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SOME ADDUCTS OF OXOBIS(ACETYLACETONATO)VANADIUM(IV) WITH PHENOL OR ITS PARA-SUBSTITUTED DERIVATIVES

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Oxobis(acetylacetonato)vanadium(IV) reacts with phenol or its para-substituted derivatives in methanol, affording a stable adduct of the composition VO(acac)$_2$(p-XC$_6$H$_4$OH), where X=H, NO$_2$, CHO, COOH, Cl or CH$_3$. The magnetic and spectral data reveal that these are vanadium(IV) complexes containing the phenol as a neutral ligand. They show an unusually low ν(V=O) frequency of ~900 cm^{-1} compared to a value of 1000 cm^{-1} for the parent complex, and are presumed to have a polymeric structure with a phenol molecule connecting with an adjacent vanadyl oxygen via the hydrogen bond. The behavior of the adduct in solution is also reported.

Solid oxobis(acetylacetonato)vanadium(IV), VO(acac)$_2$, consists of discrete molecules of the square-pyramidal structure with vanadium near its center of gravity.$^{1)}$ The sixth spatial position is chemically accessible as evidenced by the remarkable change in the electronic and infrared spectra in coordinating solvents as compared with those in solid and non-coordinating solvents.$^{2)}$ In fact some adducts with nitrogen and oxygen donors such as pyridine$^{3)}$ and dioxane$^{4)}$ have been prepared, and their structure determined. The present communication reports several adducts containing a molecule of phenol or its derivatives as the sixth ligand.

To a solution of VO(acac)$_2$ in methanol was added a methanol solution containing an equimolar amount of phenol or its para-substituted derivatives, and the mixture was heated at about 80°C for half an hour until the blue-green color turned dark brown. Then the solvent was allowed to evaporate at room temperature, depositing a crystalline product. Each compound listed in Table 1 affords correct analysis for VO(acac)$_2$-(XC$_6$H$_4$OH) except the adduct with unsubstituted phenol which has the composition VO(acac)$_2$(C$_6$H$_5$OH)$\cdot\frac{1}{2}$ H$_2$O.

Table 1. The magnetic, spectral and molecular weight data of the VO(acac)$_2$(p-XC$_6$H$_4$OH) complexes.

X	Magnetic moment B.M.	ν(V=O) in Nujol cm^{-1}	Reflectance spectra ν_{max} kK		Molecular weight in CH$_2$Cl$_2$	
					Found	Calc
NO$_2$	1.74	910	12.8	17.9	230	404
CHO	1.75	905	12.7	18.4	227	387
COOH	1.68	901	12.8	18.0	——	——
Cl	1.74	908	13.1	18.0	210	393
H	1.76	904	12.9	17.9	186	359
CH$_3$	1.76	910	13.0	17.9	213	373
No adduct	1.73	1000	14.6[a]	16.8[a]		

a) Taken from the data in ref. 5.

The observed magnetic moments correspond to the vanadium(IV) state, revealing that the phenol is coordinated as a neutral ligand. The parent complex VO(acac)$_2$ exhibits two d-d absorption maxima in non-coordinating media at 15.0 and 16.8 kK except a shoulder at 11.5 kK, which are shifted to around 13 and 17 kK in coordinating media.$^{5)}$ The reflectance spectra of the present phenol adducts have distinct maxima at around 13 and 18 kK, indicating coordination of the phenol to the metal.

It has been well established experimentally that the ν(V=O) frequency is diminished by the adduct formation.$^{2)}$ Caira, et al.$^{3)}$ reported that ligation of a substituted pyridine to vanadium at the position cis to the oxo ligand lowers the ν(V=O) frequency by 42 ± 4 cm^{-1}, while the trans ligation by 29 ± 4 cm^{-1}. The present adducts all display the ν(V=O) band in the 900-910 cm^{-1} region irrespective of the nature of the substituent X. Such a large reduction in the ν(V=O) frequency can not be resulted by mere ligation, but suggests some interaction between the oxo and phenol ligands.

