

Vanadium. Part I. Quinaldinic Acid Complexes

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Quinaldinic acid (QH) produces with vanadyl salt (1) a cream-coloured compound, characterised as $[\text{VOQ}_2] \cdot \text{H}_2\text{O}$ and (2) an olive-green complex $[\text{VO}(\text{H}_2\text{O})\text{Q}_2]$. Both change on heating to cream-coloured $[\text{VOQ}_2]$ and finally decompose to V_2O_5 . A whole series of bluish green complexes of the type $[\text{VO}(\text{X})\text{Q}_2]$ (where X = pyridine, aniline, etc.) has been prepared by the action of aromatic amine or heterocyclic base on either $[\text{VOQ}_2] \cdot \text{H}_2\text{O}$ or on $[\text{VO}(\text{H}_2\text{O})\text{Q}_2]$. These, too, change on heating to $[\text{VOQ}_2]$. All these products are paramagnetic ($\mu = 1.6$ to 1.9 B.M.) and are extremely stable towards air.

Quinquevalent vanadium reacts with this ligand to give pale cream-coloured, diamagnetic $[\text{VO}(\text{OH})\text{Q}_2] \cdot 2\text{H}_2\text{O}$. Compounds of the type $[\text{VO}_2\text{Q}(\text{X})]$ (where X = pyridine or α -picoline) have been prepared by the action of heterocyclic bases on $[\text{VO}(\text{OH})\text{Q}_2] \cdot 2\text{H}_2\text{O}$.

Complex compounds of quadrivalent vanadium with oxalic, malonic, and salicylic acids and with catechol are already known (Sidgwick, "Chemical Elements and their Compounds", Vol. I, Oxford University Press, 1951, p. 822). The vanadyl acetylacetonate complex has been studied by Morgan and Moss (*J. Chem. Soc.*, 1913, 103, 78), by Rosenheim and Mong (*Z. anorg. Chem.*, 1925, 148, 25), and also by Jones (*J. Amer. Chem. Soc.*, 1954, 76, 5995). Drew and Dunton (*J. Chem. Soc.*, 1940, 1064) have described some fairly stable, six-covalent complexes of hydroxyazo and amino-azo dyes. Pfeiffer *et al.* (*J. prakt. Chem.*, 1937, 149, 217) and also Mukherjee and Rây (this *Journal*, 1955, 32, 508) have reported some complexes with Schiff's bases. Bradley *et al.* (*J. Chem. Soc.*, 1858, 4647) have studied some six-co-ordinated alkoxide alcoholates which exist only at a low temperature. Some vanadyl biguanidines have recently been described by Banerjee and Rây (Proceedings of the Symposium on the Chemistry of Co-ordination Complexes, Agra, National Academy of Sciences, Part III, 1959, p. 198). Trujillo *et al.* (*Chem. Abs.*, 1956, 50, 16528; 1957, 51, 11907; 1958, 52, 1966; 1959, 53, 21343; 1960, 54, 2076) have studied in solution the system vanadyl malonate, phosphotungstate, acetylacetonate, *o*-phenanthroline, etc.

Quinquevalent vanadium complexes are not many. The important ones are those with 8-hydroxyquinoline, studied in great details (Welcher, "Organic Analytical Reagents", Vol. I, p. 297; Bielg *et al.*, *Annalen*, 1953, 584, 96; Blair *et al.*, *J. Inorg. Nucl. Chem.*, 1958, 5, 316) and with salicylaldehyde (Bielg and Mollinger, *Annalen*, 1957, 805, 117).

In this laboratory, a variety of organic ligands, namely, quinaldinic acid and its derivatives, hydroxamic acids, hydroxyphenyltriazenes, benzimidazoles, benzotriazoles, oximes, etc., are now being investigated as chelating ligands towards various oxidation states of vanadium**. In this, the first paper of the series, we report the complexes of quadri-

*These have been extensively studied by Dutta and also by other workers as sensitive colorimetric reagents for vanadium (Dutta, this *Journal*, 1959, 35, 243; 1959, 36, 285, 229; Dasgupta and Singh, *J. Sci. Ind. Res.*, 1952, 11B, 268; Bhaduri and Rây, *Z. anal. Chem.*, 1957, 154, 103; Wise and Brandt, *Anal. Chem.*, 1955, 27, 1392).

** A preliminary report on the vanadium complexes of hydroxyphenyltriazenes has already appeared (Dutta and Lahiry, *Chem. & Ind.*, 1961, 78).



FIG. 1. Olive-green aquo-oxo-bis-quinaldinato-vanadium (IV).



FIG. 2. Oxo-bis-quinaldinato-vanadium (IV) monohydrate (cream).

$\Theta^\circ = 4.0; 5.5; 10.5; 11.5; 13.25; 18.00; 19.5; 21.5; 23.75.$

$d(\text{\AA}) = 11.03; 8.04; 4.22; 3.86; 3.36; 2.79; 2.31; 2.10; 1.91.$

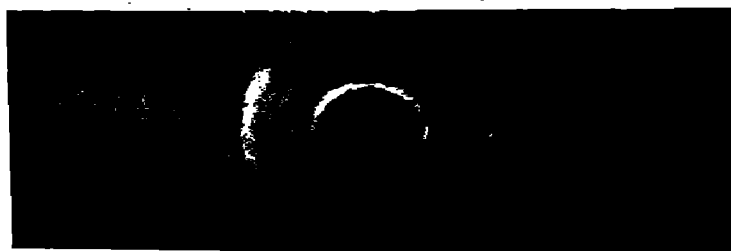
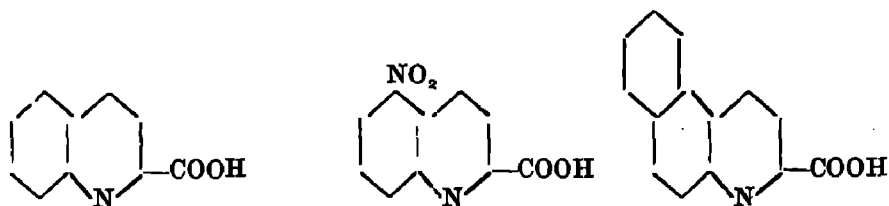


FIG. 3. Aquo-oxo-bis-quinaldinato-vanadium (IV) (olive-green).

