A Study of Metal Complexes of Analytical Importance. II[1]. *Complexes of Salicylaldoxime and C-Methyl-salicylaldoxime with Vanadium(V)*[2]

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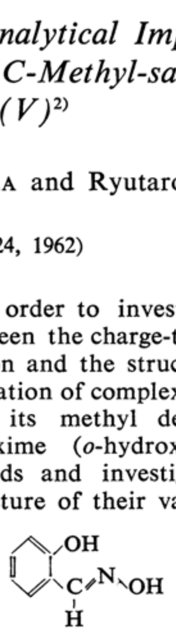
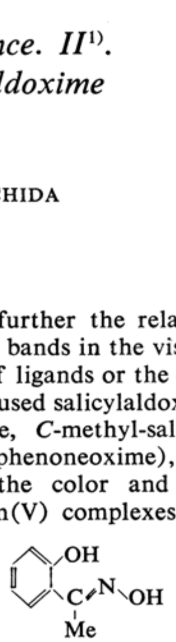
About the complexes of quinquevalent vanadium, there are few reports, and most of them concern studies of the so-called "solution complexes". Very few vanadium(V) complexes have been isolated. One of the purposes of this work is to isolate new complexes of vanadium(V).

Quinquevalent vanadium has no d-electrons, so its complexes would show no ligand field band, which comes from the d-d transition, and they would be colorless or yellow. Some complexes of vanadium(V), however, have a deep color. One of the examples of these colored complexes is the 8-quinolinol complex, which was reported on in Part I of this series[1]. The strong bands of this complex in the visible region are considered to be electron-transfer bands.

2-Methyl-8-quinolinol was found to form two complexes[1], one of them colored black, due to the charge-transfer bands, and the other, yellow. It was concluded that in the black complex the ligands were coordinated to the central metal as bidentate ligands, while in the yellow complex the ligands were coordinated as unidentate ligands[1].

In order to investigate further the relation between the charge-transfer bands in the visible region and the structure of ligands or the configuration of complexes, we used salicylaldoxime and its methyl derivative, *C*-methyl-salicylaldoxime (*o*-hydroxyacetophenoneoxime), as ligands and investigated the color and the structure of their vanadium(V) complexes.


Salicylaldoxime
(symbol : $salmH_2$)


C-Methyl-salicylaldoxime
(symbol : $Me\text{-}salmH_2$)

Results and Discussion

Complexes of Salicylaldoxime with Vanadium(V).—The reaction of vanadate with salicylaldoxime at a pH value of 1 produces a black precipitate. Flagg and Furman[3] reported that in the black precipitate, the ratio of vanadium to salicylaldoxime was 2 : 3; i.e., the complex had the formula $C_{21}H_{21}N_3O_{10}V_2$. The complex represented by this formula is very queer, because in it vanadium should be quadrivalent. The experiments were, therefore, repeated by us. The complex which was formed under almost

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[1] Part I of this series: H. Nakamura, Y. Shimura and R. Tsuchida, This Bulletin, 34, 1143 (1961).

[2] A part of this study was presented at the Symposium on Coordination Compounds of the Chemical Society of Japan, Osaka, November, 1961.

[3] J. F. Flagg and N. H. Furman, *Anal. Chem.*, 12, 663 (1940).

the same conditions as mentioned above had the empirical formula approximately represented by $C_{21}H_{21}N_3O_{11}V_2$, and repeated experiments showed that the composition of the precipitate varied with a slight difference in the experimental conditions. As the infrared absorption spectra of the precipitate were not very sharp, it was concluded that the precipitate was not a pure substance. In order to prepare a pure complex having a structure similar to that of the 8-quinolinol vanadium(V) complex (1:2-complex), a large excess of the ligand was used, but the attempt was unsuccessful. In aqueous solution, no experiments with different pH values or temperatures were successful in the preparation of the desired complex.

As will be seen below, the recrystallization of the precipitate from benzene containing free salicylaldoxime gave the 1:2-complex in a pure crystalline state. The salicylaldoxime-vanadium(V) complex thus obtained may have a structure similar to that of the 8-quinolinol-vanadium(V) complex (Fig. 1a or 1b); its color is black in the crystalline state and violet in benzene and carbon tetrachloride. The absorption spectrum of the complex in benzene is shown in Fig. 2a. The intensity of the absorption band at 54.6×10^{13} sec^{-1} is as large as that of the corresponding band of the 8-quinolinol complex. The absorption spectrum of [VO(OH)(salmH)$_2$] in carbon tetrachloride coincided with that in benzene. In many other solvents, however, the complex changed its color as time passed after dissolution. In acetone, for example, the complex dissolved immediately after dissolution to show a violet color, which was quite like the color of the benzene solution, but it gradually changed to brown, and finally the color became almost yellow. The absorption spectrum of the complex in acetone about fifteen minutes after dissolution is shown in Fig. 2b. It is considered that the change of color is due to the decomposition of the complex.

