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Oxovanadium(IV) Complexes of Schiff Bases Obtained from Salicylaldehyde Derivatives and Arylamines

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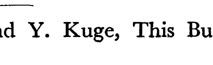
Oxovanadium(IV) complexes of Schiff bases obtained from salicylaldehyde derivatives and arylamines (abbreviated as VO(X-SAL.R)$_2$) have been synthesized, where X=H, 5,6-benzo, 5-Cl, and 5-Br, and R=Ph, CH$_3$-Ph, 2,6-(CH$_3$)$_2$-Ph and 2,6-(C$_2$H$_5$)$_2$-Ph, Ph being phenyl nucleus. Complexes of the type VO(5-X-SAL.Ph)$_2$ in the solid state, X being Cl and Br, consist of the species having a different configuration from that of the other complexes. For the latter complexes, distortion from the square-pyramidal configuration is not apparent in the solid state or in non-donor solvents, but in pyridine they combine with one pyridine molecule to form six-coordinate vanadium(IV) complexes. Comparison shows that the tendency toward the distortion in the solid state is lower with R=aryl than with R=α-branched alkyl groups.

In a previous paper[1] we reported the synthesis of oxovanadium(IV) complexes with *N*-alkylsalicylideneiminates (abbreviated as X-SAL.R, I). Their structure in the solid state and in solution was examined in connection with the steric effect caused by bulky α-branched alkyl groups.



(I)

As regards the corresponding complexes with *N*-

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[1] S. Yamada and Y. Kuge, This Bulletin, **42**, 152 (1969).

arylsalicylideneiminates, however, only a few of them have been reported,2) and no systematic examination of the aryl complexes has ever been carried out. In the present work, oxovanadium(IV) complexes with *N*-arylsalicylideneiminates have been studied, and the results have been compared with those of the *N*-alkyl-complexes and the corresponding complexes of some other metal ions.

Experimental

Materials. Complexes of the type VO(X-SAL.R)$_2$ were synthesized by a method similar to that previously reported.1,2) Analytical data of new complexes are shown in Tables 1 and 2. A typical method of preparation is given below.

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

R	Calcd, %			Found, %		
	C	H	N	C	H	N
X=H						
2-CH$_3$-Ph	68.99	4.96	5.75	68.49	4.86	6.23
3-CH$_3$-Ph	68.99	4.96	5.75	68.30	4.95	6.09
4-CH$_3$-Ph	68.99	4.96	5.75	68.80	4.92	5.55
2,6-(CH$_3$)$_2$-Ph	69.90	5.47	5.43	69.26	5.31	5.06
X=5,6-benzo						
Ph	72.99	4.32	5.01	72.76	4.29	4.77
2-CH$_3$-Ph	73.59	4.80	4.77	73.81	5.03	4.64
3-CH$_3$-Ph	73.59	4.80	4.77	72.54	4.89	4.46
4-CH$_3$-Ph	73.59	4.80	4.77	73.53	4.84	4.60
2,6-(CH$_3$)$_2$-Ph	74.13	5.24	4.55	73.83	5.19	4.67
2,6-(C$_2$H$_5$)$_2$-Ph	75.10	6.00	4.17	74.76	5.99	3.99

To a solution of oxovanadium(IV) chloride (0.01 mol) in ethanol were added salicylaldehyde or its derivative (0.02 mol) and an appropriate arylamine (0.02 mol). The solution was stirred at room temperature for about 3 hr and allowed to stand overnight. The precipitate was collected by filtration and recrystallized from ethanol containing a small amount of pyridine.

TABLE 2. ANALYTICAL DATA OF OXOVANADIUM(IV) COMPLEXES OF THE TYPE VO (X-SAL.Ph)$_2$

X	Calcd, %			Found, %			μ
	C	H	N	C	H	N	
5-Cl	59.11	3.43	5.30	59.00	3.47	5.28	1.49
5-Br	50.59	2.95	4.54	51.23	3.10	4.36	1.57

μ: magnetic moment in B. M. at room temperature

All the complexes were obtained as yellow-brown or olive-green microcrystals. They are soluble in chloroform, dichloromethane and pyridine, but almost insoluble in methanol and ethanol. Some of them undergo decomposition on dissolution.

Measurements. Electronic absorption spectra of the complexes in solution and in the solid state were determined with a Shimadzu MPS-50L spectrophotometer.