$\Theta^\circ = 6.5; 8.5; 10.5; 12.0; 13.5; 14.0; 16.5; 18.75; 21.25.$

$d(\text{\AA}) = 6.8; 5.21; 4.23; 3.70; 3.30; 3.18; 2.71; 2.30; 2.12.$

and of quinquevalent vanadium with quinaldinic acid (quinoline-2-carboxylic acid) and its 5-nitro and 5,6-benzo derivatives, describing first the quadrivalent vanadium compounds.



Quadrivalent Vanadium Complexes

On the addition of vanadyl sulphate to an aqueous solution of quinaldinic acid (QH), a cream-coloured, voluminous precipitate is obtained at *pH* about 3. The precipitation is quantitative within the *pH* range 4 to 6, but appears to be of little value for analytical purpose as the reaction can be substantially suppressed by masking agents, e.g., tartaric acid. This precipitate, after being washed with water and drying over CaCl_2 , corresponds to the composition, $\text{VOQ}_2 \cdot \text{H}_2\text{O}$ (I). On the other hand, when aqueous vanadyl sulphate is added to a methanolic solution of quinaldinic acid and the mixture is allowed to stand overnight, a highly crystalline, glistening, deep olive-green compound (vide Microphotograph, Fig. 1) is obtained, which again, corresponds to the same composition, $\text{VOQ}_2 \cdot \text{H}_2\text{O}$ (II). That these two compounds are different and that the difference in colour is not due to a difference in crystal size have been verified through a study of the two X-ray powder patterns. Comparison of the two diffraction patterns show that the structures of the two substances are different. From the data it is observed that at small angles the cream-coloured sample has two very strong lines corresponding to *d* values of 11.03 Å and 8.04 Å and further out they have two more very strong lines of *d* values 3.86 Å and 3.36 Å. On the other hand, the strongest line of the olive-green sample has the *d* value 6.80 Å. Further out it shows a pair of medium strong lines of *d* values 3.30 Å and 3.18 Å. Furthermore, compound (I) can be dehydrated by heating to the penta-co-ordinated $[\text{VOQ}_2]$. Compound (I) also loses partially its water content in vacuum. Compound (II), however, does not lose any water in vacuo, but does so on heating and changes from olive-green to the cream-coloured $[\text{VOQ}_2]$. In order to have a better insight into the nature of these two varieties, we have obtained the pyrolysis curves of these. It would appear from Fig. 4 that the cream-coloured $[\text{VOQ}_2]$ -

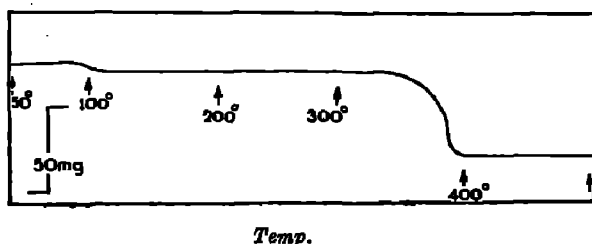
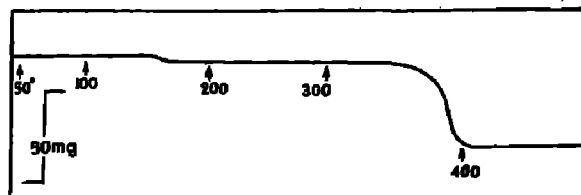


Fig. 4. Pyrolysis of cream-coloured oxo-bis-quinaldinato-vanadium (IV) monohydrate.

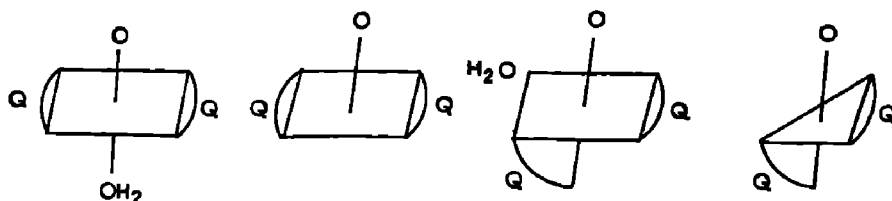
H_2O loses water at 90-100° and then the anhydrous $[\text{VOQ}_2]$ decomposes at 380-400° to V_2O_5 , which remains stable thereafter. As against this, the pyrolysis curve (Fig. 5) of the olive-

green variety (II) shows that the water is lost at 155-65° and thereafter the nature of the pyrolysis curve is identical with that of (I). This evidently shows that the water molecule in the olive-green variety is held much more strongly than in the cream-coloured one. We may therefore conclude that the H_2O molecule in (II) is present inside the co-

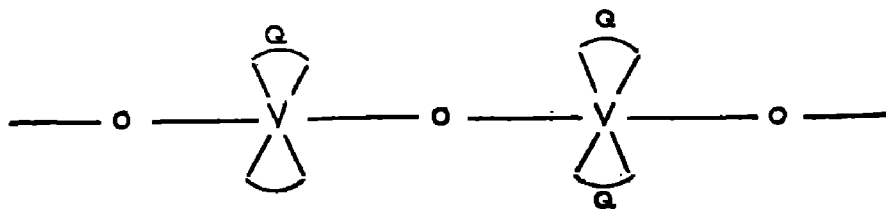


Temp.
Fig. 5. Pyrolysis curve of olive-green coloured aquo-oxo-bis-quinaldinato vanadium (IV).

ordination zone, giving the complex an octahedral structure, whereas the H_2O in (I) is held in the crystal lattice, rather than in the inner sphere. Thus the cream-coloured $[VOQ_2] \cdot H_2O$ or the anhydrous VOQ_2 is, in reality, a penta-co-ordinated complex, unless one assumes the rather improbable feature of one 'O' taking two co-ordination positions. The pyrolysis curves reveal something more. The curves of compounds (I) and of (II) are identical after the loss of the water molecule. This means in both cases the remaining $[VOQ_2]$ has the same structure. A compound, such as is $[VOQ_2]$, can have two possible structures, a square pyramid or a trigonal bipyramid.

