 18,850 (40)
H	$-N(C_6H_5)_2$	Solid	12,050, 16,800 sh, 18,850
		$CHCl_3$	12,050 (15), 16,650 (45), 18,500 (55)
		Py	13,800 (25), 16,400 ( $\approx 25$ ), 18,750 (45)
Compounds of the Series $[(X-SAL)(X-SALen-N(R)R')]VO$			
X	$-N(R)R'$	State	Absorption max, $cm^{-1}$ ( $\epsilon_{molar}$ for soln)
H	$-N(CH_3)_2$	Solid	12,100, 18,200, $\approx 20,000$
		$CHCl_3$	12,050 (45), 17,850 (220)
H	$-N(H)C_2H_5$	Solid	12,100, 18,200, 20,000
		$CHCl_3$	12,050 (45), 17,550 (210)
H	$-N(H)-n-C_8H_7$	Solid	12,100, 18,200, $\approx 20,000$
		$CHCl_3$	12,050 (40), 17,850 (205), 19,250 sh
5,6-Benzo		Solid	12,350, 16,650
		$CHCl_3$	12,500 (60), 16,950 (340)
H	$-N(H)CH_2C_6H_5$	Solid	11,900, 17,850
		$CHCl_3$	11,750 (60), 17,750 (190), $\approx 18,800$
		Py	12,250 (45), 17,750 (200), $\approx 18,500$
5,6-Benzo		Solid	12,500, 16,800
		Py	12,650 (40), 16,800 (230)
H	$-N(CH_2)_4$	Solid	11,900, 17,750, 20,000
		$CHCl_3$	11,900 (55), 17,550 (240), 19,250 (235)
		Py	12,050 (45), 17,550 (240), 19,250 (235)
5-Cl		Solid	11,750, 16,950, $\approx 18,500$
		$CHCl_3$	11,900 (45), 16,950 (250), $\approx 18,500$
		Py	12,350 (45), 16,950 (250), $\approx 18,800$
5,6-Benzo		Solid	11,900, 16,605
		$CHCl_3$	12,200 (54), 16,950 (340), 18,200 sh
		Py	12,650 (50), 16,950 (310), 18,200 sh
H	$-N(CH_2)_5$	Solid	11,650, 17,850, 20,000
5,6-Benzo		Solid	12,050, 16,650, 18,200
		$CHCl_3$	11,750 (80), 16,650 (260), $\approx 18,200$
Salicylaldimino Complexes $[SAL-NR]_2VO$			
R		State	Absorption max, $cm^{-1}$ ( $\epsilon_{molar}$ for soln)
$CH_3$		Solid	11,900, 16,650 sh, 18,300
		$CHCl_3$	11,900 (15), 16,650 sh, 18,500 (65)
		Py	13,700 (25), 16,650 sh, 19,050 (70)
$C_6H_5$		Solid	12,100, 16,100 sh, 17,850
		$CHCl_3$	11,900 (15), 16,100 sh, 18,500 (55)
		Py	13,800 (35)

The spectra of the solutions in pyridine are notably different. The first band is shifted to 13,700–13,800  $cm^{-1}$  ( $\epsilon_1' \approx 25-30$ ), the position of the second band is virtually unchanged, while the third is slightly displaced toward the violet ( $\epsilon_3' \approx 40-50$ ). In addition there is a shoulder at ca. 11,500  $cm^{-1}$  which could correspond to a symmetry lowering with subsequent removal of the degeneracy of the  $d_{zz}$  and  $d_{yz}$  levels due to the formation of pyridine adducts. Figure 1 shows the

spectrum of a typical compound of this series. The spectral data are reported in Table II.

(2) **Mixed-Ligand Complexes**  $[(X-SAL)(X-SALen-N(R)R')]VO$ .—These are formed when the substituents R and R' are alkyl groups (except when R = R' =  $C_2H_5$ ), benzyl groups, and when the terminal amino group  $-NR_2$  is  $-N(CH_2)_4$  (pyrrolidino) or  $-N(CH_2)_5$  (piperidino).

