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A Study on Adducts of Bis(8-quinolinato)-oxovanadium(IV) with Substituted Pyridines by Infrared Spectroscopy

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Henry *et al.* [1] and, more recently, Lozano *et al.* [2] have reported IR studies on adducts of bis(8-quinolinato)oxovanadium(IV), $VO(ox)_2$ (**1**), with pyridine and substituted pyridines to support the existence of a correlation between the basicity of the pyridines and V=O stretching frequency. We report here the results of an IR study on a series of adducts of **1** with substituted pyridines in solution, but with very different conclusions. Relevant IR data are summarized in Tables I and II.

TABLE I. V=O Stretching Frequencies (cm^{-1}) of $VO(ox)_2\cdot$py (**2c**)^a in Solution

Solvent		ν_I	ν_{II}
Benzene	997	969	938
Acetonitrile	993	963	939
Pyridine		963	938

^{a}Although the synthesis of **2c** was carried out by the same procedure as cited in ref. 3, elemental analysis provided the empirical formula $VC_{23}H_{17}N_3O_3$, as required for **2c** without benzene of crystallization [ν(V=O)(Nujol) = 926–936 cm^{-1} (ref. in Table II)].

As seen in Table I, three bands (sharp and strong) were present in benzene and acetonitrile solutions of (pyridine)bis(8-quinolinato)oxovanadium(IV), $VO(ox)_2\cdot$py (**2c**), in the 1000–900 cm^{-1} region. Experiments in benzene solution with varying ratios of pyridine to **2c** ca. 5×10^{-2} M (1:1, 2:1, 5:1) showed that the intensity of the band at higher frequency decreases as the pyridine concentration increases, until it completely disappears (at 5:1 ratio), while the lower absorptions (bands I and II) remain at approximately the same intensity ratio. These two bands are the only ones present in the same range of the spectra recorded for pyridine solutions of **2c**.

As shown in Table II, two peaks, at approximately the same frequency (963 ± 2 and 938 ± 1 cm^{-1}), are present in the spectra of complexes **2a–h** prepared *in loco*, following the reported procedure [2], by adding **1** to the appropriately substituted pyridine and after standing for *ca.* 20 h. Similar results (bands at 966 ± 2 and 938 ± 1 cm^{-1}) were obtained when the complex **1** was added to a benzene solution of the various substituted pyridines (*ca.* 0.8 M). The substituent on the pyridine ring affects the relative intensity of the peaks I and II, as evidenced by the ratio of their approximate absorbance values in Table II. The adducts can be divided into two groups. For five of these compounds (**2a–d**, **2g**), the intensity ratio is significantly >1, whereas for the other three adducts (**2e**, **2f**, **2h**) a drop in its value is observed. In the case of adducts **2e** and **2h** in benzene solution, peaks I and II are hardly observable because of low solubility.

The observations outlined above provide evidence for the existence of an equilibrium among three different types of complex in solution. Peaks I and II, present in all the solution experiments, can be attributed to isomers, and, most likely, to isomers where the pyridine or substituted pyridines are coordinated *cis* or *trans* to terminal oxygen. The peak at higher frequency, which falls in intensity as the pyridine concentration increases, may be reasonably assigned to a solvated species of **1***.

On this basis, equilibrium (1) is suggested.

$$\underset{cis\text{-}\mathbf{2}}{VO(ox)_2\cdot B} \rightleftharpoons \underset{\mathbf{1}}{VO(ox)_2} + B \rightleftharpoons \underset{trans\text{-}\mathbf{2}}{VO(ox)_2\cdot B} \qquad (1)$$

(B = pyridine or substituted pyridine)

Our findings on adducts of $VO(ox)_2$ with pyridines parallel those proposed for similar complexes of vanadyl acetylacetonate in chloroform solution [4]. In fact, the peak at 1003 cm^{-1} of $VO(acac)_2$ decreases on addition of pyridines, while one or two peaks at approximately fixed shifts of 31 ± 3 cm^{-1} and/or 51 ± 3 cm^{-1} are described in all cases.

The occurrence of two almost constant shifts for ν(V=O) of $VO(acac)_2$ on coordination with pyridines was reported in another paper [5].