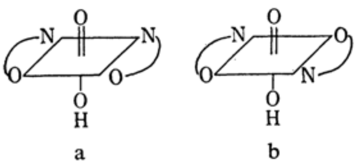

Fig. 1.

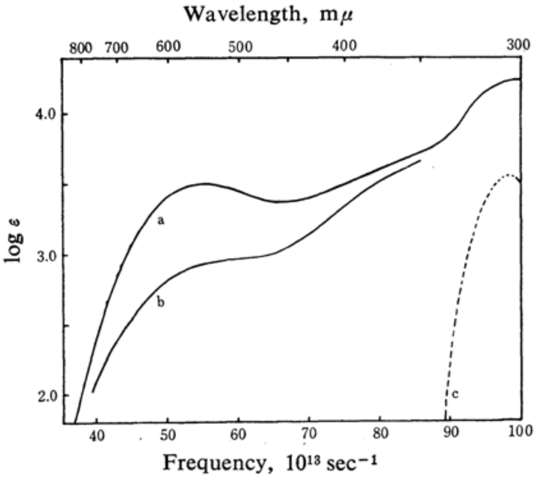

Fig. 2. Absorption spectra of salicylaldoxime-vanadium(V) complex.

a —— [VO(OH)(salmH)$_2$] in benzene
b —— [VO(OH)(salmH)$_2$] in acetone (about fifteen minutes after dissolution)
c - - - Free salicylaldoxime in benzene

The Absorption Spectrum of the Salicylaldoxime Complex in Dimethylformamide.—As was mentioned above, the salicylaldoxime complex dissolved in some solvents to show a violet color immediately after dissolution. This was not the case with dimethylformamide, which formed a solution showing a different color. Although the absorption bands of the complex in dimethylformamide decreased in intensity with time, the color of the solution immediately after dissolution was not violet, but a deep, reddish brown. The absorption curves of the complex in the 460~600 mμ range in dimethylformamide are shown in Fig. 3. In dimethylformamide the complex dissolved very rapidly, so it was possible to measure the change in the absorption intensity with time from the

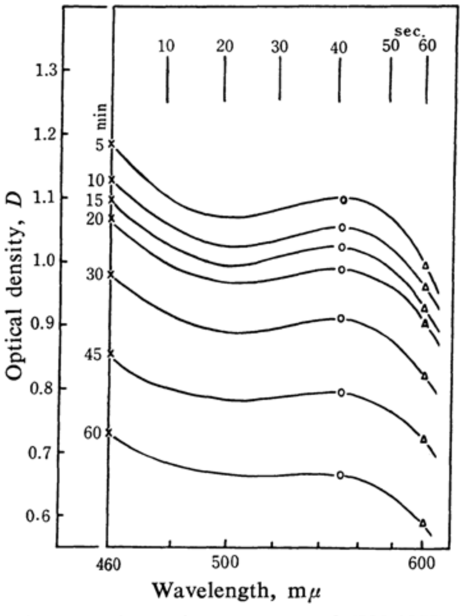

Fig. 3. Absorption spectra of [VO(OH)·(salmH)$_2$] in dimethylformamide. Concn.: 3.49×10^{-4} M

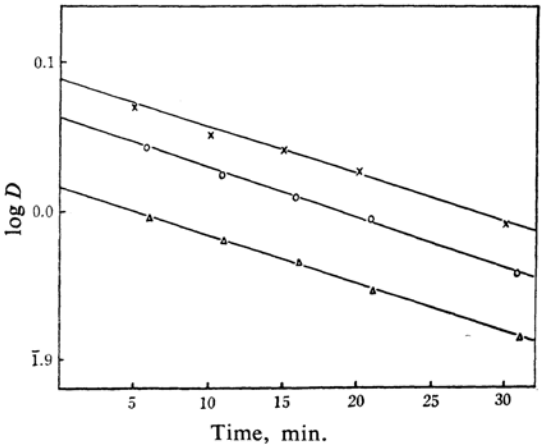

Fig. 4. Plots of log D vs. time after dissolution. ([VO(OH)(salmH)$_2$] in dimethylformamide: concn., 3.49×10^{-4} M)