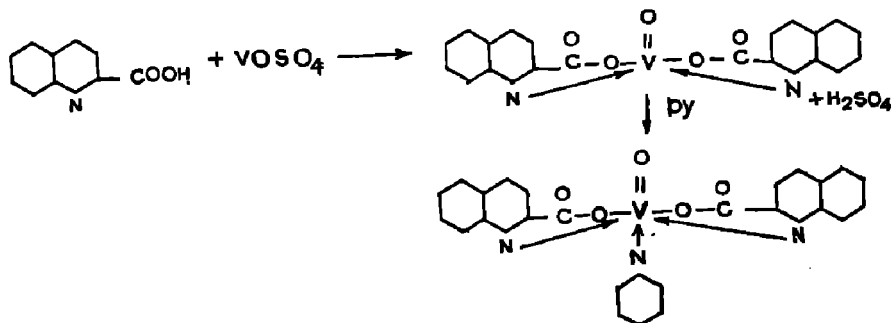


If in the olive-green compound the 'O' and ' H_2O ' are *trans* to one another, then the anhydrous compound will have a square pyramid structure. On the contrary, if ' OH_2 ' is *cis* to 'O', then the loss of ' OH_2 ' would result in a trigonal bipyramid structure. Since the *trans* structure is generally more stable than the *cis*, we would prefer to conclude that the olive-green compound has *trans* structure and that the anhydrous compound has



therefore a square pyramid configuration. One, however, cannot rule out the possibility of a polymeric structure for $[VOQ_2]$, but the very poor solubility of the substance in all

readily dissolves to produce a greenish brown solution, which soon deposits fine bluish green crystals of the composition $[\text{VO}(\text{py})\text{Q}_2]\text{H}_2\text{O}$. This compound loses its pyridine and water on heating; first water is lost, then the pyridine, and finally the colour changes to cream resulting in the formation of $[\text{VOQ}_2]$. The olive-green variety (II) on treatment with pyridine produced identical bluish green crystals of $[\text{VO}(\text{py})\text{Q}_2]\text{H}_2\text{O}$, having the same properties. The pyridine complex is quite stable at ordinary temperature. The action of pyridine on the anhydrous $[\text{VOQ}_2]$ resulted in the separation of bluish green crystals of composition $[\text{VO}(\text{py})\text{Q}_2]$. This compound furnishes an evidence to the effect that the pyridine molecule is inside the co-ordination sphere, as otherwise, with pyridine of crystallisation there is not much ground for the compound changing its colour from cream to bluish green. We have also obtained the infrared spectra of both $[\text{VO}(\text{py})\text{Q}_2]\text{H}_2\text{O}$ and also of $[\text{VO}(\text{py})\text{Q}_2]$ (Fig. 8.). Besides showing all the characteristic bands of the cream-coloured $[\text{VOQ}_2]\text{H}_2\text{O}$ and of the olive-green $[\text{VO}(\text{H}_2\text{O})\text{Q}_2]$, these bluish green varieties present a new, sharp, and strong band at $700\text{-}710\text{ cm}^{-1}$, which is certainly related to the presence of a heterocyclic pyridine in the molecule (Bellamy, *loc. cit.*). But, again, the spectra do not help to clarify the position of the aqua molecule. The sixth co-ordination position in the octahedron of vanadyl quinaldinate has also been variously filled up with amines, such as, α -picoline, aniline, methylantranilate, diphenylamine, and also by dimethylformamide. The α -picoline and the methylantranilate complexes could not be obtained by heating $[\text{VOQ}_2]\text{H}_2\text{O}$ with the amine, instead the $[\text{VOQ}_2]\text{H}_2\text{O}$ was left in contact with the amine. The dimethylformamide compound is the darkest bluish green in the whole series. β -Naphthylamine also produced a light bluish green product, which unfortunately did not provide satisfactory analytical results. Ammonia or aliphatic amines dissolved $[\text{VOQ}_2]\text{H}_2\text{O}$ producing a brown solution, indicating probably oxidation to the pentavalent state. The aliphatic amines are much stronger bases compared to aromatic amines and pyridine and hence have a strong alkaline action resulting in oxidation. Indeed, addition of VOSO_4 to an alkaline QH solution produces a light brown solution. Ligands, such as, quinoline, isoquinoline, and quinaldine, failed to produce any bluish green product. This, no doubt, is related to the bigger size of the ligand molecule, which is difficult to fit into the octahedron. We have also investigated the action of dioxan, tetrahydrofuran* (typical of co-ordination through 'O'), and also of thiophen (co-ordination through S). In all these cases light bluish green to light green products were obtained. We may therefore conclude that the tendency of quadrivalent vanadium to assume an octahedral structure is quite prominent.



Like the amine complexes, these compounds also lose on heating the co-ordinated dioxan,

*This is well known to have the ability of stabilising lower valent states of metals in complexes e.g., in $\text{Li}[\text{Ti}(\text{bipy})_2] \cdot 3.5\text{-C}_4\text{H}_8\text{O}$ (Herzog and Taube, *Angew Chem.*, 1958, 70, 469).

