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The Oxovanadium(IV) Complexes of Schiff Bases Obtained from Substituted Salicylaldehydes and Alkyl Amines[*1]

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Many new oxovanadium(IV) complexes (abbreviated as VO(X-sal.R)$_2$) of Schiff bases obtained from substituted salicylaldehydes and alkylamines have been synthesized as crystals, where X = H and 3-CH_3O and R = CH_3, C_2H_5, *n*-C_3H_7, *n*-C_4H_9, *iso*-C_3H_7, $CH(CH_3)(C_2H_5)$, $CH_2CH(CH_3)_2$ and cyclohexyl. Since all these complexes show similar electronic spectra, it is considered that they take an essentially similar configuration, that is, a square-pyramidal one in the solid state and in chloroform, even for $R = \alpha$-branched alkyls. This result is different from that of the copper (II) complexes. It is also concluded that these oxovanadium(IV) complexes, when dissolved in pyridine, take up one pyridine molecule to form a six-coordinated species. The configuration of the pyridine solvate depends upon R.

In previous papers from this laboratory,1–3) Schiff base complexes of various transition metal ions were described and their stereochemistry was discussed. As an extension of these studies, the oxovanadium(IV) complexes of these Schiff bases have been studied in the present work. The oxovanadium(IV) ion has an electronic configuration d^1, so that its complexes are expected to be somewhat similar to the complexes of copper(II) having a configuration d^9.

Some of the oxovanadium(IV) complexes of this series were previously reported,4,5) but a systematic study seems to be insufficient. The present paper describes the results of the investigations about the oxovanadium(IV) complexes of the Schiff bases obtained from substituted salicylaldehydes and alkyl amines (Fig. 1).[*3]

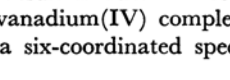

Fig. 1. VO(X-sal.R)$_2$

Experimental

Materials. The complexes of the VO(X-sal.R)$_2$

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1) S. Yamada, *Coordin. Chem. Revs.*, **1**, 415 (1966).

2) S. Yamada, H. Nishikawa, Y. Kuge and K. Yamanouchi, *Sci. Rep., Coll. Gen. Educ. Osaka Univ.*, **16**, 11 (1967).

3) S. Yamada, E. Ohno, Y. Kuge, A. Takeuchi, K. Yamanouchi and K. Iwasaki, *Coordin. Chem. Revs.*, **3**, 247 (1968).

4) J. Selbin, *ibid.*, **1**, 293 (1966).

5) L. Sacconi and U. Campigli, *Inorg. Chem.*, **5**, 606 (1966).

[*3] The complexes of this type are abbreviated in this paper as VO(X-sal.R)$_2$.

type, where X=H and 3-CH_3O, were synthesized by a method similar to that previously reported for complexes of other metal ions.[1] One of the typical examples of the syntheses is given below for VO(3-CH_3O-sal.CH_3)$_2$. To a solution of oxovanadium (IV) chloride (0.01 mol) in ethanol were added 3-methoxysalicylaldehyde (0.02 mol), a 40% aqueous solution of methyl amine (0.02 mol) and sodium acetate (0.02 mol). The solution was heated with stirring on a water-bath at about 60°C for about three hours. The solution was allowed to stand overnight, and the precipitate was collected by filtration. Recrystallization from ethanol yielded green crystals of VO(3-CH_3O-sal.CH_3)$_2$.

All the complexes were purified by recrystallization of the crude product from ethanol. Ethanol containing a small amount of pyridine was occasionally used for the recrystallization of the less soluble compounds like VO(H-sal.C_2H_5)$_2$.

The salicylideneiminato-complexes are grey-brownish green, and the 3-methoxysalicylideneiminato-complexes are green. They are soluble in chloroform and dichloromethane, but less soluble in methanol, ethanol and benzene. The complexes of the VO(H-sal.R)$_2$ type are less soluble in common organic solvents than the complexes of the VO(3-CH_3O-sal.R)$_2$ type. Analytical data of the complexes are given in Tables 1 and 2.