They are deep red or violet in color, except for those

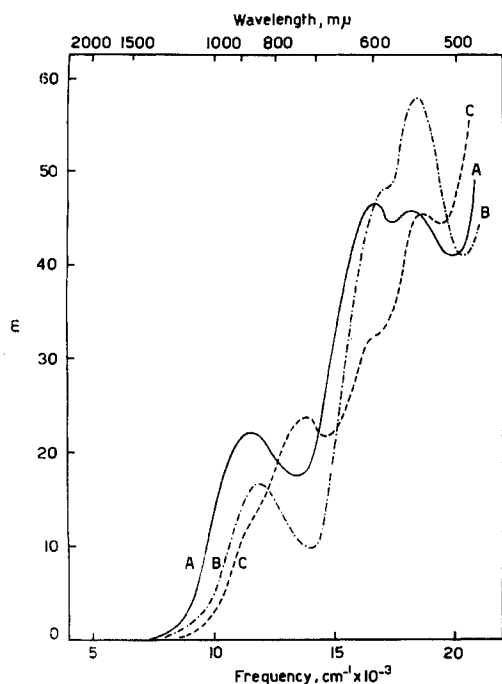


Figure 1.—Reflectance and absorption spectra of  $[(H-SALen-N(H)C_6H_5)_2VO]$  complex at room temperature: A, by reflectance absorption; B, in chloroform; C, in pyridine.

in which X = 5,6-benzo, which are green. Even at  $340^\circ$  they do not melt. Like the complexes of the previous series they have "normal" magnetic moments of *ca.* 1.7–1.9 BM. Their infrared spectra also show a strong band at *ca.*  $950\text{ cm}^{-1}$ , and both the reflectance and absorption spectra in chloroform and in pyridine show bands at approximately the same frequencies as those from the preceding series: at  $11,500\text{ (}\nu_1\text{)}$ ,  $16,650\text{--}18,000\text{ (}\nu_2\text{)}$ , and  $18,000\text{--}20,000\text{ cm}^{-1}\text{ (}\nu_3\text{)}$ . For some complexes the  $\nu_2$  and  $\nu_3$  bands are unresolved. The values of the extinction coefficients of the three peaks are, however, distinctly higher than those from series 1,  $\epsilon_1$  ranging from 40 to 80,  $\epsilon_2$  and  $\epsilon_3$  from 180 to 300. The low solubility of these compounds did not allow the determination of their molecular weights. Figure 2 shows the spectrum of a typical complex of this series and the spectral data of the studied compounds are reported in Table II.

### Discussion

The values of the magnetic moments (1.7–1.9 BM) of all the compounds under consideration are very near the spin-only value for one unpaired electron, as is expected for vanadyl(IV) compounds.<sup>5</sup> These "normal" values suggest that an interaction between vanadium atoms, such as has been proposed for other Schiff base vanadyl(IV) complexes,<sup>6</sup> can be excluded. Furthermore the presence of the  $V=O$  stretching band around  $950\text{ cm}^{-1}$  indicates that the vanadium is present as a monomeric VO unit.<sup>4</sup>

Vanadyl(IV) usually shows coordination number 5 or 6 in its complexes, with coordination geometries corresponding to a tetragonal pyramid or a distorted

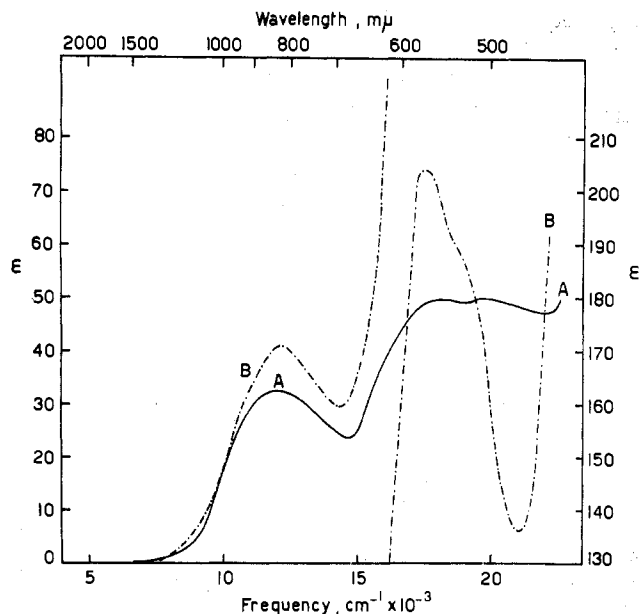


Figure 2.—Reflectance and absorption spectra of  $[(H-SAL)-N(H)-n-C_6H_7]_2VO$  complex at room temperature: A, by reflection absorption; B, in chloroform.