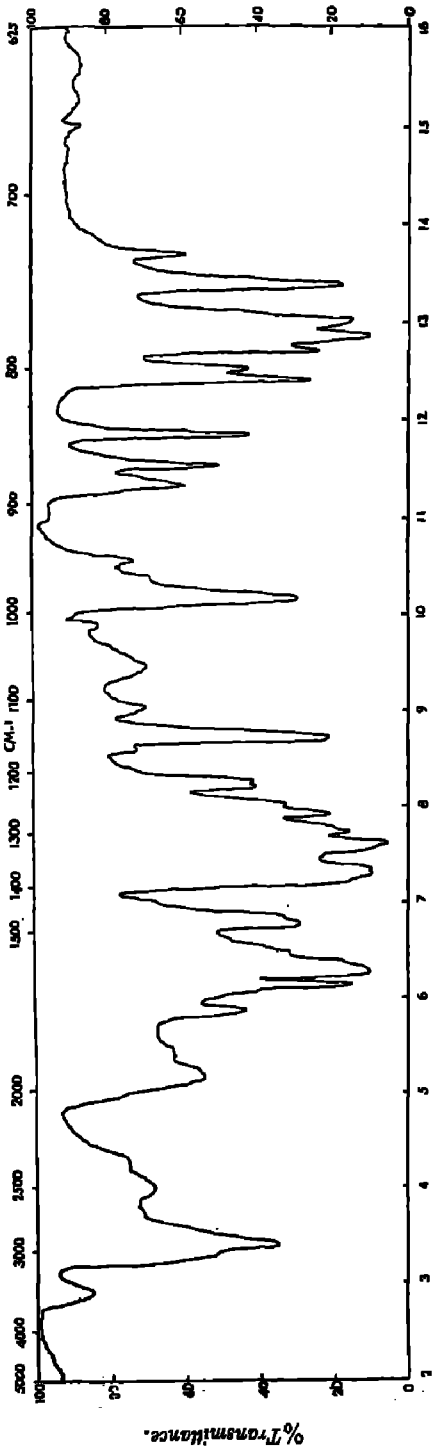


FIG. 6. I. R. spectra of quinaldinic acid.

Microns.

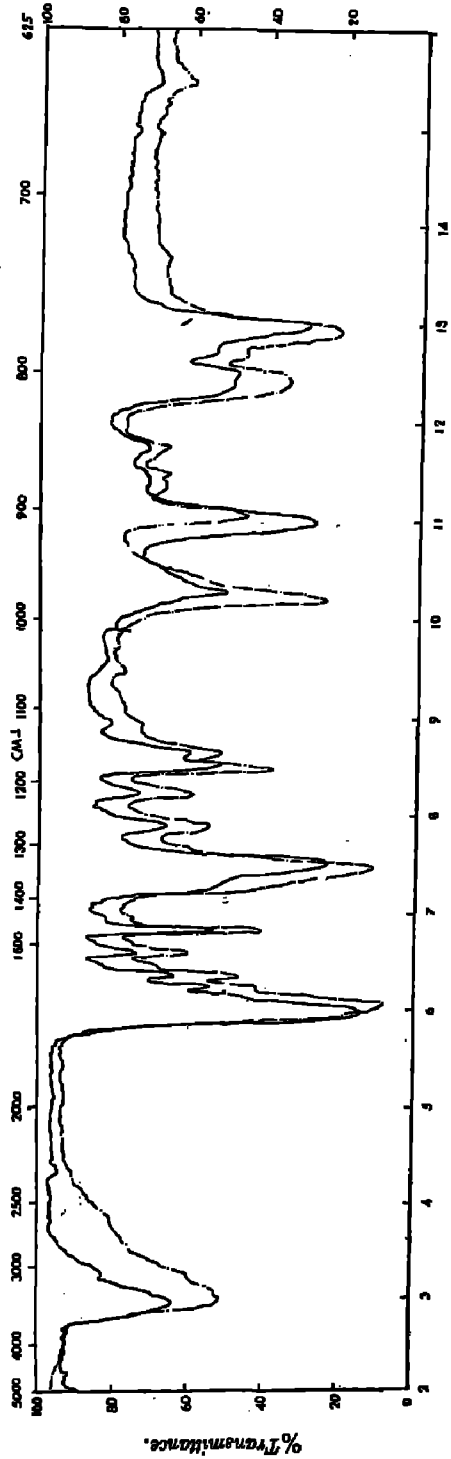


FIG. 7. I. R. spectra of oxo-bis-quinaldinato-vanadium (IV) monohydrate (—) and of aquo-bis-quinaldinato-vanadium (IV) (---).

Microns.

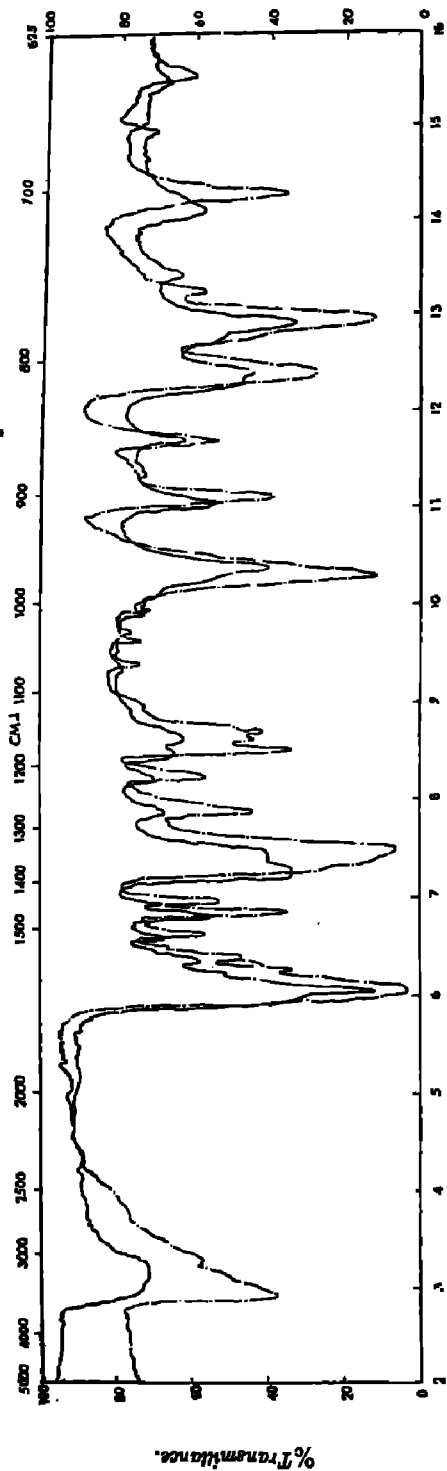


FIG. 8. I. R. spectra of pyridine-oxo-bis-quinaldinate-vanadium (IV) monohydrate (—) and of pyridine-oxo-bis-quinaldinate-vanadium (IV) (---).