TABLE 1. ANALYTICAL DATA OF OXOVANADIUM(IV) COMPLEXES OF THE VO(H-sal.R)$_2$ TYPE

	Calcd %			Found %		
R	C	H	N	C	H	N
C_2H_5	60.05	5.66	7.09	59.58	5.55	7.71
n-C_3H_7	61.38	6.18	7.16	61.21	6.11	8.04
i-C_3H_7				61.91	6.08	6.88
n-C_4H_9	63.00	6.73	6.67	62.96	6.82	6.68
$CH(CH_3)(C_2H_5)$				62.58	6.75	6.16
$CH_2CH(CH_3)_2$				62.81	6.89	6.28
Cyclohexyl	66.52	6.44	5.29	65.59	6.72	6.20

TABLE 2. ANALYTICAL DATA OF OXOVANADIUM(IV) COMPLEXES OF THE VO(3-CH_3O-sal.R)$_2$ TYPE

	Calcd %			Found %		
R	C	H	N	C	H	N
CH_3	54.69	5.09	7.09	54.72	5.07	7.48
C_2H_5	55.90	5.76	7.05	56.74	5.71	6.62
n-C_3H_7	58.54	6.25	6.21	58.53	6.40	6.37
i-C_3H_7				58.21	6.10	6.15
n-C_4H_9	60.12	6.73	5.86	59.93	6.89	6.04
$CH(CH_3)(C_2H_5)$				59.72	6.70	5.94
$CH_2CH(CH_3)_2$				59.39	6.70	6.13
Cyclohexyl	63.51	6.47	5.29	62.59	6.71	5.44

Cu(H-sal.*iso*-C_3H_7)$_2$ was prepared as previously reported.[6]

Measurements. The electronic absorption spectra of the compounds in solution and the reflection spectra of the solid were determined with a Shimadzu QR-50 spectrophotometer and a Shimadzu MPS-50L spectrophotometer.

Results and Discussion

The Oxovanadium(IV) Complexes of *N*-*n*-Alkyl-substituted Schiff Bases. Numerous new oxovanadium(IV) complexes of the Schiff bases have been synthesized in the present work. All these complexes are considered to consist of pentacoordinated molecules.[4,5] When R denotes an n-alkyl group, there is no or very little steric hindrance, so that the complexes of the VO(X-sal.R)$_2$ type are expected to be square-pyramidal, with the two groups of X-sal.R most probably taking a nearly trans-planar configuration.[5]

Electronic spectra of these complexes in non-donor solvents are essentially similar to the spectra of the same complexes in the solid state (Figs. 2 and 3, and Tables 3 and 4).[*4] It is, therefore, most likely that their configuration in such a non-donor solvent as chloroform is similar to that in the solid state, the solvent molecule not being bound with the vanadium(IV) ion. It is also concluded that all these complexes take a similar configuration, that is, a square-pyramidal one, regardless of the substituent, R, since they show similar spectra. The main features of the spectra of these complexes are in agreement with those for the related complexes.[5]

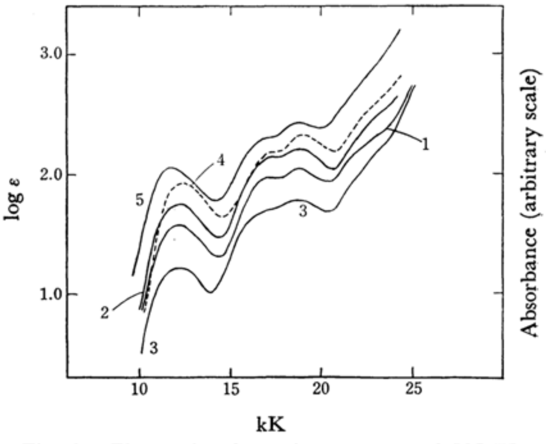

Fig. 2. Electronic absorption spectra of VO(H-sal.R)$_2$: 1, R=C_2H_5, solid; 2, R=n-C_4H_9, solid; 3, R=$CH_2CH(CH_3)_2$, in chloroform; 4, R=CH_2-$CH(CH_3)_2$, solid; 5, R=$CH(CH_3)(C_2H_5)$, solid.

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6) S. Yamada and H. Nishikawa, This Bulletin, **36**, 755 (1963).

[*4] Solubility of these complexes is rather low in common organic solvents other than chloroform and dichloromethane. In this work, the spectra were measured mostly using chloroform as a solvent. Measurements were also carried out with some of the complexes in dichloromethane, but the spectra were found to be essentially similar to the spectra of the chloroform solution.