octahedron,<sup>7</sup> respectively. However, because of the dominant axial field, the energy level diagrams, associated with these two structures, do not differ very much. The bands of both series under consideration can therefore be assigned on the basis of the same scheme. Following the MO treatment of the  $[VO(H_2O)_5]^{2+}$  ion by Ballhausen and Gray,<sup>5</sup> several studies on optical spectra of vanadyl(IV) complexes have been reported, and the limits of validity of the energy level scheme, proposed by Ballhausen and Gray, have been discussed. More recently this scheme has been revised by Ortolano, Selbin, and McGlynn in order to interpret the visible spectrum of bis(acetylacetonato)oxovanadium(IV) at low temperatures<sup>8</sup> and some spectral data concerning complexes of low symmetry with strong equatorial  $\sigma$  (and perhaps  $\pi$  equatorial) bonds.<sup>9</sup> The spectral data of the present complexes can be interpreted on the basis of this recent "clustered levels" scheme, which can account for the presence of three bands,  $\nu_1$ ,  $\nu_2$ , and  $\nu_3$ , in the range  $10,000\text{--}20,000\text{ cm}^{-1}$ , attributable to the transitions  $d_{xy} \rightarrow (d_{xz}, d_{yz})$ ,  $d_{xy} \rightarrow d_{x^2-y^2}$ , and  $d_{xy} \rightarrow d_{z^2}$ , respectively.

**Series 1.**—A close correlation between the spectroscopic data and the structure of the vanadyl complexes has not yet been established. It is, however, possible to distinguish between the pyramidal and the distorted octahedral structure, inasmuch as the sixth coordination position in tetragonal pyramidal complexes may be occupied by ligands with a small steric hindrance like pyridine.<sup>10</sup> This variation in the stereochemistry generally gives rise to significant shifts of the stretch-

(7) J. Selbin, *Chem. Rev.*, **65**, 153 (1965).

(8) T. R. Ortolano, J. Selbin, and S. P. McGlynn, *J. Chem. Phys.*, **41**, 262 (1964).

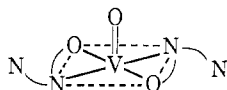
(9) J. Selbin and L. Morpurgo, *J. Inorg. Nucl. Chem.*, **27**, 673 (1965).

(10) R. T. Claunch, T. W. Martin, and M. M. Jones, *J. Am. Chem. Soc.*, **83**, 1073 (1961).

(5) C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **1**, 111 (1962).

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ing frequency of the V=O group in infrared spectra<sup>11</sup> and the bands in optical spectra.<sup>12</sup> In the optical spectra of complexes of this series in pyridine solution the first band is shifted by 800–1300  $\text{cm}^{-1}$  and the third by 300–500  $\text{cm}^{-1}$  both toward higher energies. These effects can be understood if we assign a tetragonal pyramidal structure of the type



to the compounds under consideration. The strongly donor nitrogen of pyridine, when coordinated to vanadium in *trans* position with respect to the oxygen linked through a double bond to the central atom, modifies considerably the axial perturbation due to this oxygen. The levels arising from metal d orbitals with axial character, *i.e.*,  $d_{zz}$ ,  $d_{yz}$ , and  $d_{xz}$ , are therefore destabilized with respect to the others. Thus the shifts of both the first band and the third toward the violet can be explained. It must be noted, however, that the shift of the third band is very small if compared with that of the first one, in spite of the fact that we are dealing with a transition from the fundamental to another level, to which the orbital  $d_{z^2}$  of the metal is the main contributor.

In the proposed structure the vanadium is surrounded by a *trans*  $\text{N}_2\text{O}_2$  set and the terminal nitrogen atoms ( $\beta$ ) of the ethylenediamine chains are not linked to the metal. This hypothesis is supported by the fact that the spectra of two typical salicylaldimino complexes, bis(N-methylsalicylaldimino)oxovanadium(IV) and bis(N-phenylsalicylaldimino)oxovanadium(IV), in which the set of coordinating atoms is in all probability *trans*, when dissolved in inert solvents like chloroform and benzene, are quite similar to those of complexes of this series. Moreover, the spectra of these salicylaldimino complexes in pyridine solution show shifts of the first and third band of the same magnitude as those found in compounds of this series (Figure 3).