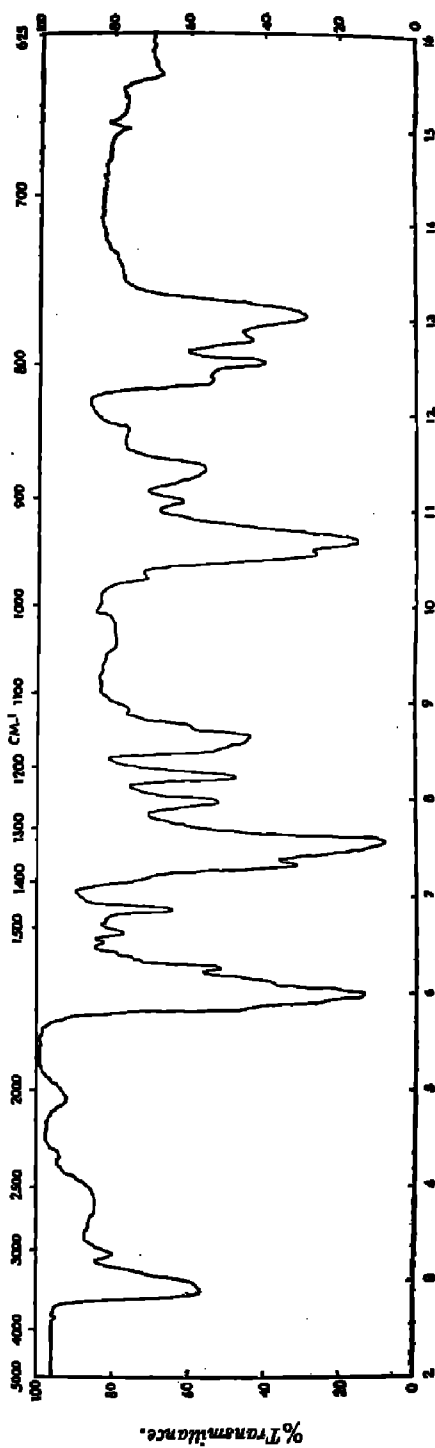


FIG. 9. I. R. spectra of oxo-hydro-bis-quinaldinate-vanadium (IV).

tetrahydrofuran, and thiophen, though somewhat more readily. By the action of KCN on $[\text{VOQ}_2]$ we have obtained a greenish black powder which is now under investigation. We intend to study thoroughly the action of KCN on a variety of stable vanadium (IV) complexes.

The quadrivalency of vanadium in the above described complexes has been established through the determination of the magnetic moments. Vanadium in the 4^+ oxidation state is a d^1 ion, so that a magnetic moment of the order of 1.73 B.M. is expected. The compounds, so far described, show moment values lying between 1.6 and 1.9 B.M. An octahedral d^2sp^3 or a square pyramid d^2sp^2 hybrid co-ordination is indicated. Attempts were also made to determine the oxidation state by titrimetry against standard permanganate. The results were not to our entire satisfaction, the end point being rather fleeting. It is not unlikely that the ligand is also affected by the permanganate.

Two other derivatives of quinaldinic acid, namely, 5-nitroquinaldinic acid and 5,6-benzoquinaldinic acid, were found to give only the paramagnetic pale apple-green to cream-coloured variety of quadrivalent vanadium complexes. The compounds lose one molecule of water at $140-50^\circ$, indicating that the complexes are octahedral with the H_2O inside the co-ordination sphere. Surprisingly enough, they failed to give any bluish green product with aromatic amines or the heterocyclic bases, the original compounds being recovered unchanged.

Quinquevalent Vanadium Complexes

A curdy white precipitate appears on the addition of quinaldinic acid to aqueous ammonium vanadate. This on purification from hot ethanol gives the composition $[\text{VO}(\text{OH})\text{Q}_2] \cdot 2\text{H}_2\text{O}$. The compound is diamagnetic. That the alternative formula $\text{H}[\text{VO}_2\text{Q}_2] \cdot 2\text{H}_2\text{O}$ does not reveal the exact state, is proved through its poor conductance (2.24 mhos) in methanol. On allowing a methanolic solution (0.001 *M*) of the product to stand for two weeks, there appeared some glistening olive-green crystals. The compound was then prepared by repeated refluxing of $[\text{VO}(\text{OH})\text{Q}_2] \cdot 2\text{H}_2\text{O}$ with a large volume of methanol. This was found to be identical with the compound (II), described under quadrivalent vanadium. Thus on standing or on refluxing in methanol $[\text{VO}(\text{OH})\text{Q}_2]$ is reduced to $[\text{VO}(\text{H}_2\text{O})\text{Q}_2]$. On heating $[\text{VO}(\text{OH})\text{Q}_2]$ with pyridine, two products were obtained: (a) the first is colorless $[\text{VO}_2\text{Q}\cdot\text{py}]$, one QH being knocked off; (b) the mother liquor on standing furnishing low yields of $[\text{VO}(\text{py})\text{Q}_2] \cdot \text{H}_2\text{O}$. The compound $[\text{VO}_2\text{Q}\cdot\text{py}]$ is diamagnetic, indicative of the quinquevalency of vanadium. The pyridine in the compound is held very strongly and is not lost before 160° . The product after the loss of pyridine gave analyses for $[\text{VO}_2\text{Q}]$, which should be regarded as a four co-ordinated complex of vanadium (V). The second product has a bluish green colour, identical with the one obtained from $[\text{VO}_2(\text{H}_2\text{O})\text{Q}_2]$ by the action of pyridine. A similar reaction also occurred with α -picoline. The compound, $[\text{VO}_2\text{Q}\cdot\text{py}]$ presumably has a square pyramid structure. Corresponding products with aniline and dimethylformamide did not give very satisfactory analyses.