TABLE 3. ABSORPTION MAXIMA OF OXOVANADIUM(IV) COMPLEXES OF THE $VO(H\text{-}sal.R)_2$ TYPE

R	State	$\nu(\log\varepsilon)$	$\nu(\log\varepsilon)$	$\nu(\log\varepsilon)$
C_2H_5	Solid	12.1	16.9sh	18.9
	Pyridine	14.0*(1.40)	17.0sh(1.46)	19.3(1.72)
n-C_3H_7	Soild	12.2	17.0sh	18.8
	Pyridine	14.0*(1.28)	17.0sh(1.45)	19.3(1.70)
i-C_3H_7	Solid	12.1	16.8sh	18.9
	Pyridine	12.2*(1.51)	17.0sh(1.52)	19.5(1.78)
n-C_4H_9	Solid	12.1	16.8sh	18.8
	Pyridine	14.0*(1.31)	17.0sh(1.35)	19.3(1.68)
$CH_2CH(CH_3)_2$	Solid	12.5	17.0sh	19.0
	$CHCl_3$	12.3 (1.22)	16.7sh(1.60)	18.8(1.75)
	Pyridine	14.1*(1.40)	17.0sh(1.35)	19.1(1.64)
$CH(CH_3)(C_2H_5)$	Solid	11.8	16.8sh	18.9
	Pyridine	12.2*(1.76)	flat	flat
Cyclohexyl	Solid	11.9	16.7sh	18.3
	Pyridine	12.9*(1.37)	17.0sh(1.52)	19.5(1.80)

* With a shoulder on the lower frequency side. ν: cm^{-1} sh: shoulder. The values of ν and ε for the shoulders are intended to be only approximate.

TABLE 4. ABSORPTION MAXIMA OF OXOVANADIUM(IV) COMPLEXES OF THE $VO(3\text{-}CH_3O\text{-}sal.R)_2$ TYPE

R	State	$\nu(\log\varepsilon)$	$\nu(\log\varepsilon)$	$\nu(\log\varepsilon)$
CH_3	Solid	12.2	17sh	18.9
	$CHCl_3$	12.1 (1.10)	16.7sh(1.56)	18.7(1.78)
	Pyridine	13.8*(1.27)	16.9sh(1.52)	19.0(1.75)
C_2H_5	Solid	12.1	16.3sh	18.4sh
	$CHCl_3$	12.1 (1.05)	16.7sh(1.55)	18.8(1.83)
	Pyridine	13.0*(1.30)	16.6sh(1.55)	18.7(1.70)
n-C_3H_7	Solid	12.2	16.0sh	18.4sh
	$CHCl_3$	12.3 (1.19)	16.7sh(1.60)	18.7(1.78)
	Pyridine	13.9*(1.25)	16.7sh(1.53)	18.8(1.71)
i-C_3H_7	Solid	11.8	16.2sh	18.7
	$CHCl_3$	12.2 (1.32)	16.6sh(1.66)	18.8(1.85)
	Pyridine	12.8*(1.29)	16.4sh(1.46)	18.4(1.71)
n-C_4H_9	Solid	12.2	16.7sh	18.6
	$CHCl_3$	12.2 (1.20)	16.7sh(1.60)	18.7(1.77)
	CH_2Cl_2	12.3 (1.27)	16.6sh(1.62)	18.8(1.81)
	Pyridine	13.8*(1.27)	16.5sh(1.55)	18.7(1.70)
$CH_2CH(CH_3)_2$	Solid	12.4	16.7sh	18.7
	$CHCl_3$	12.2 (1.16)	16.5sh(1.58)	18.9(1.76)
	Pyridine	14.0*(1.25)	16.5sh(1.55)	18.8(1.68)
$CH(CH_3)(C_2H_5)$	Solid	12.0	16.3sh	18.7
	CH_2Cl_2	12.4 (1.51)	16.6sh(1.76)	19.1(1.98)
	Pyridine	12.7*(1.42)	16.6sh(1.50)	19.0(1.75)
Cyclohexyl	Solid	12.2	16.3sh	18.3sh
	$CHCl_3$	12.1 (1.42)	16.6sh(1.75)	18.8(1.90)
	Pyridine	13.4*(1.20)	17.1sh(1.50)	19.3(1.71)

* With a shoulder on the lower frequency side. ν: cm^{-1} sh: shoulder. The values of ν and ε for the shoulders are intended to be only approximate.

It is interesting to note that three band maxima are observed in the region of *d–d* bands for these complexes. About an unambiguous assignment of the *d–d* absorption bands of the oxovanadium(IV) complexes there still seems to remain some dipute.[4,7] The three bands at about 12 kK,

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[7] J. Selbin, *Chem. Revs.*, **65**, 153 (1965).