× : 460 mμ ○ : 550 mμ △ : 600 mμ

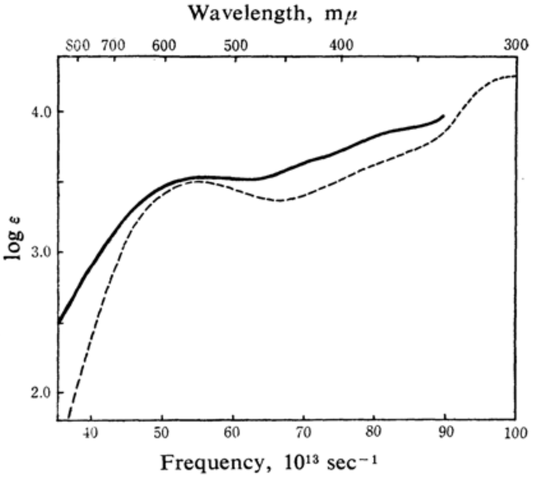

Fig. 5. Absorption spectra of [VO(OH)·(salmH)$_2$].

—— in dimethylformamide
- - - in benzene

instant when the complex was dissolved. From Fig. 3, optical densities at 5, 10, 15, 30, 45 and 60 min. after dissolution at 460 mμ were obtained. Similarly, the values at 600 mμ after 6, 11, 16, 31, 46 and 61 min. were obtained. (It took one minute for the curves to be drawn from 460 mμ to 600 mμ). Optical densities at other wavelengths were also obtained. The logarithmic plot of the optical densities vs. time gave straight lines, showing that the decomposition of the complex was of the first order reaction (Fig. 4). By extrapolating the lines to zero, the optical densities of the complex at "zero time" were obtained. Thus, with similar measurements of other ranges, the absorption spectrum of the complex in dimethylformamide was obtained (Fig. 5). A comparison of the absorption spectra of the salicylaldoxime complex in benzene and in dimethylformamide shows a distinct difference which cannot be regarded as the effect of the solvent. In dimethylformamide the bands are broader and are situated at longer wavelengths than in benzene. 8-Quinolinol-vanadium(V) complex has two isomers, the cis and the trans$^{1)}$ (Fig. 1). The absorption spectra of these isomers are shown in Fig. 6. From a comparison of the spectra of the salicylaldoxime complex with those of 8-quinolinol complexes, it has been concluded that the salicylaldoxime complex has the trans structure (Fig. 1b) in benzene or in carbon tetrachloride and the cis structure (Fig. 1a) in dimethylformamide.

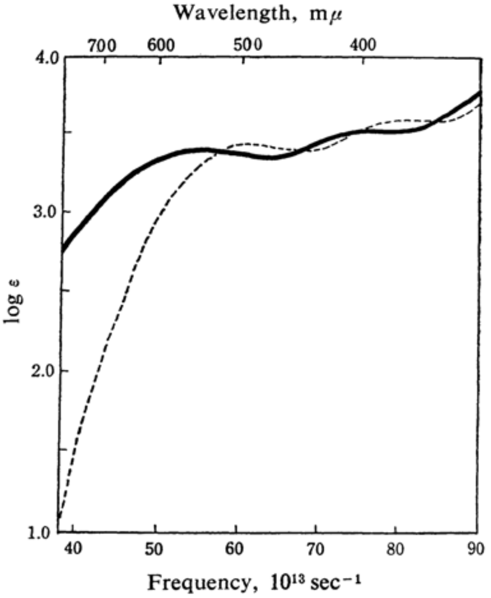

Fig. 6. Absorption spectra of 8-quinolinol-vanadium(V) complexes$^{1)}$.

—— cis-form - - - trans-form

The Esterified Complex of Salicylaldoxime with Vanadium(V).—The 1:2-complex of salicylaldoxime could be recrystallized from ethanol. The complex thus recrystallized from ethanol was esterified in OH, that is, [VO·(O–Et)(salmH)$_2$]. The absorption spectrum of [VO(O–Et)(salmH)$_2$] in benzene is shown in Fig. 7. It has large charge-transfer bands which are quite similar to that of [VO(OH)·(salmH)$_2$], and the esterification does not effect any such remarkable change of color as was reported for 8-quinolinol complexes$^{1)}$.