Magnetic susceptibilities were determined by the Gouy method at room temperature.

Results and Discussion

It is known that the vanadium(IV) ion in most oxovanadium(IV) complexes assumes a square-pyramidal configuration.1,2) Therefore, when R denotes such a group as phenyl and 3- or 4-substituted phenyl causing very little steric hindrance, the complexes of the type VO(X-SAL.R)$_2$ are expected to have a square-pyramidal configuration, with the two X-SAL.R groups most

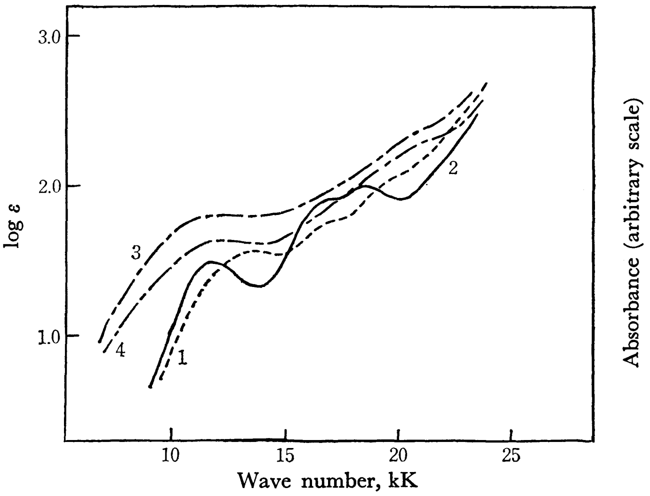

Fig. 1. Electronic absorption spectra of VO(H–SAL.R)$_2$: 1, R=Ph, solid; 2, R=2,6-(CH$_3$)$_2$-Ph, in pyridine; 3, R=2-CH$_3$-Ph, in pyridine; 4, R=2,6-(CH$_3$)$_2$-Ph, in pyridine.

TABLE 3. ABSORPTION MAXIMA OF OXOVANADIUM (IV) COMPLEXES OF THE TYPE VO (X–SAL.R)$_2$

R	State	Absorption max, kK (log ε for solution)
X=H		
Ph	solid	12.0 16.6sh, 18.6
	CHCl$_3$	11.9(1.25), 16.5(1.65)sh, 18.5(1.79)
	pyridine	13.6(1.28)
2-CH$_3$–Ph	solid	11.9, 16.8, 18.6
	CHCl$_3$	11.9(1.40), 16.4(1.72)sh, 18.6(1.86)
	pyridine	12.1(1.81)br
3-CH$_3$–Ph	solid	11.7, 16.9sh, 18.7
	pyridine	12.9(1.58)
4-CH$_3$–Ph	solid	11.6, 16.9sh, 18.7
	pyridine	12.9(1.57)
2,6-(CH$_3$)$_2$–Ph	solid	11.9, 17.0sh, 18.6
	pyridine	12.0(1.60)br
X=5,6-benzo		
Ph	solid	11.9, 16.7sh, 18.5
	pyridine	13.4(1.72)
2-CH$_3$–Ph	solid	11.9, 16.5sh, 18.5
	CHCl$_3$	12.0(1.51), 16.4(1.91)sh, 18.4(2.04)
	pyridine	13.4(1.76)
3-CH$_3$–Ph	solid	11.8, 16.7sh, 18.5
	pyridine	13.4(1.76)
4-CH$_3$–Ph	solid	11.9, 16.9sh, 18.6
	pyridine	13.3(1.74)
2,6-(CH$_3$)$_2$–Ph	solid	12.2, 16.5sh, 18.2
	pyridine	13.3(1.76)
2,6-(C$_2$H$_5$)$_2$–Ph	solid	12.3, 16.5sh, 18.0
	pyridine	13.3(1.70)

br: broad, sh: shoulder

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

probably having a nearly planar configuration.[1,2] This is borne out by their electronic absorption spectra in non-donor solvents and in the solid state, as shown in Figs. 1 and 2, and Table 3. The spectra are similar to each other and also to those of the N-alkyl-substituted complexes.[1] The absorption maxima at about 12, 16, and 18 kK may be assigned to transitions $d(xy) \to d(xz)$ $d(yz)$, $d(xy) \to d(x^2-y^2)$ and $d(xy) \to d(z^2)$, respectively, as in the previous papers.[1,2] Comparison of their band maxima with those of the *N*-alkyl-substituted complexes[1] shows that the ligand field produced by X-SAL·aryl is slightly weaker than that by X-SAL·alkyl.

