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Reactions of Bis(acetylacetonato)oxovanadium(IV) with Phenol and Its *para*-Substituted Derivatives

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Bis(acetylacetonato)oxovanadium(IV) reacts with phenol or its *para*-substituted derivatives in methanol, affording stable adducts with the composition of 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 $\approx$900 cm^{-1} as compared with the value of 1000 cm^{-1} for the parent complex, and are presumed to have a polymeric structure with an infinite chain of V=O···V=O···. The phenol is connected by a hydrogen bond to one oxygen atom of an acetylacetonate ligand. The behavior of the complex in solution is also discussed. The addition of 1,10-phenanthroline or 2,2′-bipyridine to a reaction mixture of VO(acac)$_2$ and nitrophenols results in phenolato complexes VO(OC$_6$H$_{5-n}$X$_n$)(acac)(phen or bpy), where X=NO$_2$ and n=1, 2, or 3. Two isomers of VO(OC$_6$H$_2$(NO$_2$)$_3$)(acac)(bpy) are isolated and characterized.

Acetylacetone usually acts as a monoionic bidentate ligand in complexes with a variety of metal ions.[1] In recent years there have been reported several metal complexes which contain the acetylacetone molecule as a neutral ligand.[2] As one of the preparative methods, the reaction of the enolate chelates with dry hydrogen bromide was effective in obtaining CrBr$_2$(acac)(acacH), MnBr$_2$(acacH)$_2$, CoBr$_2$(acacH), and NiBr$_2$(acacH)$_2$.[2a] With the aim of extending the method to the preparation of similar oxovanadium(IV) complexes, the reactions of bis(acetylacetonato)oxovanadium(IV), VO(acac)$_2$, with phenol and its derivatives have now been examined. Although their acidities are appreciably different, neither phenol nor p-nitrophenol, afforded the desired complexes such as VO(acac)(acacH) (phenolate), but produced molecular adducts instead.

It is well known that the square pyramidal VO(acac)$_2$ forms 1:1 adducts in solution with a variety of bases, filling the sixth coordination site,[3] but little is known as to the interaction with acids. This paper will report on the phenol adducts and the phenolato complexes produced by these reactions.

Experimental

Bis(acetylacetonato)oxovanadium(IV) was prepared according to the method reported by Rowe and Jones.[4] Acetylacetone and methanol were distilled before use. Dichloromethane and diethyl ether were also distilled over phosphorus pentoxide and metallic sodium respectively. Commercially available phenols, 1,10-phenanthroline, and 2,2′-bipyridine were used without further purification.

*Reactions of VO(acac)$_2$ with the Phenols in Methanol: Preparation of the VO(acac)$_2$(*p*-X-C$_6$H$_4$OH) Adducts (X=H, NO$_2$, CHO, COOH, Cl, or CH$_3$).* To a solution of VO(acac)$_2$(1 g, 3.8 mmol) in methanol (30 ml) was added a methanol solution (10 ml) containing an equimolar amount of phenol or its *para*-substituted derivatives, and the mixture was kept at 70 °C for about 1 h in order to vaporize the solvent slowly. The concentrated dark brown mixture (*ca.* 5 ml) was then cooled to room temperature to deposit reddish brown needles. The yields and analytical data are summarized in Table 1.

Preparation of the Phenolato Complexes VO(OC$_6$H$_{5-n}$X$_n$)(acac)(phen or bpy)(X=NO$_2$; n=1, 2, or 3). To a solution of VO(acac)$_2$(1 g, 3.8 mmol) in methanol (30 ml) was added a methanol solution (10 ml) containing an equimolar amount of 4-nitro-, 2,4-dinitro- or 2,4,6-trinitrophenol, after which the mixture was kept at 70 °C in order to vaporize the solvent slowly. The resulting dark brown mixture (*ca.* 5 ml) was cooled to 0 °C. The addition of a methanol solution ($\approx$5 ml) containing an equimolar amount of a bidentate nitrogen base, phen or bpy, gave a crystalline product. The picrato complexes were also deposited from the dichloromethane solution of the 4-nitrophenolato complex containing an excess of picric acid when the solution stood at room temperature for a few hours. Two kinds of products, yellow and yellow-green, with the same composition of VO(OC$_6$H$_2$(NO$_2$)$_3$)(acac)(bpy) were obtained by these alternative routes. The phenolato complexes were all stable in air. The analytical data and some physical properties are listed in Table 2.

