# *Study on Metal Complexes of Analytical Importance. I. Vanadium Complexes of 8-Quinolinol and 2-Methyl-8-quinolinol*[1]

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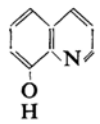
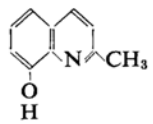
8-Quinolinol (A) is a popular analytical reagent, being used in the analysis of vanadium.



A

8-Quinolinol
(symbol: oxinH)



B

2-Methyl-8-quinolinol
(symbol: $CH_3$-oxinH)

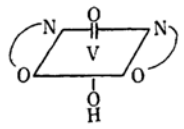
The reaction of vanadate with 8-quinolinol in aqueous solution at pH 4~5 produces a bluish-black complex. This complex dissolves in lower aliphatic alcohols to give red solutions, while in chloroform it gives a violet one[2]. From boiling alcohol solutions saturated with this complex is deposited a brownish black complex on cooling, which dissolves in chloroform to show red color instead of violet.

Bielig and Bayer[2] reported that these two complexes were geometrical isomers which had a molecular formula $[VO(OH)(oxin)_2]$, and they named the bluish-black complex "violet form" and the brownish black complex "red form" by the colors of the chloroform solutions of these complexes.

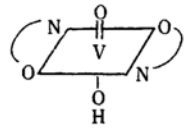
1) A part of this study was presented at the Symposium on Coordination Compounds of the Chemical Society of Japan, Sendai, September, 1960.

2) H.-J. Bielig and E. Bayer, *Ann.*, **584**, 96 (1953).

Based on rather weak experimental evidences, they reported that the violet form had the cis structure and that the red form had the trans structure which are shown in Fig. 1.



cis structure
Fig. 1 (a)



trans structure
Fig. 1 (b)

Contrary to their conclusion, Blair and Pantony[3] assumed that the red form had the molecular formula [VO(O–R)(oxin)$_2$] (R is an alkyl group), namely that the complex was an alkyl ester of [VO(OH)(oxin)$_2$]. As for the violet form, Blair and Pantony explained that it had the trans structure, but no experimental evidence was given.

In order to decide the configurations of the complexes, we have prepared new complexes of 2-methyl-8-quinolinol, and from experimental data of these complexes have discussed the problem.

## Results and Discussion

**Complexes of 2-Methyl-8-quinolinol with Vanadium(V).**—As will be seen in the experimental part, 2-methyl-8-quinolinol produces with vanadate a yellow complex, not a black one. In the case of 8-quinolinol a bluish-black complex (violet form) is separated under the same conditions. In this respect, the yellow complex resembles neither the violet nor the red form.

Recrystallization of the yellow complex from 98% methanol also produces a yellow complex. The complex thus obtained is yellow in crystalline state, but shows red color in absolute methanol giving an absorption band at 60.6 $\times 10^{13}$ sec$^{-1}$ (Fig. 2a). The solution in 98% methanol gives a weaker band at the same frequency (Fig. 2b). The higher the water content of the solvent is, the weaker is the absorption band (Fig. 2b–f). Thus, the color in 90% methanol solution is almost yellow.

Elementary analysis of the yellow complex shows that it has the formula of VO(OH)(CH$_3$-oxin)$_2$·2H$_2$O, and over phosphorus pentoxide in vacuo the complex gradually changes black with decrease of its weight. In three weeks the color changes completely to black, and the decrease of weight corresponds to two molecules of water. The black complex thus obtained has the empirical formula VO(OH)(CH$_3$-