The Complex of *C*-Methyl-salicylaldoxime with Vanadium(V).—As was reported in Part I of this series$^{1)}$, the difference between the reactions of 8-quinolinol and 2-methyl-8-quinolinol

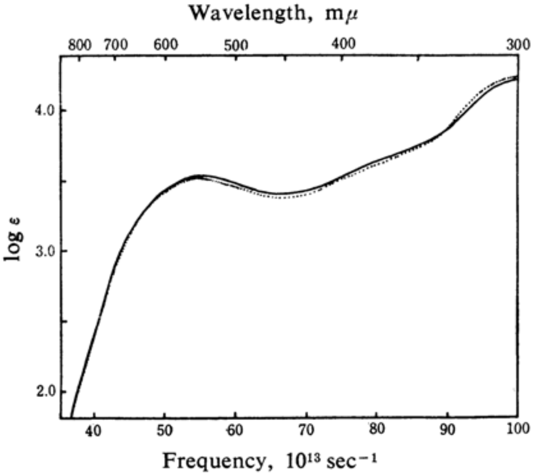

Fig. 7. Absorption spectra of [VO(O-Et)·(salmH)$_2$] (——) and [VO(OH)(salmH)$_2$] (······) in benzene.

with vanadate is a very interesting problem. At pH values between 3 and 5 the former produced a black complex, whereas the latter gave a yellow complex under the same experimental conditions[1]. Concerning this phenomenon, the color and the structure of the complexes of salicylaldoxime and *C*-methyl-salicylaldoxime with vanadium(V) are problems of great interest.

C-Methyl-salicylaldoxime produced, with vanadate at a pH value of 1, a reddish-brown precipitate, not a black one. It was found that the color of the precipitate depended on the pH value of the solution of vanadate. At a higher pH value, the color of the precipitate was yellow. Contrary to the 2-methyl-8-quinolinol complex, the yellow precipitate did not change in color upon heating or drying. The yellow precipitate has no water of crystallization.

The preparation of a black complex like that of the salicylaldoxime complex was attempted. Lowering of the pH value of the solution of vanadate was effective in producing a rather dark-colored precipitate, but from an aqueous solution it was not possible to obtain a black complex. The precipitate which had been separated from the aqueous solution dissolved in many solvents to show yellow colors. After many attempts, it was found that the precipitate dissolved gradually in boiling benzene and that the color of the solution became violet. Evaporation of the solvent from the violet solution, however, produced a brown precipitate. Therefore, the benzene solution saturated with the complex at the boiling point was cooled rapidly and frozen. After separation of the frozen solvent, brownish-black crystals were obtained. It was observed under a microscope that the crystals were a mixture of yellow and black crystals. As the yellow crystals were soluble in warm alcohol, the black crystals were obtained in a pure state by washing the mixture repeatedly with warm alcohol. The black complex was the 1:2-complex of *C*-methyl-salicylaldoxime corresponding to that of salicylaldoxime. The absorption spectrum in benzene of the former was quite similar to that of the latter (Fig. 8).

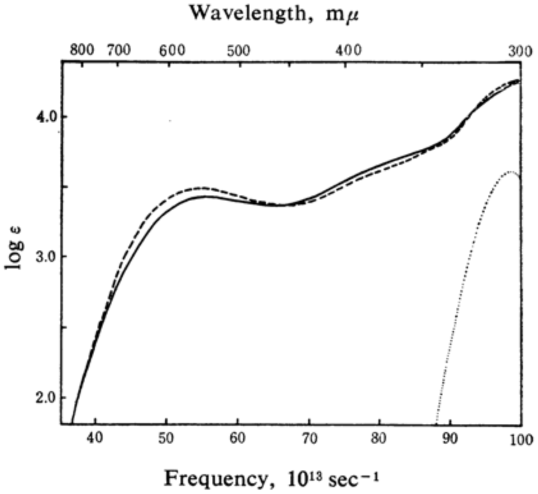

Fig. 8. Absorption spectra of [VO(OH)(Me-salmH)$_2$] (——), [VO(OH)(salmH)$_2$] (- - -) and free *C*-methyl-salicylaldoxime (······) in benzene.

The Absorption Spectrum of *C*-Methyl-salicylaldoxime in Dimethylformamide. — In a way similar to that used for the salicylaldoxime complex, the absorption spectrum of the *C*-methyl-salicylaldoxime complex in dimethylformamide was determined (Fig. 9a).

By a comparison of Figs. 6 and 9, it can be seen that the *C*-methyl-salicylaldoxime complex has the cis structure in dimethylformamide and the trans structure in benzene, as has the salicylaldoxime complex.