Measurements. The absorption spectra in solution and the reflectance spectra were obtained using a Hitachi EPS-3T recording spectrophotometer. The IR spectra of solid specimens were measured by means of JASCO IR-E (4000—700 cm^{-1}) and Hitachi EPI-L (700—200 cm^{-1}) infrared spectrophotometers.

The electric conductance of 10^{-3} M solutions of the phenolato complexes in methanol was measured at 25 °C by using a Yanagimoto-type MY conductivity apparatus. Tetraethylammonium iodide was used as the standard of the uni-univalent electrolytes. The molecular weight was determined by means of vapor-pressure osmometry in a dichloromethane solution [(1—2)$\times$10^{-2}M] with an apparatus manufactured by Knauer, Berlin, Germany.

The magnetic susceptibility was measured at room temperature on a Shimadzu automatically recording magnetic balance by the Faraday method. Mercury(II) tetraisothiocyanatocobaltate(II) was used as the reference.

Results and Discussion

Recently Aly[5] examined the reactions of neutral acetylacetonato complexes of Zn(II), Ni(II), Co(II), Al(III), and Fe(III) with nitrophenols in a refluxing mixture (1:1 by volume) of benzene and ethanol. In most of the reactions with 2,4,6-trinitro- and 2,4-dinitrophenols, cationic complexes of the [M(acac)$_n$(H$_2$O)$_m$](nitrophenolate)type were obtained, although 4-nitrophenol did not react. On the contrary, the neutral adducts VO(acac)$_2$(p-X-C$_6$H$_4$OH) are the only products in the reactions of VO(acac)$_2$ with phenol and its *para*-substituted derivatives in methanol, in spite of the

TABLE 1. ANALYTICAL DATA[a)] OF THE $VO(acac)_2(p\text{-}XC_6H_4OH)$ ADDUCTS

Adduct	Mp/°C	C/%	H/%	N/%	Yield/%
$VO(acac)_2(p\text{-}NO_2C_6H_4OH)$	118	47.23(47.54)	4.66(4.74)	3.42(3.46)	43
$VO(acac)_2(p\text{-}CHOC_6H_4OH)$	114	52.65(52.72)	5.19(5.21)		69
$VO(acac)_2(p\text{-}COOHC_6H_4OH)$	153	50.18(50.63)	5.00(5.00)		34
$VO(acac)_2(p\text{-}ClC_6H_4OH)$	91	48.88(48.81)	4.80(4.86)		42
$VO(acac)_2(C_6H_5OH)\cdot 1/2H_2O$	65	52.28(52.18)	5.75(5.75)		39
$VO(acac)_2(p\text{-}CH_3C_6H_4OH)$	80	54.56(54.70)	5.87(5.94)		25

a) Calculated values in parentheses.

TABLE 2. ANALYTICAL DATA[a)] AND SOME PHYSICAL PROPERTIES OF THE PHENOLATO COMPLEXES

Complex[b)]	Color	Mp/°C	C/%	H/%	N/%	Yield/%
$VO(OC_6H_4NO_2)(acac)phen$	red-violet	191	56.36(57.03)	4.12(3.95)	8.52(8.68)	80
$VO(OC_6H_4NO_2)(acac)bpy$	red-brown	187	54.33(54.79)	4.25(4.16)	8.96(9.13)	84
$VO(OC_6H_3(NO_2)_2)(acac)phen$	orange	186	51.45(52.18)	3.26(3.43)	10.84(10.53)	89
$VO(OC_6H_3(NO_2)_2)(acac)bpy$	orange	170	49.66(49.91)	3.51(3.59)	11.22(11.09)	87
$VO(OC_6H_2(NO_2)_3)(acac)phen$	yellow-green	187	47.37(48.10)	3.57(2.98)	12.00(12.19)	89
$VO(OC_6H_2(NO_2)_3)(acac)bpy$						
Yellow isomer	yellow	180	45.45(45.83)	3.12(3.11)	12.63(12.73)	93
Yellow-green isomer	yellow-green	193	46.28(45.83)	3.17(3.11)	12.04(12.73)	49