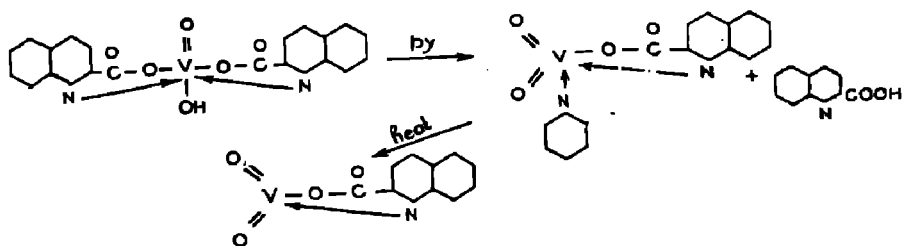
The infrared spectral characteristics of the compound $[\text{VO}(\text{OH})\text{Q}_2] \cdot 2\text{H}_2\text{O}$ were also studied. Besides showing the same absorption characteristics as shown by $[\text{VO}(\text{H}_2\text{O})\text{Q}_2]$ and $[\text{VOQ}_2] \cdot \text{H}_2\text{O}$, this compound reveals one extra band, sharp but of low intensity at about 3100 cm^{-1} . Bielig *et al.* (*loc. cit*) attribute a weak band at about 3400 cm^{-1}

to be due to OH in the compound oxo-hydroxo-bis-oxinato-vanadium (V). At the region 3400 cm^{-1} all our samples, however, show prominent absorption bands. As the band at 3100 cm^{-1} does not appear in our other compounds, this may be assigned to the OH in the compound, oxo-hydroxo-bis-quinaldinato-vanadium (V). In fact, there are evidences to show that the OH band appears near 3100 cm^{-1} (Cross, "Practical Infrared Spectroscopy", Butterworths Publication, 1960).**

TABLE I
Magnetic measurements.
Temp. = 35° .

Compounds.	Dia. corr. $\times 10^6$.	χ_M (corr.) $\times 10^6$.	μ_{eff} (B.M.) ^a .
[VOQ ₂]H ₂ O	208.4	1236	1.75
[VO(H ₂ O)Q ₂]	208.4	1264	1.77
[VO(C ₅ H ₅ N)Q ₂]H ₂ O	259.0	1307	1.86
[VO(CH ₃ .C ₅ H ₄ N)Q ₂]	257.0	1320	1.91
[VO(C ₅ H ₅ .NH ₂)Q ₂]	258.8	1312	1.805
[VO(C ₆ H ₄ $\left\langle \begin{array}{l} \text{NH}_2 \\ \text{COOCH}_3 \end{array} \right\rangle$ Q ₂]	284.9	1550	1.96
[VO(HN $\left\langle \begin{array}{l} \text{C}_6\text{H}_5 \\ \text{C}_6\text{H}_5 \end{array} \right\rangle$ Q ₂]	308.0	1506	1.93
[VO(HCON $\left\langle \begin{array}{l} \text{CH}_3 \\ \text{CH}_3 \end{array} \right\rangle$ Q ₂)H ₂ O]	250.4	1216	1.74
[VO(C ₄ H ₈ O ₂)Q ₂]	252.0	1129.6	1.66
[VO(C ₄ H ₈ O)Q ₂]	247.0	1172.0	1.695
[VO(C ₄ H ₄ S)Q ₂]H ₂ O	260.5	1238.0	1.74
[VO(H ₂ O)(BzQ) ₂]	269.6	1383.8	1.84
[VO(H ₂ O)(nQ) ₂]	232.9	1056.4	1.61
[VO(OH)Q ₂]2H ₂ O			Diamagnetic
[VO ₂ Q(C ₅ H ₅ N)]			"
[VO ₂ Q(CH ₃ .C ₅ H ₄ N)]			"

*Calculated from χ_M (corr.) using the Curie equation $\mu_{\text{eff}} = 2.84 (\chi_M \text{ (corr.) } T)^{\frac{1}{2}}$
(BzQH = 5:6-Benzoquinaldinic acid. nQH = 5-nitroquinaldinic acid).



Picolinic acid, though has the same disposition of the N and COOH, failed to react like quinaldinic acid. Quinolinic acid (pyridine-2,3-dicarboxylic acid), having a molecular weight close to quinaldinic acid, also did not furnish any positive results. Further work with other pyridine and quinoline carboxylic acids is progressing in this laboratory. Investigation are also being carried out on the complexes of VOCl₃, VCl₄ and VCl₅ with quinaldinic acid and its derivatives.

**We have just succeeded in isolating some vanadium (III) complexes of quinaldinic acid. This will be reported in due course.

Reference may be made here to the formation of two differently coloured modifications of Fe(II)—quinaldinic acid complex (Rây and Bose, *Z. anal. Chem.*, 1933, **95**, 400) as also of cobalt(II)—quinaldinate (Dutt, this *Journal*, 1937, **14**, 572). It is worthwhile therefore to study the reactions of quinaldinic acid with other transition metals. We have already undertaken works in this direction.

EXPERIMENTAL

Quinaldinic acid was prepared from quinaldine (B.D.H.) by following Hammick's procedure (*J. Chem. Soc.*, 1923, **123**, 2882) and was recrystallised twice from hot glacial acetic acid, furnishing light cream-coloured fine needles. Vanadyl sulphate pentahydrate was E. Merck's product. 5-Nitroquinaldinic acid was obtained by nitration of quinaldinic acid (Welcher, "Organic Analytical Reagent", Vol. II, p. 206). 5,6-Benzoquinaldinic acid was prepared according to De (D. Phil. thesis, Calcutta University, 1952).

Oxo-bis quinaldinato-vanadium (IV) Monohydrate (Cream).—Quinaldinic acid (0.5 g.), dissolved in water (200 c.c.), was treated under stirring with an aqueous solution of vanadyl sulphate (0.25 g. in 10 c.c.). A voluminous cream-coloured precipitate was formed, which was digested on a water bath for half an hour, filtered, washed with water, and dried over CaCl_2 . { Found: V, 11.58; C, 56.1; H, 3.8; N, 6.57; H_2O (by loss at 110°), 3.80. $[\text{VO}(\text{C}_{10}\text{H}_6\text{O}_2\text{N})_2]\text{H}_2\text{O}$ requires V, 11.88; C, 55.94; H, 3.26; N, 6.53; H_2O , 4.20% }.