It is interesting to note that, even for R=2-CH_3-Ph, 2,6-$(CH_3)_2$-Ph and 2,6-$(C_2H_5)_2$-Ph, a significant distortion from the square-pyramidal configuration does not occur in these complexes, since their absorption maxima in the solid state and in non-donor solvents are nearly the same as those of VO(X-SAL·Ph)$_2$ as shown in Figs. 1 and 2, and Table 3. A similar result was obtained with the corresponding nickel(II) and copper(II) complexes.[3]

The electronic spectra of the complexes of the type VO(5,6-benzo-SAL.R)$_2$ in pyridine clearly differ from those of the same complexes in the solid state or in chloroform as shown in Fig. 2 and Table 3. Since their spectral change on going from the solid state to the pyridine solution is nearly the same, irrespective of whether R denotes 2,6-$(CH_3)_2$-Ph, 2,6-$(C_2H_5)_2$-Ph or Ph, and resembles that of VO(X-SAL·*n*-alkyl)$_2$,[1] their pyridine adducts are considered to have a similar configuration to that of VO(X-SAL·*n*-alkyl)$_2$.

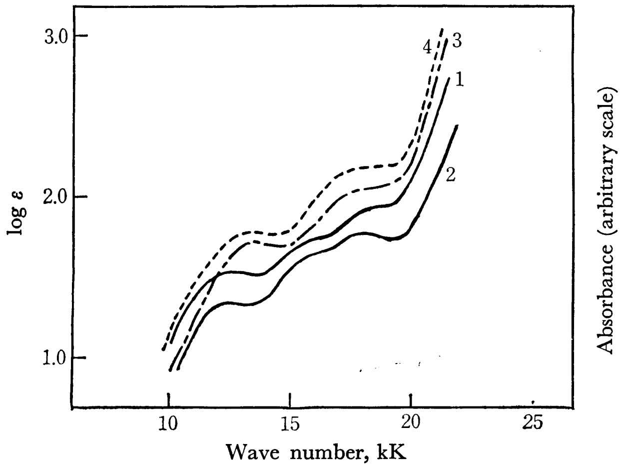

Fig. 2. Electronic absorption aspectr of VO(5,6-benzo-SAL. R)$_2$: 1, R=Ph, solid; 2, R=2,6-$(CH_3)_2$-Ph, solid; 3, R=Ph, in pyridine; 4, R=2,6-$(CH_3)_2$-Ph, in pyridine.

Table 4. The configuration of complexes of the type M(H-SAL.R)$_2$ in the solid state and in pyridine

M	R=*iso*-C_3H_7		R=2,6-$(CH_3)_2$-Ph	
	solid	in pyridine	solid	in pyridine
VO(IV)[a]	pl	dist. add.	pl	dist. add.
Co(II)[b]	td	equil.	td	equil.
Ni(II)[c]	td	oct. add.	pl	pl
Cu(II)[d]	td	td	pl	5-co. add.

pl: planar; td: tetrahedral; dist. add.: adduct with a distorted configuration; equil.: equilibrium consisting of two or more different species; 5-co. add.: 5-coordinate adduct; oct.: octahedral

a) Present study and ref. (1). b) Ref. (4).
c) Ref. (3). d) S. Yamada, unpublished.

The complexes of the type VO(H-SAL.R)$_2$ in pyridine, R being Ph, 3-CH_3-Ph and 4-CH_3-Ph, exhibit similar spectra to those of the corresponding 5,6-benzo-complexes. On the contrary, for R=2-CH_3-Ph and 2,6-$(CH_3)_2$-Ph and X=H, the spectral change on going to the pyridine solution is different from the other complexes of the type VO(H-SAL.aryl)$_2$, as shown in Fig. 1 and Table 3, the *d-d* bands of the former in pyridine being shifted toward much lower frequencies than in the solution of the latter. This anomalous spectral change indicates that VO(H-SAL.2-CH_3-Ph)$_2$ and VO(H-SAL.2,6-$(CH_3)_2$-Ph)$_2$ in pyridine form six-coordinate pyridine adducts having a more distorted configuration than that of the corresponding adduct of VO(H-SAL. Ph)$_2$. This difference between the complexes with X=H and those with X=5,6-benzo may be ascribed to the effect of the field strength produced by the in-plane ligands. A similar difference in the stereochemistry of the complex, as a result of the introduction of a substituent in the benzene nucleus, was sometimes observed with the corresponding complexes of cobalt(II), nickel(II) and copper(II).[4]

Comparison of the present results with those of the previous papers[3,4] is summarized in Table 4. We see that the distortion in the solid state occurs more easily with R=α-branched alkyl groups than with R=aryl groups.