**Series 2.**—The infrared data are in accordance with the presence of coordinate aldehyde groups and imine groups in the molecule of these complexes. The assignment of some significant bands in the range 1700–1500  $\text{cm}^{-1}$  for some representative complexes are reported in Table III. As can be seen, the compounds 4 and 5 show two bands, the first of which at 1625–1630  $\text{cm}^{-1}$  is attributable to C=N stretching<sup>13</sup> and the second at 1645  $\text{cm}^{-1}$  is attributable to the stretching vibration of the coordinated C=O group.<sup>14</sup> The first band is in fact present in the spectra of the salicylaldimino complexes 1 and 2 and of typical compounds of series 1; the second in the spectrum of bis(5-chlorosalicylaldehyde)oxovanadium(IV).

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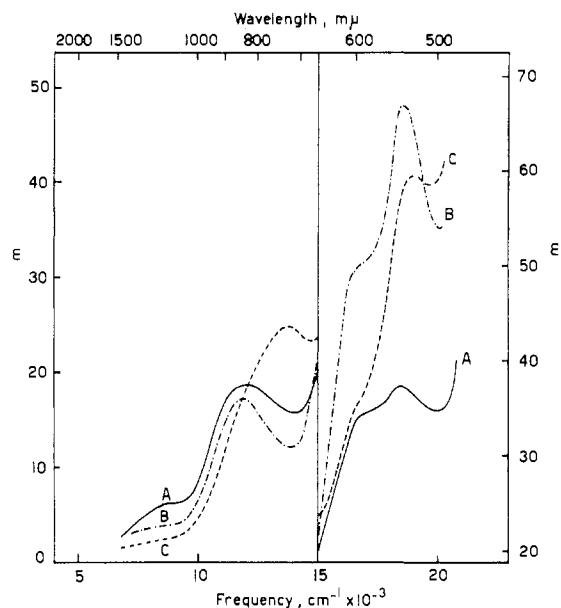


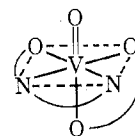
Figure 3.—Reflectance and absorption spectra of  $[\text{SAL}-\text{NCH}_3]_2\text{VO}$  complex at room temperature: A, by reflectance absorption; B, in chloroform; C, in pyridine.

TABLE III  
OBSERVED FREQUENCIES (IN  $\text{CM}^{-1}$ ) OF THE  
INFRARED SPECTRA

Compound	Observed bands			
	C=O str	C=N str	Aromatic	C=C
(1) $(\text{SAL}-\text{NCH}_3)_2\text{VO}$		1630	1600	1550
(2) $(\text{SAL}-\text{NC}_6\text{H}_5)_2\text{VO}$		1600	1585	1540
(3) $[\text{SALen}-\text{N}(\text{H})\text{C}_6\text{H}_5]_2\text{VO}$		1610	1600	1550
(4) $[(\text{SAL})(\text{SALen}-\text{N}(\text{H})\text{C}_2\text{H}_5)_2\text{VO}$	1645	1630	1600	1540
(5) $[(\text{SAL})(\text{SALen}-\text{N}(\text{H})-n\text{-C}_3\text{H}_7)_2\text{VO}$	1645	1630	1600	1540
(6) $(5\text{-ClSAL})_2\text{VO}^a$	1645		1600	1525

<sup>a</sup> Bis(5-chlorosalicylaldehyde)oxovanadium(IV).

In the crystal field region the spectra of the compounds of this second series, dissolved in coordinating or inert solvents, are quite similar, if a slight shift of the first band around 12,000  $\text{cm}^{-1}$ , in the spectra of the solution of some compounds in pyridine, is neglected. This indicates that in these compounds with mixed ligands the vanadium is coordinatively saturated. The most likely structure is of the type



where the metal is linked with a salicylaldehyde group and with a Schiff base, acting tridentately. It will be remembered that some Schiff bases of this series, with R, R' = alkyl groups, also function as tridentate ligands with nickel(II)<sup>1a,1b</sup> and cobalt(II),<sup>1c</sup> with which they form octahedral complexes. As in these last complexes it is reasonable to assume that in the vanadyl compounds the three donor atoms O, N, and N( $\beta$ ) are arranged in an equatorial plane. The geometry of the group  $-\text{N}-\text{CH}_2-\text{CH}_2-\text{N}(\text{R})\text{R}'$  does not, however, permit a regular octahedral structure. In fact spec-

tral and structural evidence in nickel(II)<sup>1a, 1b</sup> and cobalt(II)<sup>1c</sup> complexes, mentioned above, indicates some distortion of the regular structure. The high values of the extinction coefficients at the peaks in the spectra of the vanadyl compounds may also be attributed to such distortions.