The Yellow Form of the *C*-Methyl-salicylaldoxime Complex. — Recrystallization of the crude complex from toluene gave a yellow complex. The absorption spectrum of the yellow form is shown in Fig. 9c. The great difference between the colors of the black and the yellow forms cannot be ascribed only to the cis-trans isomerization.

The infrared absorption spectra of these black and yellow complexes give us some suggestions about their structures. Although the black form exhibits an O–H stretching band of =N–OH[4] at 3380 cm^{-1}, the yellow form

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[4] G. Duyckaerts, *Bull. soc. roy. sci. Liège*, **21**, 196 (1952).

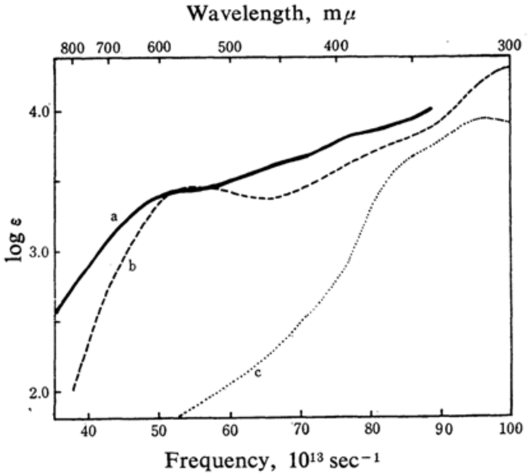

Fig. 9. Absorption spectra of *C*-methyl-salicylaldoxime-vanadium(V) complexes.
- a ━━ $[VO(OH)(Me\text{-}salmH)_2]$ in dimethylformamide
- b - - - $[VO(OH)(Me\text{-}salmH)_2]$ in benzene
- c ······ $[V(OH)(Me\text{-}salm)_2]$ in dimethylformamide

does not show any band above the 4000∼3000 cm^{-1} region. This suggests that in the yellow form the oxygen atoms of a oxime character are bound to the vanadium ion. That is, it is probable that in the yellow form, the ligands are coordinated to the vanadium ion with two oxygen atoms. This view is supported by the elementary analysis of $V(OH)(Me\text{-}salm)_2$ and also by the fact that the band at 1620 cm^{-1} of the black form shifts to 1642 cm^{-1} in the yellow form[5].

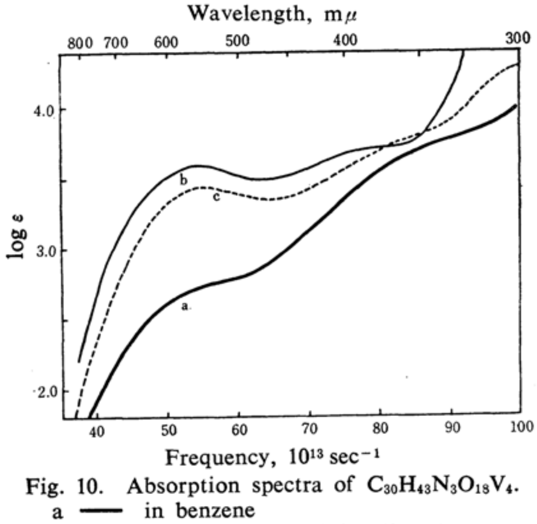

Fig. 10. Absorption spectra of $C_{30}H_{43}N_3O_{18}V_4$.
- a ━━ in benzene
- b —— in benzene containing ligand
- (c - - - represents $[VO(OH)(Me\text{-}salmH)_2]$ in benzene)

The Complex Recrystallized from Methanol.—Recrystallization of the yellow form from methanol gave brown planar crystals. The color of the benzene solution of the crystals was also brown (Fig. 10a). Adding *C*-methyl-salicylaldoxime to the solution made its color violet, a color which was similar to that of the black form in the same solvent (Fig. 10b). The composition of the brown crystals was, however, very complicated ($C_{30}H_{43}N_3O_{18}V_4$), and further investigation is nescessary to solve this problem.

Experimental

Preparation of the Salicylaldoxime-Vanadium Complex. — The 1 : 2-complex was prepared as follows: 1.9 g. (1/100 mol.) of sodium metavanadate tetrahydrate ($NaVO_3 \cdot 4H_2O$) was dissolved in 50 ml. of 0.2 N sodium hydroxide. The pH value of the solution was adjusted to about 1 by the use of 2 N sulfuric acid. After the solution had been stirred for thirteen minutes, the black precipitate was filtered, washed and dried in the air. Six hundred milligrams of dried precipitate were refluxed with 200 ml. of benzene containing 500 mg. of salicylaldoxime for one hour. After filtration, the solution was concentrated to about 30 ml. and was left to cool. The black crystals separated were filtered and washed with benzene.