Oxo[N,N'-bis(salicylidene)propane-1,3-diamino]vanadium(IV) has a polymeric structure of an infinite chain of square-pyramidal molecules connected by V=O···V=O··· bonds,$^{6)}$ and exhibits an unusually low ν(V=O) frequency of 861 cm^{-1} in Nujol.$^{7)}$

Oxobis(trifluoroacetylacetonato)- and oxobis(thenoyltrifluoroacetonato)-vanadium(IV) complexes also display the ν(V=O) bands at 1015 and 1012 cm^{-1} in methylene chloride, but at 932 and 900 cm^{-1} in Nujol respectively, and are presumed to have similar polymeric structures in solid.[8)]

In the present complexes the phenol molecule must be coordinated to vanadium through the oxygen atom, and might be connected with the vanadyl oxygen of an adjacent molecule via the hydrogen bond. The fact that neither anisole nor sodium phenolate forms such an adduct seems to support this assumption.

As is seen in Table 1 the molecular weight determined in methylene chloride at 25°C is close to half the calculated value, revealing the extensive dissociation of the adduct in solution. The IR spectrum of the p-nitrophenol adduct in methylene chloride is quite different from that in Nujol and nearly coincides with that of $VO(acac)_2$ (Fig. 1). This fact indicates that the phenol molecule is released in solution. If successive portions of p-nitrophenol are added to the solution, a new absorption band (980 cm^{-1}) grows up gradually at the expense of the 1000 cm^{-1} band. The new band can be assigned to the ν(V=O) vibration of the phenol adduct formed by the following equilibrium in solution.

$$VO(acac)_2 + p\text{-}NO_2C_6H_4OH \rightleftarrows VO(acac)_2(p\text{-}NO_2C_6H_4OH)$$

Selbin and his collaborators[9)] examined the effect of various ligands on the ν(V=O) frequency of $VO(acac)_2$ in chloroform. Addition of phenol gave no effect at the mole ratio of 1:1, but displayed a new band at 1:25 whose frequency was lower by 23 cm^{-1} than that of the parent complex.

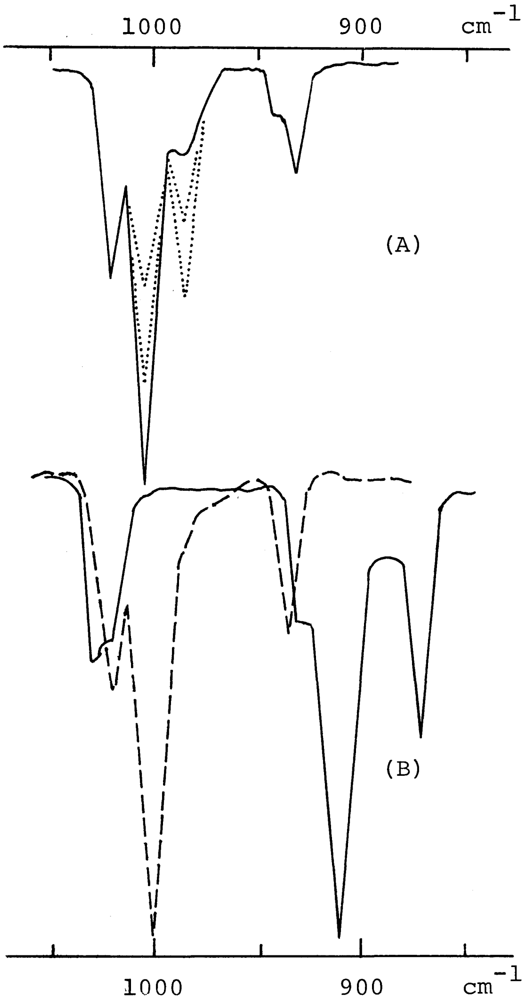

Fig. 1. IR spectra in CH_2Cl_2 (A) and in Nujol (B).

——— $VO(acac)_2(p\text{-}NO_2C_6H_4OH)$

……… $VO(acac)_2(p\text{-}NO_2C_6H_4OH) + p\text{-}NO_2C_6H_4OH$

– – – – $VO(acac)_2$

These data together with the present results indicate that a molecule of phenol or its derivatives merely occupies the sixth coordination site of vanadium(IV) in solution without any interaction with the oxo ligand.

The X-ray analysis of oxobis(acetylacetonato)(p-nitrophenol)vanadium(IV) is now in progress.

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