Aquo-oxo-bis-quinaldinato-vanadium (IV) (Olive-green).—(a). An aqueous solution of vanadyl sulphate (0.25 g. in 5 c.c.) was added to a hot methanolic solution of quinaldinic acid (0.5 g. in 40 c.c.), when the cream-coloured compound separated. On keeping the mixture overnight the product turned olive-green. The olive-green crystals were filtered, washed with methanol, and dried over CaCl_2 . { Found: V, 11.65; C, 56.2; H, 3.6; N, 6.42; H_2O (by loss at 150°), 4.60. $[\text{VO}(\text{H}_2\text{O})(\text{C}_{10}\text{H}_6\text{O}_2\text{N})_2]$ requires V, 11.88; C, 55.94; H, 3.26; N, 6.53; H_2O , 4.20% }.

(b). The oxo-hydroxo-bis-quinaldinato-vanadium(V) was dissolved in methanol (150 c.c.), refluxed on a water bath for 15-20 hrs., and then allowed to stand. A crop of olive-green crystals appeared which were treated as above. The mother liquor on further refluxing with methanol produced a fresh crop of the olive-green crystals.

Pyridine-oxo-bis-quinaldinato-vanadium(IV) Monohydrate.—The freshly prepared cream-coloured compound was washed with water, sucked dry, and then heated with distilled pyridine (10 c.c.) on the water bath under reflux. The cream-coloured compound readily dissolved producing a greenish solution which soon deposited a fine bluish green crystalline product. After half an hour, the mixture was cooled, the product washed with ethanol first by decantation and then on the filter till free of pyridine, and dried over CaCl_2 . { Found: V, 9.80; N, 8.46; $(\text{C}_5\text{H}_5\text{N} + \text{H}_2\text{O})$, 19.3. $[\text{VO}(\text{C}_5\text{H}_5\text{N})(\text{C}_{10}\text{H}_6\text{O}_2\text{N})_2] \cdot \text{H}_2\text{O}$ requires V, 10.04; N, 8.27; $(\text{C}_5\text{H}_5\text{N} + \text{H}_2\text{O})$, 19.1% }.

The same compound was also obtained from the freshly prepared olive-green variety. [Found: V, 9.86; $(\text{C}_5\text{H}_5\text{N} + \text{H}_2\text{O})$, 19.1%]. The substance liberates pyridine on heating with NaOH solution.

Pyridine-oxo-bis-quinaldinato-vanadium (IV) was obtained using anhydrous $[\text{VOQ}_4]$

and anhydrous pyridine. { Found: V, 10.70; C_5H_7N (by loss at 130°), 16.70. $[VO(C_5H_5N)(C_{10}H_6O_2N)_2]$ requires V, 10.41; C_5H_5N , 16.12% }.

α -Picoline-oxo-bis-quinaldinato-vanadium (IV).—To quinaldinic acid (0.5 g.), dissolved in ethanol (10 c.c.), was added α -picoline (10 c.c.), followed by an aqueous solution of vanadyl sulphate (0.25 g. in 5 c.c.). A clear greenish brown solution was formed, which slowly deposited fine bluish green crystals. These were filtered next day, washed with ethanol, and finally dried over $CaCl_2$. The compound, however, could not be prepared by following the procedure for the pyridine complex. { Found: V, 10.30; $CH_3C_5H_4N$, 18.11 (by loss at 130°). $[VO(CH_3C_5H_4N)(C_{10}H_6O_2N)_2]$ requires V, 10.12; $CH_3C_5H_4N$, 18.45% }.

Aniline-oxo-bis-quinaldinato-vanadium (IV) was obtained as light green microcrystals as in the case of the pyridine complex, using aniline (15 c.c.). { Found: V, 10.15; N, 8.10; $C_6H_5NH_2$, 19.0. $[VO(C_6H_5NH_2)(C_{10}H_6O_2N)_2]$ requires V, 10.12; N, 8.33; $C_6H_5NH_2$, 18.45% }.

Methylantranilate-oxo-bis-quinaldinato-vanadium (IV) was prepared like the α -picoline compound using methylantranilate in place of α -picoline. The cream-coloured compound, first formed, slowly changed to pale bluish green. After keeping overnight, the crystals were filtered, washed with ethanol and dried over $CaCl_2$. { Found: V, 9.30; N, 7.20. $[VO(C_6H_4(NH_2)(CO_2Me)(C_{10}H_6O_2N)_2]$ requires V, 9.08; N, 7.47% }.

Diphenylamine-oxo-bis-quinaldinato-vanadium (IV).—Quinaldinic acid (0.5 g.) and diphenylamine (5 g.) were heated in ethanol (70 c.c.) on a water bath under reflux. Vanadyl sulphate (0.25 g. in 5 c.c. water) was then added and the mixture refluxed for 2 hours. The cream-coloured precipitate changed to light green. This was then filtered, washed, and dried as usual. { Found: V, 9.03; N, 7.11. $[VO(HN(Ph)_2)(C_{10}H_6O_2N)_2]$ requires V, 8.79; N, 7.24% }.

Dimethylformamide-oxo-bis-quinaldinato-vanadium (IV) monohydrate was prepared like the pyridine complex using dimethylformamide instead of pyridine. This formed beautiful dark bluish green crystals. { Found: V, 9.96; N, 8.38; $HCON(CH_3)_2 + H_2O$ (by loss at 130°), 18.62. $[VO(HCONMe_2)(C_{10}H_6O_2N)_2]H_2O$ requires V, 10.16; N, 8.37. $(HCONMe_2 + H_2O)$, 18.12% }.

The dioxane and the tetrahydrofuran compounds also were obtained as above.