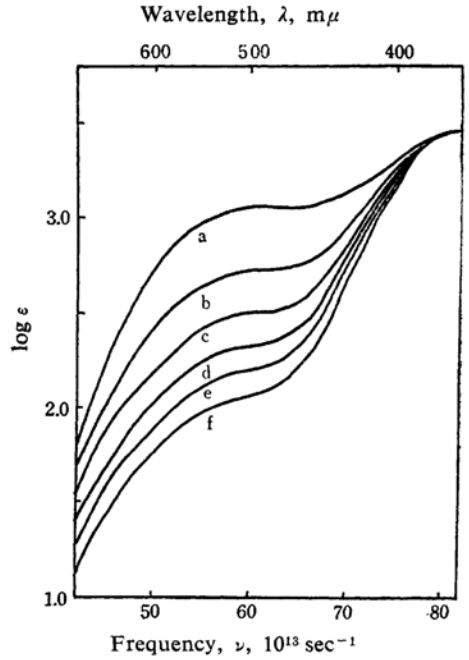



Fig. 2. Absorption spectra of [VO(OH)(CH$_3$-oxin)$_2$(OH$_2$)$_2$] in absolute methanol and in diluted methanol.
a, absolute; b, 98%; c, 96% d, 94%; e, 92%; f, 90%.

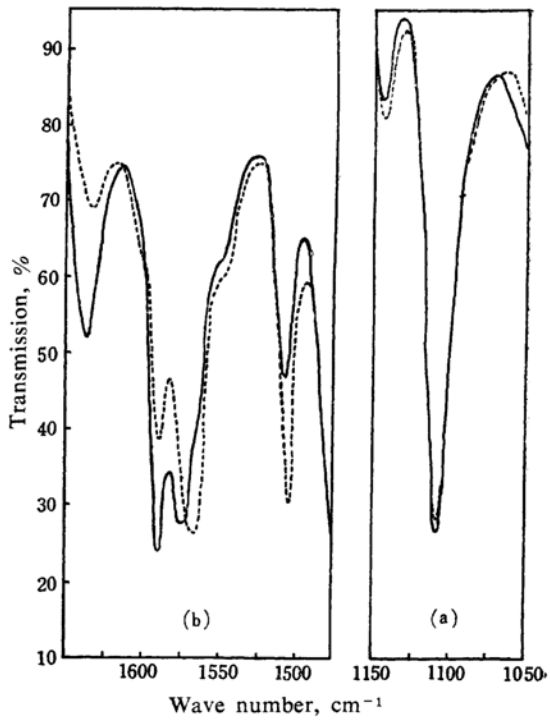



Fig. 3. Infrared absorption spectra of [VO(OH)(CH$_3$-oxin)$_2$(OH$_2$)$_2$] (——) and [VO(OH)(CH$_3$-oxin)$_2$] (----).
(a): C–O stretching band
(b): C=N or C=C stretching bands

3) A. J. Blair and D. A. Pantony, *J. Inorg. Nucl. Chem.*, 5, 316 (1958).

oxin)$_2$. Accordingly it is clear that the difference between the yellow and the black colors is due to the water molecules. Judging from the marked change of the color, the water molecules are not merely of crystallization character but are coordinated. The black complex cannot have the cis structure owing to the steric hindrance between the methyl groups of the ligands. It is considered to have the trans structure (Fig. 1).

Since the maximum coordination number of the quinquevalent vanadium is six, the yellow complex [VO(OH)(CH$_3$-oxin)$_2$(OH$_2$)$_2$] must have an octahedral configuration. Consequently the two 2-methyl-8-quinolinol ions are coordinated as unidentate ligands. The difference between 8-quinolinol and 2-methyl-8-quinolinol is only that the latter has a methyl group at the carbon atom adjacent to the nitrogen atom. Therefore, it seems that the nitrogen atoms are not bound to the vanadium ion. Infrared absorption spectra of these two complexes show that this consideration is correct.

Both the yellow and the black complexes exhibit a strong band of C–O stretching[4] at the same wave number 1108 cm$^{-1}$ (Fig. 3). This shows that in each complex, oxygen atoms are bound to the vanadium ion. If the bond V–O were broken in the yellow complex, the position of the C–O stretching band of the complex would differ from that of the black. Moreover, these complexes show four bands over the region between 1640 and 1500 cm$^{-1}$ which are considered to be C=N or C=C stretching vibrations[5] in the ligands. Considerable differences are recognized between the corresponding bands of the two complexes not only in their positions, but also in intensities (Fig. 3). These differences suggest that in the yellow complex the nitrogen atoms are not bound to the central vanadium ion.