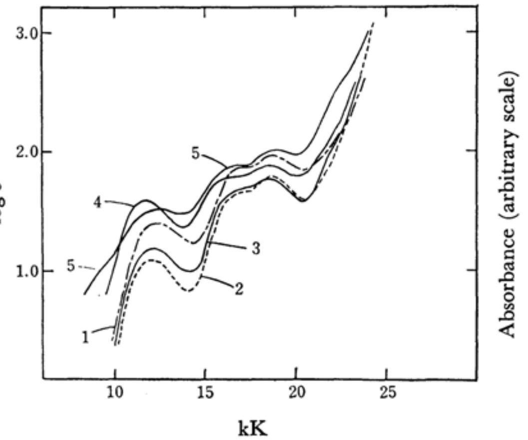

Fig. 3. Electronic absorption spectra of VO-(3-CH_3O-sal.R)$_2$: 1, R=CH_3, solid; 2, R=CH_3, in chloroform; 3, R=*n*-C_4H_9, in chloroform; 4, R=*iso*-C_3H_7, solid; 5, R=$CH(CH_3)(C_2H_5)$, in dichloromethane.

16—17 kK and 18.5—19 kK may tentatively be assinged as transitions $d(xz)$, $d(yz) \leftarrow d(xy)$, $d(x^2-y^2) \leftarrow d(xy)$ and $d(z^2) \leftarrow d(xy)$, respectively, on the basis of the "clustered levels" scheme.[5,7)]

These complexes in pyridine show electronic spectra, which are different from the spectra of the same complexes in the solid state and in chloroform (Figs. 4 and 5, and Tables 3 and 4). The change in the spectrum on going from a non-donor solvent to pyridine is not very large, but quite characteristic. This fact seems to indicate that the oxovanadium(IV) complexes, when dissolved in pyridine, combine with one molecule of pyridine to form six-coordinated solvates. It is to be noted that for the pyridine solution there appears a shoulder at about 12 kK, in addition to the peak at about 13—14 kK and two other peaks. The two peaks at the lower frequencies may tentatively be assigned as the transitions $d(xz) \leftarrow d(xy)$ and $d(yz) \leftarrow d(xy)$.

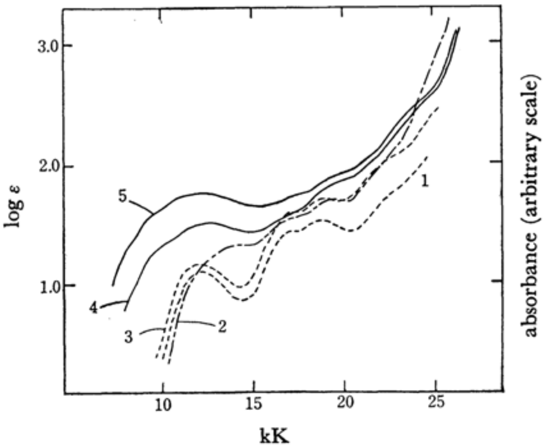

Fig. 4. Electronic absorption spectra of VO(H-sal.R)$_2$: 1, R=*n*-C_3H_7, solid; 2, R=*n*-C_3H_7, in pyridine; 3, R=*iso*-C_3H_7, solid; 4, R=*iso*-C_3H_7, in pyridine; 5, R=$CH(CH_3)(C_2H_5)$, in pyridine.

The Oxovanadium(IV) Complexes of *N*-α-Branched Alkyl-substituted Schiff Bases. For

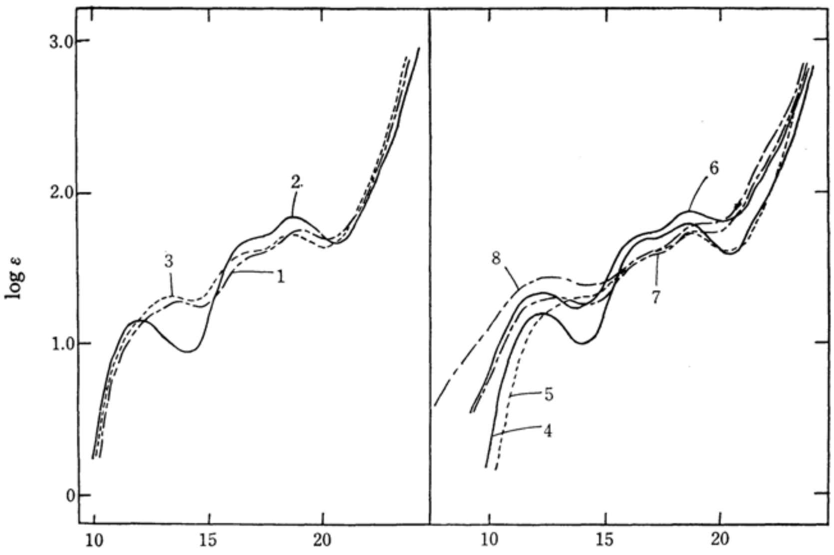

Fig. 5. Electronic absorption spectra of VO(3-CH_3O-sal.R)$_2$: 1, R=CH_3, in pyridine; 2, R=C_2H_5, in chloroform; 3, R=C_2H_5, in pyridine; 4, R=*n*-C_3H_7, in chloroform; 5, R=*n*-C_3H_7, in pyridine; 6, R=*iso*-C_3H_7, in chloroform; 7, R=*iso*-C_3H_7, in pyridine; 8, R=$CH(CH_3)(C_2H_5)$, in pyridine.