Found: C, 55.38; H, 4.24; N, 6.75; V, 11.80. Calcd. for $C_{20}H_{19}N_2O_6V=[VO(OH)(salmH)_2]\cdot C_6H_6$: C, 55.30; H, 4.41; N, 6.45; V, 11.73%.

The ethyl ester of the complex was prepared by recrystallization from ethanol.

Found: C, 49.70; H, 4.13; N, 7.59; V, 13.42. Calcd. for $C_{16}H_{17}N_2O_6V=[VO(O\text{-}Et)(salmH)_2]$: C, 49.99; H, 4.46; N, 7.28; V, 13.27%.

Preparation of the *C*-Methyl-salicylaldoxime-Vanadium(V) Complex.—*C*-Methyl-salicylaldoxime was prepared by the method of Poddar[6].

The complex was prepared as follows: 1.9 g. (1/100 mol.) of sodium metavanadate tetrahydrate was dissolved in 50 ml. of 0.2 N sodium hydroxide. The pH value of the solution was adjusted to 1.2 by diluted sulfuric acid. To the solution was added 3.1 g. (2/100 mol.) of *C*-methyl-salicylaldoxime dissolved in 6 ml. of acetone. After three hours, the crude precipitate was filtered and washed with water.

The black form was prepared as follows: 1.0 g. of the crude precipitate was refluxed for three hours with one liter of benzene. After filtration, the solution was cooled with ice and left in a refrigerator. The frozen colorless solvent, which did not contain the complex was removed from the frozen mass with a spoon. The residue was melted at room temperature, and the crystals were separated by filtration. A mixture of yellow and black crystals was thus obtained. The mixture was put into 100 ml. of warm alcohol and stirred. After filtration the crystals were washed several times more with warm alcohol. The crystals thus obtained

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[5] L. J. Bellamy, "The Infrared Spectra of Complex Molecules", 2nd Ed., John Wiley & Sons, Inc., New York (1958).

[6] S. N. Poddar, *Z. anal. Chem.*, **154**, 254 (1957).

were black in color. The absence of yellow crystals was confirmed microscopically.

Found: C, 52.63; H, 4.68; N, 7.10; V, 12.20. Calcd. for $C_{18}H_{19}N_2O_6V$=[VO(OH)(Me-salmH)$_2$]·1/3C_6H_6: C, 52.75; H, 4.67; N, 6.83; V, 12.42%.

The yellow form was prepared as follows: 0.75 g. of the crude complex was dissolved in 500 ml. of toluene at 95°C. After filtration, the solution was left in a refrigerator. The reddish-brown crystals which separated were washed repeatedly with carbon tetrachloride to remove the black form.

Found: C, 52.32; H, 4.16; N, 7.29; V, 13.70. Calcd. for $C_{16}H_{15}N_2O_5V$=[V(OH)(Me-salm)$_2$]: C, 52.47; H, 4.13; N, 7.65; V, 13.91%.

Measurement. — Visible and ultraviolet absorption spectra were determined with a Beckman DU and a Hitachi EPS-2 spectrophotometer using cells with light paths 1.0 and 0.10 cm. in length respectively.

The infrared absorption measurements were made by the KBr pressed-disk technique in a Hitachi EPI-2 infrared spectrophotometer.

Summary

New complexes of salicylaldoxime (symbol: salmH_2) and *C*-methyl-salicylaldoxime (symbol: Me-salmH_2) with vanadium(V), [VO(OH)·(salmH)$_2$] (A), [VO(O–Et)(salmH)$_2$] (B), [VO·(OH)(Me-salmH)$_2$] (C) and [V(OH)(Me-salm)$_2$] (D) were prepared. A, B and C complexes were dark-colored, while the D complex was light-colored.

The absorption spectra of A and C in dimethylformamide were determined. Based on the measurements of the visible, ultraviolet and infrared absorption spectra of these complexes, the following conclusions were drawn:

1) In benzene complex A has the trans structure, while in dimethylformamide it has the cis structure.

2) Complex C has the same properties as A.

3) The esterification of A does not cause any remarkable change in color.

4) The great difference between the color of C and that of D comes from the difference in the donor atoms of the ligand. In the former the ligands are coordinated as N, O-chelates, and in the latter, as O, O-chelates.

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