a) Calculated values in parentheses. b) $OC_6H_4NO_2$: 4-nitrophenolate; $OC_6H_3(NO_2)_2$: 2,4-dinitrophenolate; $OC_6H_2(NO_2)_3$: 2,4,6-trinitrophenolate = picrate.

TABLE 3. THE MAGNETIC, SPECTRAL, AND mol wt[a)] DATA OF THE $VO(acac)_2(p\text{-}XC_6H_4OH)$ ADDUCTS

X	Magnetic moment B. M.	$\nu(V{=}O)$ [b)] cm^{-1}	$\nu(V\cdots O)$[b)] cm^{-1}	Reflectance spectra $\nu_{max}/10^3$ cm^{-1}		Mol wt in CH_2Cl_2
NO_2	1.74	910	280	12.8	17.9	230(404)
CHO	1.75	905	280	12.7	18.4	227(387)
COOH	1.68	901	283	12.8	18.0	—
Cl	1.74	908	281	13.1	18.0	210(393)
H	1.76	904	281	12.9	17.9	186(359)
CH_3	1.76	910	278	13.0	17.9	213(373)
No adduct	1.73	1000	—	14.6	16.8	

a) Calculated values in parentheses. b) In Nujol.

widely different acidities of the phenols. Moreover, 2,4-dinitro- and 2,4,6-trinitrophenols do not react with $VO(acac)_2$ under the same reaction conditions. 2,2′-Bipyridine and 1,10-phenanthroline, however, induce reactions with the nitrophenols, resulting in the phenolato complexes $VO(X_nC_6H_{5-n}O)(acac)$(phen or bpy) ($X{=}NO_2$; $n{=}1$, 2 or 3).

The Phenol Adducts $VO(acac)_2(p\text{-}X\text{-}C_6H_4OH)$. The magnetic, spectral, and molecular-weight data of the $VO(acac)_2(p\text{-}X\text{-}C_6H_4OH)$ complexes are shown in Table 3. The observed magnetic moments correspond to those of the vanadium(IV) state.

A crystal of $VO(acac)_2$ consists of discrete molecules of a square-pyramidal structure, with the vanadium atom near its center of gravity.[6)] On the contrary, the present 4-nitrophenol adduct was disclosed by preliminary X-ray analysis[7)] to have a polymeric structure of an infinite chain of square-pyramidal molecules connected by $V{=}O\cdots V{=}O\cdots$ bonds, as is depicted in Fig. 1. The phenol molecule is connected to one oxygen atom of an acetylacetonate ligand *via* the hydrogen bond with the $OH\cdots O$ distance of 2.68 Å. Our attempts to isolate the 1:1 adducts of $VO(acac)_2$ with anisole and sodium phenolate were unsuccessful. Thus, the presence of the phenolic hydrogen atom might be essential for making such a 1:1 adduct bearing a polymeric chain.

The $\nu(V{=}O)$ band of $VO(acac)_2$ appears at 1000 cm^{-1}, but the frequency decreases on adduct formation.[3)] Caira *et al.*[8)] reported that the ligation of a substituted pyridine to vanadium at the position cis to the oxo ligand lowers the $\nu(V{=}O)$ frequency by 42±4 cm^{-1}, while the trans ligation by 29±4 cm^{-1}. As may be seen in Table 3, the observed $\nu(V{=}O)$ frequencies for the present compounds are too low to be taken as those for simple phenol adducts. Such a low $\nu(V{=}O)$ frequency is characteristic of the oxovanadium(IV) complex bearing $V{=}O\cdots V{=}O\cdots$ bonds. For example, bis(trifluoroacetylacetonato)- and bis(thenoyltrifluoroacetonato)oxovanadium(IV) complexes display the $\nu(V{=}O)$ band at 1015 and 1012 cm^{-1} in dichloromethane, but at 932 and 900 cm^{-1} in Nujol, respectively, and so may be presumed to have the polymeric structure[9)] in a solid. A similar polymeric structure has been