Now we have been led to the conclusion that the yellow complex [VO(OH)(CH$_3$-oxin)$_2$(OH$_2$)$_2$] has an octahedral structure and that the 8-quinolinol ions are not bidentate but unidentate ligands which are bound to the central vanadium ion by their oxygen atoms.

**Structure of the Red Form.**—As was described in the preceding section, the black complex [VO(OH)(CH$_3$-oxin)$_2$] has the trans structure. Therefore, the comparison of the absorption spectrum of [VO(OH)(CH$_3$-oxin)$_2$] with those of the red and the violet forms may give us some suggestions about the structures of these complexes.

The absorption spectra of these three complexes in chloroform are shown in Fig. 4. [VO(OH)(CH$_3$-oxin)$_2$] shows two bands at $60.6\times10^{13}$ and $80.6\times10^{13}$ sec$^{-1}$. The positions

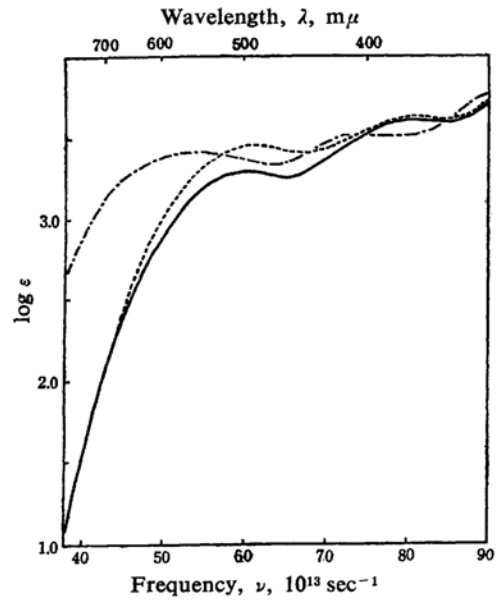



Fig. 4. Absorption spectra of 8-quinolinol-vanadium complexes and 2-methyl-8-quinolinol-vanadium complex in chloroform.
—·— violet form
---- red form
—— [VO(OH)(CH$_3$-oxin)$_2$] (trans)

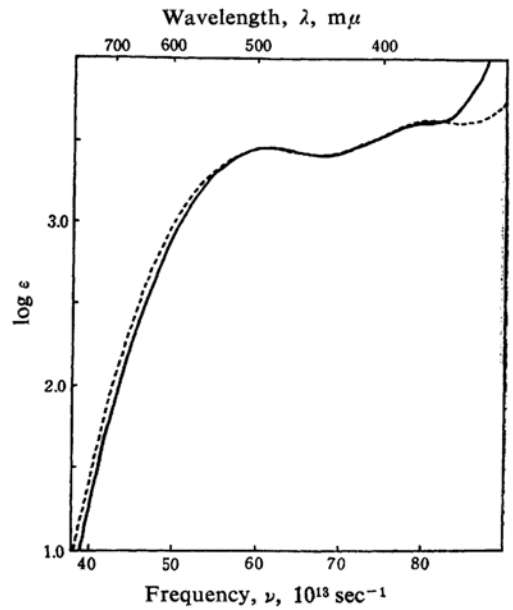



Fig. 5. Absorption spectra of [VO(OH)(oxin)$_2$] (red form) (——) and [VO(O-CH$_3$)(oxin)$_2$] (----) in benzene. The enhancement of the curve (——) at the shorter wavelength region is owing to the absorption of 8-quinolinol which is added in excess.

