cis-Dioxovanadium(V) and Mixed-Valence Divanadium(IV, V) Complexes Containing β-Diketonate and Heterocyclic Nitrogen-base Ligands

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Diamagnetic dioxovanadium(V) complexes, VO_2(β-dik)(phen or bpy),† were prepared by the direct reactions of VO(β-dik)$_2$ with 1,10-phenanthroline and 2,2′-bipyridine in dichloromethane under aerobic conditions as well as by two other methods. These compounds were concluded to have a *cis* configuration on the basis of the IR and Raman data. These complexes are solvolyzed to afford the di-μ-methoxo- or di-μ-hydroxo-divanadium(V) species, and are reduced by hydrogen bromide to the oxovanadium(IV) species in dichloromethane. In methanol instead of dichloromethane, VO(acac)$_2$ reacted with 2,2′-bipyridine to produce a novel mixed-valence divanadium(IV, V) complex, V_2O_3(acac)$_3$(bpy), which was revealed by the magnetic, spectral, and polarographic data to be a trans adduct of VO(acac)$_2$ with VO_2(acac)(bpy) *via* an oxide ligand.

Bis(acetylacetonato)oxovanadium(IV), VO(acac)$_2$, acts as an effective and highly selective catalyst for the epoxidation of olefins[1] and olefinic alcohols[2] by *t*-butyl hydroperoxide. Gould *et al.*[1] provided some evidence showing that a vanadium(V) hydroperoxide complex produced by the reaction of VO(acac)$_2$ with a hydroperoxide served as an effective catalyst for the epoxidation. The intermediary vanadium(V) complex, however, was neither isolated nor characterized.

Solid VO(acac)$_2$ is stable in air for a long period, but in solution it is slowly oxidized by atmospheric oxygen to some as yet unknown quinquevalent species.[3] In general, VO^{2+} ions are stable for 6 months or more in concentrated strong acids, but they are rapidly oxidized above pH 2.45, especially in alkaline solutions.[4]

The reaction of VO(acac)$_2$ with a slight excess of 1,10-phenanthroline in methanol yielded a mixed ligand V(IV) complex with the composition of VO (acac)$_2$(phen)·2MeOH,[5] but the same reaction in dichloromethane under aerobic conditions resulted in a V(V) complex, VO_2(acac)(phen).[6] We wish now to report more detailed results on the reactions of several bis(β-diketonato)oxovanadium(IV) complexes with 1,10-phenanthroline and 2,2′-bipyridine under the latter reaction conditions to afford diamagnetic VO_2(β-dik)(phen or bpy).

Experimental

Materials. The oxovanadium(IV) complexes, VO(acac)$_2$,[7] VO(tfac)$_2$,[8] and VO(bzac)$_2$,[9] were prepared by the methods described in the literature and gave satisfactory elemental analyses and IR spectra. Commercially available β-diketones, 1,10-phenanthroline, and 2,2′-bipyridine were used without further purification. The organic liquids were dried and distilled before use. A stock solution of hydrogen bromide was prepared by dissolving in dichloromethane the gas which had been generated by the reaction of tetralin with bromine and by then drying through a tube containing calcium bromide.

Preparation of the Diamagnetic cis-*Dioxovanadium(V) Complexes.* These complexes were prepared by the following methods.

Method A: Direct Reaction of Bis(β-diketonato)oxovanadium(IV) with 1,10-Phenanthroline and 2,2′-Bipyridine under Aerobic Conditions. cis-*Dioxo(acetylacetonato)(1,10-phenanthroline)vanadium(V),* cis-*VO_2(acac)(phen) (**1**):* To a dichloromethane solution (40 ml) of VO(acac)$_2$ (1.0 g, 3.8 mmol) we added a solution of an excess of 1,10-phenanthroline monohydrate in dichloromethane (40 ml); oxygen was bubbled through the mixture for about 5 h to deposit reddish brown crystals. They were then filtered off, washed with diethyl ether, and dried *in vacuo*, but they still contained dichloromethane as the solvent of crystallization. Recrystallization from a mixture (1:1 by volume) of methanol and acetylacetone freed the complex from the solvent of crystallization.