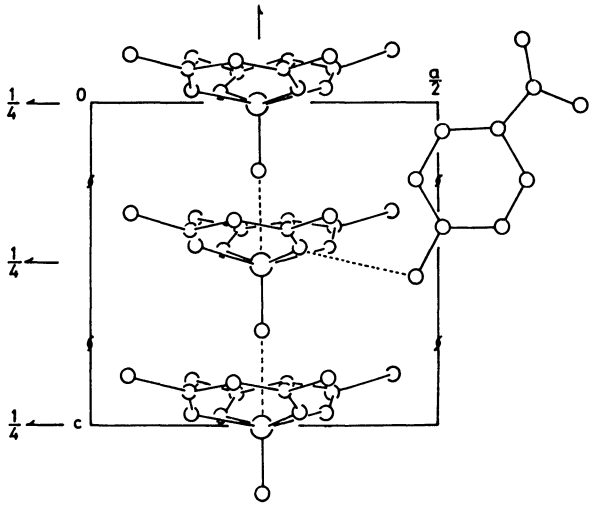

Fig. 1. The structure of VO(acac)$_2$(p-NO$_2$C$_6$H$_4$OH) (from Ref. 7).

established by the X-ray analysis for (N,N'-disalicylidene-1,3-propanediaminato)oxovanadium(IV), VO(sal)$_2$tn,[10] the ν(V=O) vibration of which appears at 854 cm^{-1} in a solid.

We may now assign the new band at 280 cm^{-1}, which is not involved in the spectra of the parent complex and the free phenol, to the stretch of the bridging V···O linkage in the polymeric structure, according to the literature.[9] On the basis of the similarity of the IR spectra, the other adducts seem also to have an analogous chain structure. The anomalous orange-brown color of these complexes also supports the chain structure.[10-12]

It is worth noting that the order of each V=O bond length in VO(acac)$_2$ (1.56 Å, Ref. 6), VO(acac)$_2$(p-NO$_2$C$_6$H$_4$OH) (1.60 Å, Ref. 7), and VO(sal)$_2$tn (1.633 Å, Ref. 10) is reflected in the ν(V=O) frequencies: 1000, 910, and 854 cm^{-1} in series. The reverse order of the V···O distance in VO(acac)$_2$(p-NO$_2$C$_6$H$_4$OH) (2.32 Å) and VO(sal)$_2$tn (2.213 Å) is also reasonable.

The parent complex, VO(acac)$_2$, exhibits two d-d absorption maxima in non-coordinating media at 15000 and 16800 cm^{-1}, with a shoulder at 11500 cm^{-1}; those maxima are shifted to around 13000 and 17000 cm^{-1} in coordinating media.[13] As may be seen in Table 3, the reflectance spectra of the present phenol adducts have distinct maxima at around 13000 and 18000 cm^{-1}, indicating the formation of hexa-coordinate complexes. This is compatible with the polymeric structure discussed above. In dichloromethane, however, these two maxima for, *e.g.*, the 4-nitrophenol adduct are observed at 14700 and 16800 cm^{-1}. These shifts imply the V···O bond cleavage and the release of the phenol molecule, resulting in monomeric penta-coordinate species, even in such a non-coordinating medium. In methanol, these maxima revert again to 12700 and 17200 cm^{-1} due to the formation of the hexa-coordinate species by the ligation of a solvent molecule.

Such a dissociation of the adduct in solution is also indicated by the molecular-weight and IR data. The molecular weight determined in dichloromethane at 25 °C (Table 3) is close to half the value calculated for the monomeric adduct, revealing the extensive liberation of the phenol in solution in addition to the V···O bond cleavage. The IR spectrum of the 4-nitrophenol adduct in dichloromethane is quite different from that in Nujol and nearly coincides with that of VO(acac)$_2$ (Fig. 2), in accordance with the dissociation scheme noted before. If successive portions of 4-nitrophenol are added to the solution, the shoulder at 980 cm^{-1} grows gradually to a new absorption band at the expense of the 1000 cm^{-1} band. According to the assignment by Selbin *et al.*,[14] the new band can be assigned to the ν(V=O) vibration of the phenol adduct, in which the site trans to the exo ligand of VO(acac)$_2$ is occupied by the phenol molecule.