R = 2-methylpropyl, there is no serious steric hindrance to the planar coordination of the two ligands around the vanadium(IV) ion. For R = isopropyl, 1-methylpropyl and cyclohexyl, however, there may be more or less remarkable steric hindrance to the planar coordination, since the corresponding copper(II) complexes of the Cu(X-sal.R)$_2$ type were found to be planar or distorted from the planar configuration, depending upon the nature of X.[6,8] On the contrary, the complexes of the VO(X-sal.R)$_2$ type for R = α-branched alkyls in chloroform and in the solid state show electronic absorption spectra quite similar to the corresponding complexes with R = *n*-alkyl groups. It is, therefore, most likely that for all these oxovanadium(IV) complexes the coordination of the two ligand groups may be nearly planar. This difference between the oxovanadium(IV) complexes and the corresponding copper(II) complexes indicates that the configuration distorted from the planar one is destabilized to a more or lesser extent for the oxovanadium(IV) ion, as compared with the copper(II) ion. This may be due, at least partly, to the steric effect of the oxygen atom bound to the vanadium(IV) ion, in addition to the difference in the bonding nature of the metal ions. It is, however, to be noted that the intensity of the *d–d* bands, particularly that of the band at the lowest frequency, becomes higher on going from R = *n*-alkyl to R = α-branched alkyl or cyclohexyl for X = 3-CH$_3$O, as shown in Fig. 5 and Table 4. The change is not quite large but definite, and it is most likely that the coordination of the two Schiff bases to the vanadium(IV) ion may be distorted from the planar one to an only small extent.

For R = α-branched alkyl groups, the electronic spectra of VO(3-CH$_3$O-sal.R)$_2$ in pyridine are clearly different from the spectra of the same complexes in the solid state and in chloroform, as shown in Fig. 5 and Table 4. This fact indicates that the oxovanadium(IV) complexes of this series, when dissolved in pyridine, take up a pyridine molecule. Since, for R = α-branched alkyl groups as well as 2-methylpropyl, the change in the spectra of VO(3-CH$_3$O-sal.R)$_2$ on going from a non-donor solvent to pyridine is essentially similar to that of VO(3-CH$_3$O-sal.*n*-alkyl)$_2$, the configuration of the pyridine solvates for these substituents, R, may be similar to the corresponding solvates for R = *n*-alkyl groups.

On the contrary, for R = α-branched alkyl groups or cyclohexyl, the electronic spectra of VO(H-sal.R)$_2$ in pyridine are quite different from the spectra of the same complexes in chloroform and in the solid state (Fig. 4 and Table 3). The *d–d* bands at the lowest frequencies of these complexes are found to become much broader, extending into a considerably lower frequency region on going from chloroform to pyridine. This result is different from that for VO(H-sal.*n*-alkyl)$_2$ and VO(3-CH$_3$O-sal.alkyl)$_2$. It is most likely that this anomalous change of spectra in VO(H-sal.α-branched alkyl)$_2$ may be due to the steric hindrance leading to a distorted configuration for the pyridine solvates.

For R = α-branched alkyl groups, it is thus found that the behavior of VO(H-sal. R)$_2$ is different from that of VO(3-CH$_3$O-sal.R)$_2$. This difference provides one of the examples showing that a small difference in the electronic factor due to the substituent X may cause a drastic change in the stereochemistry of the Schiff base metal complexes.

It is also interesting to compare VO(H-sal.*iso*-C$_3$H$_7$)$_2$, for example, with the corresponding copper(II) complexes, Cu(H-sal.*iso*-C$_3$H$_7$)$_2$. This copper(II) complex, which takes a distorted tetrahedral configuration in non-donor solvents,[6,8] retains the same configuration in pyridine, since its electronic spectrum in pyridine is essentially similar to the spectrum in non-donor solvents. This is another example showing that the distorted tetrahedral configuration is more stable in the copper(II) complex than in the oxovanadium(IV) complex.

Support of this work by the Ministry of Education is gratefully acknowledged.

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[8] L. Sacconi, "Essays in Coordination Chemistry," ed. by W. Schneider, G. Anderegg and R. Gut, Birkhäuser Verlag, Basel (1964), p. 148.