### Conclusions

The electronic characteristics of the substituents R, R' seem to be the main factor which governs the stereochemistry of the complexes. Even when only one of the substituents is an aryl group, the electron-withdrawing effect on the  $\beta$  nitrogen prevents the coordination of this atom to the central vanadium and complexes with the same ligand are the result. When the R, R' groups have an electron-releasing effect, the  $\beta$  nitrogen becomes a strong donor, the Schiff base therefore functions tridentately, and hexacoordinate complexes are formed. While in five-coordinate nickel(II) complexes with X-SALen-N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> the bidentate ligand is a Schiff base, it is remarkable that with vanadyl the bidentate ligand is a salicylaldehyde group. This occurs even if the reaction is carried out using stoichiometric amounts of preformed Schiff bases and a vanadyl salt dissolved in aqueous ethanol. Part of the Schiff base is hydrolyzed and the salicylaldehyde, thus liberated, links itself to the vanadyl unit. The low solubility of the mixed-ligand chelates in aqueous ethanol is probably an important factor in directing the reaction toward the formation of complexes of this

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type. The nature of the ring substituent X does not seem to have any influence, in contrast to the behavior of cobalt(II) and nickel(II) complexes with these Schiff bases.

The Schiff bases with the terminal amino group -NR<sub>2</sub> = -N(CH<sub>2</sub>)<sub>4</sub>, -N(CH<sub>2</sub>)<sub>5</sub>, -N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> deserve further consideration. Among these, only the last does not act tridentately but forms complexes with the same ligand, in which the  $\beta$  nitrogen is not linked to the central atom. If we arrange the various groups according to increasing steric hindrance, the following order is obtained: -N(CH<sub>2</sub>)<sub>4</sub> < -N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> < -N(CH<sub>2</sub>)<sub>5</sub>. The series of increasing donor power of the nitrogen atom, estimated on the basis of the p*K* values of the corresponding amines HNR<sub>2</sub> in equilibria with the reference acceptor NiDBH,<sup>16</sup> is: HN(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> < HN(CH<sub>2</sub>)<sub>4</sub> < HN(CH<sub>2</sub>)<sub>5</sub>. It can be deduced that in the competition between the bulkiness and the electronic characteristics of the substituents R, the latter predominates, enabling the nitrogen to coordinate in pyrrolidino and piperidino derivatives. In the case of a terminal diethylamino group, on the contrary, the donor power does not succeed in compensating for the bulkiness of the two ethyl groups.

**Acknowledgments.**—Thanks are expressed to Dr. Nicoletta Nardi for assisting with some spectrophotometric measurements, to Dr. Jolanda Gelsomini for Microanalysis, and the Italian National Research Council (C.N.R.) for the financial support.

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## Addition Compounds of Bis(dibenzoylmethano)oxovanadium with Pyridine

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Received September 7, 1965

The formation of mono- and diaddition compounds of pyridine with bis(dibenzoylmethano)oxovanadium was shown by measuring the amount of pyridine adsorbed with a silica balance and by visible and infrared spectroscopy. While coordination of the first molecule of pyridine causes the V=O stretching band to shift to lower frequency, further addition of the second molecule of pyridine was found to cause a shift in the reverse direction. An equilibrium constant for the monoadduct of bis(dibenzoylmethano)oxovanadium with pyridine in chloroform solution was estimated from the visible spectra and was compared with that for the acetylacetonate chelate.

### Introduction

Bis(acetylacetonato)oxovanadium and bis(benzoylacetonato)oxovanadium have been established from chemical and X-ray determinations to have a penta-coordinated structure with a V=O bond and two chelate rings.<sup>2-4</sup> Pyridine coordinates to the vanadium

atom, and the monoaddition compound of bis(acetylacetonato)oxovanadium with pyridine has been known and studied spectroscopically.<sup>5-7</sup>

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