Compounds **2**, **3**, **4**, and **6** in Table 1 were prepared by similar methods, but the oxidation was continued for 7—9 h. In the preparation of 2,2′-bipyridine derivatives the solution after oxidation was concentrated to 10 ml to deposit crystals.

Method B: Replacement Reactions of VO_2(acac)(phen or bpy) by Other β-Diketonate Ligands. The VO_2(acac)(phen or bpy) complex (1 mmol) was added to a methanol solution (20 ml) containing twice the molar amounts of a β-diketone other than acetylacetone, and the mixture was heated to dissolve the complex. The solution was then filtered and cooled to room temperature to separate out crystals of the corresponding β-diketonate complex, VO_2(β-dik)(phen or bpy).

This method was useful for the preparation of *cis*-dioxo complexes **3**—**10**. The low yield of *cis*-dioxo(2,2′-bipyridine)(dibenzoylmethanido)vanadium(V) monohydrate *cis*-VO_2(dbm)(bpy)·H_2O is caused by partial methanolysis. Thus, a reddish brown methanolysis product was first precipitated and analyzed to fit $VO(OCH_3)_2$(dbm) (Found: C, 57.84; H, 4.85. Calcd for $C_{17}H_{17}O_5V$: C, 57.96; H, 4.86%). The desired red compound separated out from the filtrate.

Method C: Replacement of the 2,2′-Bipyridine in VO_2(β-dik)(bpy) by 1,10-Phenanthroline. A methanol solution (10 ml) of 1,10-phenanthroline (3 mmol) was added to a methanol solution (25 ml) containing VO_2(β-dik)(bpy) (1 mmol) and the same kind of β-diketone ligand (3 mmol). The mixture was heated to 60 °C for 1 h, and then kept at room temperature to precipitate the phen complex.

Compounds **1**, **3**, and **5** were prepared according to this method. The analytical data, decomposition temperatures, and yields (by each synthetic method, A, B, or C) of these dioxovanadium(V) complexes are listed in Table 1.

Solvolysis Reactions of cis-*VO_2(β-dik)(phen or bpy).* When the *cis*-VO_2(β-dik)(phen or bpy) complex (1 mmol) was heated to dissolve it in methanol (20 ml), a solvolytic reaction occurred and a product with the composition of $V_2O_4(OCH_3)_2$(phen or bpy) was separated out on cooling

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† β-dikH (β-diketone) = acacH(acetylacetone), bzacH (benzoylacetone), tfacH (trifluoroacetylacetone), dbmH (dibenzoylmethane), and hfacH (hexafluoroacetylacetone); phen and bpy stand for 1,10-phenanthroline and 2,2′-bipyridine respectively.

TABLE 1. ANALYTICAL DATA,[a] DEC TEMP, AND YIELDS

No.	Compound	C/%	H/%	N/%	Dec temp / °C	Yield/% A[b]	B[b]	C[b]
1	VO_2(acac)(phen)	55.67(56.36)	4.39(4.17)	7.45(7.73)	143—144	36		63
2	VO_2(acac)(bpy)	53.09(53.27)	4.45(4.47)	8.01(8.28)	170—171	63		
3	VO_2(bzac)(phen)	61.60(62.27)	4.13(4.04)	6.76(6.60)	191—193	86	80	45
4	VO_2(bzac)(bpy)·1/2H_2O	58.93(58.69)	4.45(4.43)	6.93(6.84)	167—168	86	91	
5	VO_2(tfac)(phen)	49.06(49.06)	2.91(2.91)	6.83(6.73)	177—179		82	29
6	VO_2(tfac)(bpy)	45.08(45.94)	3.00(3.08)	6.89(7.14)	176—177	54	31	
7	VO_2(dbm)(phen)	66.52(66.67)	3.95(3.94)	5.52(5.76)	215—217		88	
8	VO_2(dbm)(bpy)·H_2O	62.97(62.51)	4.58(4.41)	5.61(5.83)	200—203		6	
9	VO_2(hfac)(phen)	43.26(43.24)	1.94(1.92)	5.77(5.93)	167—168		70	
10	VO_2(hfac)(bpy)	40.82(40.38)	2.23(2.03)	6.25(6.28)	159—161		42	
11	VOBr(acac)(phen)·2H_2O	43.64(44.18)	4.11(4.14)	6.12(6.06)	203—204		42	
12	VOBr(acac)(bpy)·2H_2O	40.91(41.12)	4.32(4.37)	6.30(6.39)	191—193		62	
13	VOBr(bzac)(phen)·1/2H_2O	53.78(53.14)	3.81(3.65)	5.68(5.63)	170—172		57	
14	VOBr(bzac)(phen)·H_2O	50.15(49.81)	3.90(3.55)	5.71(5.81)	149—151		40	
15	$V_2O_3(acac)_3$(bpy)	49.75(49.76)	4.90(4.84)	4.46(4.64)	165—167	55		62[c]