Table 4 also shows that the vanadium(IV) ion seems to take up an additional ligand such as pyridine to form a six-coordinate adduct more readily than do the cobalt(II), nickel(II), and copper(II) ions.

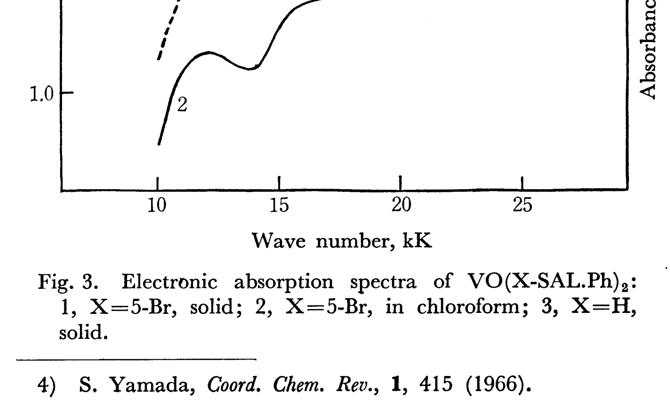

Fig. 3. Electronic absorption spectra of VO(X-SAL.Ph)$_2$: 1, X=5-Br, solid; 2, X=5-Br, in chloroform; 3, X=H, solid.

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[3] S. Yamada, A. Takeuchi, K. Yamanouchi, and K. Iwasaki, This Bulletin, **42**, 131 (1969).

[4] S. Yamada, *Coord. Chem. Rev.*, **1**, 415 (1966).

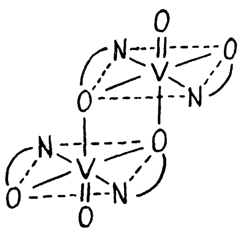

Fig. 4. A possible structure for VO(5-X-SAL.Ph)$_2$ in the solid state, X being Cl and B .

TABLE 5. ABSORPTION MAXIMA OF OXOVANADIUM(IV) COMPLEXES OF THE TYPE VO(5-X-SAL.Ph)$_2$

X	State	Absorption max, kK (log ε for solution)
Cl	solid	13.1, 18.2
	pyridine	13.5(1.62)
Br	solid	13.0, 18.0
	$CHCl_3$	12.0(1.24), 16.5(1.56)sh, 18.7(1.70)sh
	pyridine	13.7(1.58)

sh: shoulder

The spectra of VO(5-Cl-SAL.Ph)$_2$ and VO(5-Br-SAL.Ph)$_2$ in the solid state, shown in Fig. 3 and Table 5, differ remarkably from those of other complexes such as VO(H-SAL.Ph)$_2$ and VO(5,6-benzo-SAL.Ph)$_2$. Moreover, their magnetic moments (Table 2) are lower than the spin-only moment 1.73 B. M. for the d^1 system, showing that some sort of interaction may be present between vanadium(IV) ions. It is therefore likely that their configuration differs from the square pyramidal one. One of the probable configurations for these two complexes in the soid state is a binuclear one, as shown in Fig. 4. For a definite conclusion, however, an X-ray study is necessary. Examination of their infrared spectra yielded no significant conclusion. The low solubility of these compounds did not allow the determination of their molecular weights.

The 5-bromo-substituted complex is moderately soluble in non-coordinating solvents, although the 5-chloro-substituted complex is only slighlty soluble. The spectrum of VO(5-Br-SAL.Ph)$_2$ in chloroform, as shown in Fig. 3, is different from that of the same complex in the solid state but similar to the spectrum typical of the square-pyramidal oxovanadium(IV) complex of this series. It is thus found that the 5-bromo-substituted complex has a uninulcear, square-pyramidal configuration in the non-donor solvent. Inspection of the spectra also indicates that these complexes in pyridine form pyridine adducts having a similar configuration to that of VO(H-SAL.Ph)$_2$ or VO(5,6-benzo-SAL.Ph)$_2$.

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