4) R. G. Charles, H. Freiser, R. Friedel, L. E. Hillard and W. D. Johnstone, *Spectrochim. Acta*, 8, 1 (1956).
5) L. J. Bellamy, "The Infrared Spectra of Complex Molecules", 2nd ed. (1958), pp. 270-286.

of the bands coincide with those of the red form. Accordingly it seems that the red form has the trans and the violet form has the cis structure. In this respect, these results support Bielig's opinion. But as will be seen in the experimental part, Blair's opinion that the red form has a formula $[VO(O\text{–}R)(oxin)_2]$ is also correct. 8-Quinolinol complexes which are recrystallized from boiling methanol and isopropyl alcohol respectively have the empirical formulae corresponding to $[VO(O\text{–}CH_3)(oxin)_2]$ and $[VO(O\text{–}C_3H_7)(oxin)_2]$. To obtain a red 8-quinolinol complex without using alcohols, we examined many solvents. No solvent, however, was effective. Next, the reaction between vanadium(V) quinaldinate and 8-quinolinol in benzene was tried. Instantly the color changed to red and the absorption spectrum of the solution was quite like that of the red form which was obtained from boiling methanol solution (Fig. 5).

Now we can conclude that the violet form has the cis structure, while the red form has the trans structure, and further that the esterification of the red form does not induce any striking change of color.

**Yellow 8-Quinolinol Complex.** — Both the violet and the red forms are almost black in the crystalline state, as was described in the preceding section. But a yellow 8-quinolinol complex can also be obtained, which is prepared as a sodium salt at higher pH[2]. Bielig and Bayer gave the formula $Na[VO(O)(oxin)_2]\cdot H_2O$ to the yellow complex salt. They carried out the chemical analysis of the yellow complex after drying it over phosphorus pentoxide at 100°C in a high vacuum. The sodium salt which was dried in air has an empirical formula $NaVO(O)(oxin)_2\cdot 4H_2O$. The yellow color of this salt may be understandable on the assumption that it has the formula $Na[VO(O)(oxin)_2(OH_2)_2]\cdot 2H_2O$ corresponding to the yellow 2-methyl-8-quinolinol complex $[VO(OH)(CH_3\text{-}oxin)_2(OH_2)_2]$.

## Experimental

**Preparation of 2-Methyl-8-quinolinol Complexes of Vanadium.**—The yellow complex was prepared as follows: 3.2 g. of 2-methyl-8-quinolinol was dissolved in 60 ml. of 1 N acetic acid and was diluted to 250 ml. To the solution was added drop by drop 2.0 g. of sodium metavanadate tetrahydrate ($NaVO_3\cdot 4H_2O$) dissolved in 100 ml. of 0.2 N sodium hydroxide. A muddy yellow precipitate appeared. The pH of the mixture was adjusted to 5.0 by the use of 1 N acetic acid and it was digested for two hours at 70°C. The crude complex thus obtained was recrystallized three times from 98% methanol by evaporating the solvent at 40°C in vacuo. The yellow complex obtained as pure crystals was dried over calcium chloride. For analyzing the coordinated water of this complex, heating is not suitable, since the complex decomposes at a high temperature. Therefore, drying over phosphorus pentoxide was adopted for the analysis of the coordinated water.

Found: $H_2O$, 8.10; C, 54.96; H, 4.85; N, 6.40; V, 11.51. Calcd. for $C_{20}H_{17}O_4N_2V\cdot 2H_2O = [VO(OH)(CH_3\text{-oxin})(OH_2)_2]$: $H_2O$, 8.26; C, 55.04; H, 4.85; N, 6.42; V, 11.68%.

The complex is soluble in lower aliphatic alcohols, cyclohexanone, pyridine and diluted solution of alkali, and insoluble in ethyl ether, 2-butanone, cyclohexane, benzene, chloroform, carbon tetrachloride and water.

The black complex was prepared by expeling the water molecules of the yellow complex over phosphorus pentoxide in vacuo.

Found: C, 60.04; H, 4.18; N, 7.10; V, 12.65. Calcd. for $C_{20}H_{17}O_4N_2V = [VO(OH)(CH_3\text{-oxin})_2]$: C, 60.00; H, 4.28; N, 7.00; V, 12.73%.

The black complex is soluble in chloroform, benzene and whatever the yellow complex is soluble in, sparingly soluble in ethyl ether, insoluble in cyclohexane, carbon tetrachloride and in water, and soluble with decomposition in dioxane, acetone and 2-butanone.

**Violet Form of 8-Quinolinol-Vanadium Complex.** —This complex was prepared by the method of Bielig and Bayer[2] and also of Blair and Pantony[3].