a) Calculated values in parentheses. b) Yield by each synthetic method (A, B or C) described in Exptl Section. c) Yield by an equimolar reaction between $VO(acac)_2$ and VO_2(acac)(bpy).

to room temperature. The yields were 54% for $V_2O_4(OCH_3)_2$(phen) (Found: C, 40.67; H, 3.37; N, 6.83. Calcd for $C_{14}H_{14}N_2O_6V_2$: C, 41.20; H, 3.46; N, 6.86%. Dec 179—180 °C), and 63% for $V_2O_4(OCH_3)_2$(bpy) (Found: 37.17; H, 3.70; N, 7.12. Calcd for $C_{12}H_{14}N_2O_6V_2$: C, 37.52; H, 3.67; N, 7.29%. Dec 169—170 °C). The latter compound was also prepared by stirring for a few days a suspension of vanadium(V) pentoxide in methanol containing 2,2'-bipyridine. The subsequent heating of the complex in other organic solvents, such as chloroform, dichloromethane, acetone, and nitromethane, resulted in $V_2O_4(OH)_2$(phen)·3/2H_2O or $V_2O_4(OH)_2$(bpy)·2H_2O. The yield was 67% for $V_2O_4(OH)_2$(phen)·3/2H_2O (Found: C, 35.38; H, 2.49; N, 6.55. Calcd for $C_{12}H_{13}N_2O_{7.5}V_2$: C, 35.37; H, 3.22; N, 6.88%. Dec 194—196 °C). The yield was 48% for $V_2O_4(OH)_2$(bpy)·2H_2O (Found: C, 30.97; H, 2.74; N, 6.60. Calcd for $C_{10}H_{14}N_2O_8V_2$: C, 30.89; H, 3.60; N, 7.14%. Dec 156—158 °C). The products of methanolysis and hydrolysis were all unstable in air and were insoluble in most solvents, thus precluding physical measurements.

Reduction of cis-*VO_2(acac)(phen or bpy) with Hydrogen Bromide.* The *cis*-VO_2(acac)(phen or bpy) complex (2 mmol) was dissolved in dichloromethane (60 ml) containing acetylacetone (9 mmol), and to the mixture we then added, drop by drop, a solution (0.16 M, 25 ml) of hydrogen bromide in dichloromethane. The resultant white-green precipitate was found to be dibromooxo(1,10-phenanthroline)vanadium(IV) $VOBr_2$(phen) or dibromo(2,2'-bipyridine)oxovanadium(IV) $VOBr_2$(bpy) on the basis of elemental analysis. The filtrate was concentrated to 20 ml to deposit yellow-green crystals with the composition of VOBr(acac)(phen)·2H_2O (**11**) or VOBr(acac)(bpy)·2H_2O (**12**). The corresponding VOBr(bzac)(phen)·1/2H_2O (**13**) and VOBr(bzac)(bpy)·H_2O (**14**) complexes were produced in a similar manner and gave satisfactory analyses (Table 1).

*Preparation of the Mixed-Valence Divanadium(IV, V) Complex. Tris(acetylacetonato)(2,2'-bipyridine)trioxo-divanadium(IV, V), $V_2O_3(acac)_3$(bpy) (**15**):* A methanol solution (30 ml) containing $VO(acac)_2$ (1.6 g, 6.2 mmol) and 2,2'-bipyridine (1.0 g, 6.4 mmol) was concentrated to about 10 ml at 60 °C on a water bath and then cooled to room temperature to deposit green crystallites of $V_2O_3(acac)_3$(bpy). The complex was also prepared by simple adduct formation between $VO(acac)_2$ and **2**: equimolar amounts of $VO(acac)_2$ (0.58 g, 2.2 mmol) and VO_2(acac)(bpy) (0.74 g, 2.2 mmol) were dissolved in methanol (50 ml) containing acetylacetone (2 ml), and then the mixture was concentrated to 20 ml to separate $V_2O_3(acac)_3$(bpy).