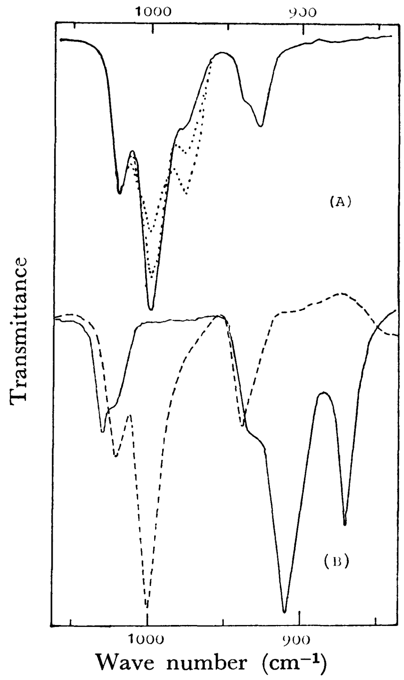

Fig. 2. IR spectra in CH$_2$Cl$_2$ (A) and in Nujol (B): VO(acac)$_2$(p-NO$_2$C$_6$H$_4$OH) (——), VO(acac)$_2$(p-NO$_2$C$_6$H$_4$OH) + p-NO$_2$C$_6$H$_4$OH(······), and VO(acac)$_2$ (----).

In the case of β-diketonato complexes, the driving force for the V=O···V=O stacking has been attributed mainly to the inductive effect of electron-withdrawing groups introduced in the parent acetylacetonate ligand.[9] The present case, however, involves only VO(acac)$_2$, in which the β-diketonate ligand does not bear any substituent exerting an electron-withdrawing effect on the metal acidity. It is not clear how the hydrogen bonding between the phenol and an acetylacetonate oxygen can exert an electronic and/or steric effect to make possible the V=O···V=O stacking in crystals.

The Phenolato Complexes VO($OC_6H_{5-n}X_n$)(acac)(phen or bpy) (X=NO_2; n=1, 2, or 3). The magnetic, spectral, molecular-weight, and conductance data of the phenolato complexes are shown in Table 4. The observed magnetic moments correspond to the d^1 spin state of the vanadium ion, indicating that no redox process of vanadium occurs during these reactions.

Caira *et al.*[8] examined the IR spectra of the substituted pyridine adducts VO(acac)$_2$L, as has been de-

TABLE 4. THE MAGNETIC, SPECTRAL, mol wt,[a] AND CONDUCTANCE DATA OF THE $VO(OC_6H_{5-n}X_n)(acac)L$ COMPLEXES

$X_nC_6H_{5-n}O^-$	L	Magnetic moment B. M.	$\nu(V=O)$ cm^{-1} (in Nujol)	Visible spectra in CH_2Cl_2, ν_{max} $10^3\ cm^{-1}$		Mol wt in CH_2Cl_2	Molar conductance in CH_3OH $ohm^{-1}\ cm^2\ mol^{-1}$
$4\text{-}NO_2C_6H_4O^-$	phen	1.74	970	12.3	17.0	509(484)	18
	bpy	1.67	968	12.5	17.1	414(460)	8
$2,4\text{-}(NO_2)_2C_6H_3O^-$	phen	1.70	965	12.5	16.9	d)	50
	bpy	1.74	962	12.4	17.4	539(505)	41
$2,4,6\text{-}(NO_2)_3C_6H_2O^-$	phen	1.72	972	13.0	17.1	584(574)	95
	bpy[b]	1.71	901	d)		d)	80
	bpy[c]	1.72	973	13.0	16.9	555(550)	81[e]

a) Calculated values in parentheses. b) Yellow isomer. c) Yellow-green isomer. d) Not determined because of poor solubility. e) This complex behaves in the same manner as the yellow isomer in methanol.