**Red Forms of 8-Quinolinol-Vanadium Complex.** —The methyl ester was prepared as follows: 1.0 g. of violet form was refluxed for 90 min. with 400 ml. of methanol. After filtration, the solution was concentrated to about 40 ml. The brownish black crystals then separated were filtered and dried in air.

Found: C, 59.16; H, 4.20; N, 7.35; V, 13.01. Calcd. for $C_{19}H_{15}O_4N_2V = [VO(O\text{–}CH_3)(oxin)_2]$: C, 59.09; H, 3.91; N, 7.25; V, 13.19%.

The isopropyl ester was prepared in almost the same way as was the methyl ester.

Found: C, 61.61; H, 4.66; N, 6.81; V, 12.08. Calcd. for $C_{21}H_{19}O_4N_2V = [VO(O\text{–}C_3H_7)(oxin)_2]$: C, 60.80; H, 4.62; N, 6.80; V, 12.30%.

**Yellow 8-Quinolinol Complex of Vanadium.**— This complex was prepared by the method of Bielig and Bayer[2] and was analyzed after being dried in air.

Found: C, 45.52; H, 4.25; N, 5.91; V, 10.60. Calcd. for $C_{18}H_{20}O_8N_2NaV = Na[VO(O)(oxin)_2(OH_2)_2]\cdot 2H_2O$: C, 45.87; H, 4.27; N, 5.94; V, 10.81%.

**Preparation of Sodium Salt of 2-Methyl-8-quinolinol-Vanadium Complex.**—The same method as that used in the preparation of $Na[VO(O)(oxin)_2(OH_2)_2]\cdot 2H_2O$ was not effective for the preparation of this complex. So the desired complex was prepared as follows: 2.1 g. of $[VO(OH)(CH_3\text{-oxin})_2(OH_2)_2]$ was dissolved in 200 ml. of 0.2 N sodium hydroxide. After being filtered, the solution was concentrated at 50°C in vacuo to 20 ml. The complex salt thus obtained was recrystallized twice from 98% methanol.

Found: C, 48.59; H, 4.65; N, 5.42; V, 10.05. Calcd. for $C_{20}H_{24}O_8N_2NaV = Na[VO(O)(CH_3\text{-oxin})_2(OH_2)_2]\cdot 2H_2O$: C, 48.59; H, 4.89; N, 5.67; V, 10.30%.

**Absorption Spectrum of the Red Form which is Not Esterified.**—For the first time, vanadium quinaldinate was prepared as follows: 0.97 g. of $NaVO_3 \cdot 4H_2O$ was dissolved in 50 ml. of 2 N sodium hydroxide. To this solution was added 1.73 g. of quinaldinic acid dissolved in 50 ml. of 2 N sodium hydroxide. This mixture was acidified with 10 ml. of 2 N acetic acid. The white precipitate which appeared was separated by filtration after it had been digested for two hours at 60°C.

The benzene solution of this complex was colorless. To the solution was added a benzene solution of 8-quinolinol (almost colorless). The solution instantly became red, which was quite similar to the color of the solution of the red form prepared from the violet form by the use of methanol (Fig. 5). The same behavior was recognized in dioxane too.

**Measurements.**—Visible and ultraviolet absorption spectra were determined with a Beckman DU and a Hitachi EPU-2A spectrophotometers using the cells which have 1 and 10 cm. light paths.

Infrared absorption measurements were made by the pressed disk technique in a Hitachi EPI-2 infrared spectrophotometer, the disks being 200 mg. of dried potassium bromide containing 1.5 mg. of complexes.

**Summary**

New complexes, $[VO(OH)(CH_3\text{-oxin})_2]$, $[VO(OH)(CH_3\text{-oxin})_2(OH_2)_2]$ and $Na[VO(O)(CH_3\text{-oxin})_2(OH_2)_2] \cdot 2H_2O$ have been prepared and discussed in relation to the structures.

From experimental evidences of these complexes and of 8-quinolinol-vanadium complexes, we have concluded that the violet form of 8-quinolinol-vanadium complex has a cis configuration and that the red form has a trans one.

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