The analytical data, decomposition temperature, and yield of the complex are listed in the last row of Table 1.

Measurements. Each specimen of the complexes was dried *in vacuo* at room temperature before being subjected to elemental analysis. The absorption spectra of the solutions and the reflectance spectra of the solid specimen were measured by means of a Hitachi EPS-3T autorecording spectrophotometer equipped with an RIO reflectance attachment. The infrared spectra were taken in Nujol on JASCO IR-E (4000—700 cm^{-1}) and Hitachi EPI-L (700—200 cm^{-1}) infrared spectrophotometers. The Raman spectra were recorded with the aid of a JRS-S1 Laser Raman spectrophotometer by exciting a solid specimen in a rotating cell with a 5145 Å Argon laser.

The magnetic susceptibility was measured by means of a Shimadzu MB-2 automatically recording magnetic balance, employing mercury tetraisothiocyanatocobaltate(II) as a reference. The electric conductivities of compounds **11** and **12** were measured in methanol by means of an MY-7 apparatus of the Yanagimoto Seisakusho, Ltd.

Results and Discussion

As has been described in the Experimental Section, each VO_2(β-dik)(phen or bpy) complex could be prepared by one or more of three synthetic methods. The complexes are all yellow to red crystals. The magnetic susceptibilities of the representative compounds, **1** and **2**, were measured at room temperature. They are both diamagnetic, χ_M being -1.52×10^{-4} and -4.72×10^{-5} c.g.s. unit respectively. This implies that the vanadium atom is in a quinquevalent state with the d^0 configuration in these complexes,

TABLE 2. THE CHARACTERISTIC IR BANDS OF THE $VO_2(\beta\text{-dik})$(phen OR bpy) COMPLEXES (cm^{-1})

No.	Compound	$\nu_s(C=O)$	$\nu_{as}(C=C=C)$	$\nu_s(VO_2)$	$\nu_{as}(VO_2)$	$\delta(VO_2)$
1	VO_2(acac)(phen)	1613	1515	916	891	340
2	VO_2(acac)(bpy)	1613	1513	911	886	344
3	VO_2(bzac)(phen)	1612	1515	915	891	337
4	VO_2(bzac)(bpy)$\cdot 1/2H_2O$	1615	1516	914	881	336
5	VO_2(tfac)(phen)	1653	1545	923	900	326
6	VO_2(tfac)(bpy)	1651	1537	922	901	328
7	VO_2(dbm)(phen)	1600	1515	918	892	327
8	VO_2(dbm)(bpy)$\cdot H_2O$	1610	1518	915	887	337
9	VO_2(hfac)(phen)	1662	1554	932	907	322
10	VO_2(hfac)(bpy)	1663	1555	939	912	327

The diamagnetism of the other dioxo complexes can also be inferred by analogy with **1** and **2**.

Geometrical Structure. To our knowledge, only the *cis* arrangement of two oxide ligands has been elucidated by X-ray analysis for octahedral dioxovanadium(V) complexes, such as ammonium salts of dioxobis(oxalato)vanadate(V)[10] and (dihydrogenethylenediaminetetraacetato)dioxovanadate(V),[11] and trisodium (ethylenediaminetetraacetato)dioxovanadate(V) tetrahydrate.[12] Hence, it is of interest to explore whether or not the two oxo groups in the present complexes are in a *cis* configuration. As has been described in a preliminary communication,[6] the *cis* structure was also established by a single crystal X-ray analysis of compound **1**.

Griffith and Wickins[13,14] proposed that the strong π-donor effect of the oxo ligand in octahedral complexes will make the d^0 species of the $[MO_2X_4]^{n-}$ type take the *cis* configuration. From the theoretical treatment of the vibrational modes they[14] showed that, for the *cis* form, the three vibrational modes of $\nu_s(MO_2)$, $\nu_{as}(MO_2)$, and $\delta(MO_2)$ are active in both IR and Raman spectra, while for the trans form only the symmetric stretching mode is Raman-active, with the other modes being IR-active only. They examined the IR and Raman spectra of a number of d^0 species of the $[MO_2X_4]^{n-}$ type (Mo^{VI}, W^{VI}, or V^V; X=F, Cl, or ½ox). All of them exhibited three bands due to the vibrational modes described above at around 950, 900, and 370 cm^{-1} respectively in either the IR or Raman spectra. Thus, these d^0 complexes were concluded to have a *cis* rather than a *trans* arrangement of the oxo ligands.