Dioxan-oxo-bis-quinaldinato-vanadium (IV): { Found: V, 10.01; $C_4H_8O_2$ (by loss at 130°), 18.1. $[VO(C_4H_8O_2)(C_{10}H_6O_2N)_2]$ requires V, 10.22; $C_4H_8O_2$, 17.60% }.

Tetrahydrofuran-oxo-bis-quinaldinato-vanadium (IV): { Found: V, 10.40; C_4H_8O , 14.74. $[VO(C_4H_8O)(C_{10}H_6O_2N)_2]$ requires V, 10.55; C_4H_8O , 14.90% }.

Thiophen-oxo-bis-quinaldinato-vanadium (IV) Monohydrate.—The solution of quinaldinic acid (0.7 g.) in thiophen (10 c.c.) and ethanol (10 c.c.) was heated under reflux (water bath) and treated with the vanadyl sulphate solution (0.5 g. in 5 c.c. water). Immediately a bluish green compound separated; the mixture was refluxed for half an hour, filtered, washed, and dried as usual. { Found: V, 9.6; $(C_4H_4S + H_2O)$, 19.57. $[VO(C_4H_4S)(C_{10}H_6O_2N)_2]H_2O$ requires V, 9.94; $(C_4H_4S + H_2O)$, 19.88% }.

Aquo-oxo-bis-5-nitroquinaldinato-vanadium (IV).—To 5-nitroquinaldinic acid (0.5 g.), dissolved in almost boiling water (300 c.c.), vanadyl sulphate (0.2 g. in 10 c.c. water) was

added. A pale apple-green compound was obtained, which was washed with hot water, then with ethanol, and dried over CaCl_2 . { Found: V, 9.48; N, 10.96; H_2O (by loss at 150°), 4.3. $[\text{VO}(\text{H}_2\text{O})(\text{NO}_2\text{C}_{10}\text{H}_5\text{O}_2\text{N})_2]$ requires V, 9.78; N, 10.75; H_2O , 3.4% }.

Aquo-oxo-bis-5,6-benzoquinaldinato-vanadium (IV).—To 5,6-benzoquinaldinic acid (0.6 g.), dissolved in ethanol (50 c.c.), was added $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$ (0.25 g. in 5 c.c. water). A deep cream-coloured compound separated which was filtered, washed with ethanol, and dried over CaCl_2 . { Found: V, 9.23; N, 5.26; H_2O (by loss at 150°), 3.5. $[\text{VO}(\text{H}_2\text{O})(\text{C}_{14}\text{H}_{14}\text{O}_2\text{N})_2]$ requires V, 9.56; N, 5.26; H_2O , 3.37% }. The vanadium (IV) complex could not be prepared in aqueous medium only due to the extreme insolubility of the reagent.

Oxo-hydroxo-bis quinaldinato-vanadium (V) Dihydrate.—Ammonium vanadate (0.2g. in 15c.c. water) was added to quinaldinic acid (1 g. in 150 c.c. water) when a yellowish white precipitate separated. It was digested on a water bath for half an hour, filtered, and finally recrystallised from hot ethanol. { Found: V, 10.85; N, 6.03; H_2O , 7.20. $[\text{VO}(\text{OH})(\text{C}_{10}\text{H}_5\text{O}_2\text{N})_2] \cdot 2\text{H}_2\text{O}$ requires V, 10.99; N, 6.03; H_2O , 7.75% }.

Pyridine-dioxo-monoquinaldinato-vanadium (V).—The compound, oxo-hydroxo-bis-quinaldinato-vanadium (V) was prepared, as described before, and was then treated with pyridine (7-8 c.c.). The mixture was warmed on a water bath for half an hour, when a clear solution was obtained. This, on cooling in ice, furnished colorless crystals which were filtered, washed with ice-cold water, and dried as usual. { Found: V, 15.01; N, 8.44. $\text{C}_5\text{H}_5\text{N}$ (by loss at 170°), 23.25. $[\text{VO}_2(\text{C}_5\text{H}_5\text{N})(\text{C}_{10}\text{H}_5\text{O}_2\text{N})]$ requires V, 15.26; N, 8.38; $\text{C}_5\text{H}_5\text{N}$, 23.65%. Found: V, 19.54; N, 5.91. $[\text{VO}_2(\text{C}_{10}\text{H}_5\text{O}_2\text{N})]$ requires V, 20.00, N, 5.49% }.

α -Picoline-dioxo-monoquinaldinato-vanadium (V) was obtained as above using α -picoline in place of pyridine. { Found: V, 14.63; N, 7.99; $\text{CH}_3\text{C}_5\text{H}_4\text{N}$ (by loss at 210°), 26.79. $[\text{VO}_2(\text{CH}_3\text{C}_5\text{H}_4\text{N})(\text{C}_{10}\text{H}_5\text{O}_2\text{N})]$ requires V, 14.63; N, 8.04; $\text{CH}_3\text{C}_5\text{H}_4\text{N}$, 26.72% }. Found: V, 20.00; N, 6.01 $[\text{VO}_2(\text{C}_{10}\text{H}_5\text{O}_2\text{N})]$ requires V, 20.00, N, 5.49% }.

Analytical Methods.—Vanadium content was determined either by decomposing the complex with HNO_3 and H_2SO_4 and then igniting to V_2O_5 or by igniting the complex under a thick layer of oxalic acid to the V_2O_5 stage. Nitrogen was estimated by combustion technique.

X-ray Measurement.—X-ray powder photographs were taken with Phillips PW 1010 X-ray unit with Phillips Debye-Scherrer camera with 57.3 mm diameter using $\text{CuK}\alpha$ radiation.

Magnetic Measurements.—The magnetic moments were determined by the Gouy method using a semi micro Mettler balance for measuring the difference in weight and with a field strength of 9.26 gauss. Diamagnetic corrections were taken from Selwood "Magnetochemistry", Interscience, New York, p. 7⁸, 1956).

The infrared spectra were scanned on a Perkin-Elmer 21 Infrared Spectrometer using KBr disc technique.

The pyrolysis curves (Fig. 4 and Fig. 5) were recorded in a Chevenard thermobalance (approximate rate of heating, 5° per minute).

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