scribed previously. For the *cis* configuration, the $\nu(V=O)$ frequency showed no appreciable dependence upon the electronic nature of the pyridine substituent, whereas for the *trans* one the electron release by the substituent caused a reduction in the frequency. All of the present nitrophenolates except the yellow isomer of picrate (*vide infra*) display $\nu(V=O)$ bands in the 962—973 cm^{-1} region which are higher than those for the phenol adducts and which are almost constant, irrespective of the great difference in the pK_a's of the nitrophenols ($pK_a=7.149$, 4.110, and 0.708 at 25 °C for 4-nitro-, 2,4-dinitro-, and 2,4,6-trinitrophenols respectively). If the above IR criterion for the geometrical structure of $VO(acac)_2L$ is also applicable to the present complexes, the *cis* arrangement of the phenolate to the oxo ligand would be more probable. However, at the present stage it is not clear which atom, oxygen (acac) or nitrogen (bpy), occupies the position *trans* to the oxo ligand.

As may be seen in Table 4, the present phenolato complexes exhibit two d-d absorption maxima in dichloromethane at around 12500 and 17000 cm^{-1}, with a shoulder at around 21000 cm^{-1}. These spectra are similar to those of the phenol adducts in a solid and are typical ones for octahedral oxovanadium(IV) complexes. The two band positions are almost constant for these complexes and do not relate to the change in the pK_a's of the nitrophenols, again indicating no electronic effect of the substituted phenol on vanadium.

The observed molecular weight in dichloromethane at 25 °C is close to the calculated value, indicating that these complexes exist intact in solution without liberating the phenolate ligand. This contrasts with the cationic complex derived by Aly.[5] The conductance measured in methanol, on the contrary, depends on the nature of the nitrophenol contained in these complexes. The 4-nitrophenolato complex exists as a non-electrolyte even in methanol, while the picrato complex behaves practically as a uni-univalent electrolyte in this solution, presumably with the release of the picrate ion. The conductance of the 2,4-dinitrophenolato complex is intermediate between those of the 4-nitro- and the 2,4,6-trinitrophenolato complexes, suggesting partial ionization to a complex cation and a 2,4-dinitrophenolate ion in solution. The enhanced ionization with the increase in the number of the nitro substituent on the phenol ring appears to reflect the increase V–O(phenolate)-bond instability in these complexes resulting from the electronic and/or steric effect of the substituent.

Two kinds of $VO(OC_6H_2(NO_2)_3)(acac)(bpy)$ complexes were produced by different synthetic routes. The yellow-green isomer was prepared by the picrate substitution of the 4-nitrophenolato complex in dichloromethane, while the yellow isomer was obtained by the direct reaction of $VO(acac)_2$, 2,4,6-trinitrophenol, and bpy in methanol. However, it is likely that the difference in kind was caused by the difference in the donor abilities of the solvents used rather than by that in the synthetic routes, since the yellow-green isomer could also be prepared by means of a direct reaction in dichloromethane.

The $\nu(V=O)$ frequency of the yellow isomer lies at 901 cm^{-1} abnormally lower than those of other phenolato complexes, and is close to those of the phenol adducts. Thus, it is suggested that the isomer also has a $V=\dot{O}\cdots V=O$ chain structure in a solid and is formulated by [VO(acac)(bpy)](picrate). The low solubility of the complex in nonpolar solvents may be due to its polymeric and ionic character. On the other hand, the complex dissolves in methanol and behaves as a uni-univalent electrolyte, as does the yellow-green isomer.

The existence of two isomers for the picrato complex containing bpy appears to be caused by a delicate balance among the coordinating abilities of a picrate ion, an adjacent vanadyl oxygen atom, and a methanol molecule, toward the sixth coordination site of a particular vanadium cation $[VO(acac)(bpy)]^+$. The yellow-green isomer is stable in dichloromethane, but releases the picrate ion in methanol, depositing the yellow isomer on evaporation. Why a pair of isomers of the phen derivative can not be derived is a question left to be solved.

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