On the basis of these reports and our results, it is not inconceivable to suggest that the most marked differences in ν(V=O) of the 8-quinolinol adducts in the solid state, which have been correlated with the basicity of the pyridines [1, 2], could rather be derived from configurational change. Similar reasoning could also account for the significant discrepancy between the ν(V=O) values reported for solid **2f** (see Table II) prepared by different procedures.

On the other hand, the basicity of the pyridines seems to have a rather pronounced effect on the *cis*/

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*The molecular complexity of solid **1** has been discussed in ref. 3.

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TABLE II. V=O Stretching Frequencies (cm^{-1}) and Approximate Intensity Ratio for the Adducts, and pK_a Values of Substituted Pyridines

Adduct[a]		Previous data (Nujol or KBr discs)	Base solution[b]			Benzene solution[c]			pK_a
			ν_I	ν_{II}	Intensity ratio (I:II)	ν_I	ν_{II}	Intensity ratio (I:II)	
1[d]		975[e], 970[f], 963[g]							
1·4-CNpy	(2a)	960[e]				966	939	1.4	1.90
1·3-Clpy	(2b)		964	937	1.6	964	938	1.5	2.84
1·py	(2c)	950[e], 935–945[f], 945[g]	963	938	1.6	968	939	1.4	5.25
1·3-Mepy	(2d)	930[f]	965	938	1.5	968	939	1.5	5.68
1·2-Mepy	(2e)	975[e]	961	939	0.6	h	h	h	5.97
1·4-Mepy	(2f)	945[e], 965[f]	962	938	0.6	964	939	1.0	6.02
1·3,4-Dimepy	(2g)		965	939	1.2	968	939	1.5	6.46
1·2,6-Dimepy	(2h)	968[e]	962	939	0.6	h	h	h	6.60

[a] 4-CNpy = 4-cyanopyridine; 3-Clpy = 3-chloropyridine; py = pyridine; 2-, 3-, 4-Mepy = 2-, 3-, 4-methylpyridine; 3,4-, 3,5-, 2,6-Dimepy = 3,4-, 3,5-, 2,6-dimethylpyridine. [b] In the corresponding substituted pyridine. [c] In benzene containing the corresponding substituted pyridine *ca.* 0.8 M. [d] Prepared as described in ref. 3. [e] Ref. 1. [f] Ref. 2. [g] Ref. 3. [h] Peaks I and II are hardly observable because of low solubility.

trans equilibrium position in the case of acetylacetonate adducts [4]. In fact, the more basic pyridines give only the ν(V=O) of larger shift, but, as the basicity decreases, this band falls in intensity and the ν(V=O) of smaller shift becomes predominant, until for 3-cyanopyridine the former band is completely absent. On the contrary, all the 8-quinolinol adducts examined in this work show two peaks which can be ascribed to ν(V=O) of the *cis* and *trans* isomers. Furthermore, there is no evidence of a trend in their intensity ratio with pK_a values of the pyridines. For five adducts, as summarized in Table II, this value appears to be almost independent of the basicity of the pyridines. The large decreases observed for adducts **2e** and **2h** would seem to be related to the steric hindrance introduced by the *ortho*-substitution, whereas a similar behaviour found for the 4-methylpyridine adduct could be attributed to the existence of resonance forms [2].

In summary, a major conclusion can be drawn from this preliminary work: the adducts of VO(ox)$_2$ with pyridines exist in solution as *cis* and *trans* isomers in equilibrium with a solvated species of VO(ox)$_2$. The position and electronic character of the substituent on the pyridine ring does not affect the ν(V=O), but determines the *cis*/*trans* equilibrium position involving factors which have to be rationalized. With particular regard to this aspect of the problem, further investigations are necessary to clarify the role played by the electronic, steric and solvation effects.

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References

1 R. P. Henry, P. C. H. Mitchell and J. E. Prue, *Inorg. Chim. Acta, 7,* 125 (1973).
2 R. Lozano, J. Martinez, J. Roman, A. Martinez and A. Doadrio, *Polyhedron, 5,* 1341 (1986).
3 M. Pasquali, A. Landi and C. Floriani, *Inorg. Chem., 18,* 2397 (1979).
4 J. J. R. F. Da Silva and R. Wootton, *J. Chem. Soc., Chem. Commun.,* 421 (1969).
5 M. R. Caira, J. M. Haig and L. R. Nassimbeni, *J. Inorg. Nucl. Chem., 34,* 3171 (1972).