The IR spectrum of compound **1** in Nujol shows two strong bands assignable to the V–O (oxide) stretching vibration at 916 and 891 cm^{-1}, together with a band due to the O–V–O bending mode at 340 cm^{-1} (Table 2). The Raman spectrum also exhibits two stretching bands, although the O–V–O bending mode is indiscernible because of the intense background. These results are compatible with the conclusion drawn from the theoretical treatment. As may be seen in Fig. 1, the higher-frequency $\nu(VO_2)$ band is weaker in IR, but is much stronger in Raman than the lower-frequency one, revealing that the former band is attributable to the symmetric vibration, and the latter, to the anti-symmetric vibration. In many bent triatomic molecules the ν_{as} band is observed in a higher-frequency region than the ν_s band, but compound **1** shows an opposite pattern. A similar situation is also observed in $(NH_4)_3[VO_2(ox)_2]\cdot 2H_2O$,[14] while VO_2Cl, VO_2F and VO_2SbF_6[15] show the $\nu_{as}(VO_2)$ band in a higher-frequency region than the $\nu_s(VO_2)$ band. The presence of the ν_s band at a higher frequency in the oxalato complex and the present compound **1** might be attributable to the enhanced repulsion between the oxide ligands as compared with the other three compounds. Such a reversion of ν_{as} and ν_s frequencies is also observed for triatomic molecules with an isosceles-triangular structure such as O_3 and OF_2 because of the large repulsion between the two atoms on the base.[16] As may be seen in Table 2, all the dioxo complexes other than compound **1** also exhibit three IR bands assignable to the $\nu_s(VO_2)$, $\nu_{as}(VO_2)$, and $\delta(VO_2)$ vibrations, although Raman spectra of these complexes were not examined. By analogy with compound **1**, the *cis* configuration of the two oxide ligands in these complexes can also be inferred with confidence.

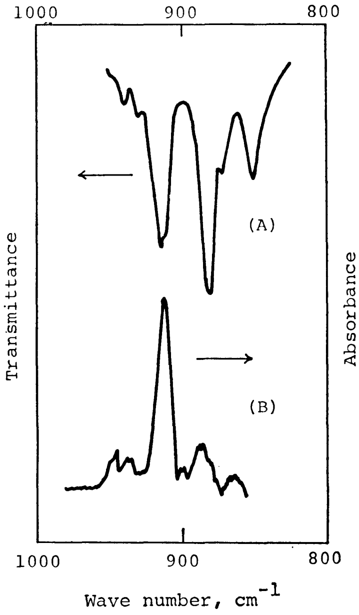
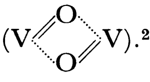
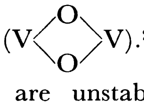


Fig. 1. The IR (in Nujol) (A) and Raman (in solid state) (B) spectra of VO_2(acac)(phen) in the V–O (oxide) stretching region.

Other Characteristics. It has been well established that the β-diketonate chelates exhibit their $\nu_s(C=O)$ and

ν_{as}(C⩵C⩵C) bands in the 1500—1600 cm^{-1} region.[17] On the contrary, the present dioxo complexes display the carbonyl band at frequencies higher than 1600 cm^{-1}, as may be seen in Table 2. A similar situation was noticed when a bidentate nitrogen base, such as ethylenediamine, 1,10-phenanthroline, or 2,2′-bipyridine, was added so as to coordinate it to a neutral metal β-diketonate.[18] The increase in frequency was attributed to the weakening of the metal-oxygen(β-dik) bond by donation of electron from the base to the metal center. In the present case, it is most likely that the strong π-donor ability of oxide ligands weakens the V–O(β-dik) bond. Such a *trans* influence of two oxide ligands essentially resulted in the elongation of one of the two V–O(acac) bonds and of one of the two V–N bonds which are *trans* to the two oxide ligands in VO_2(acac)(phen)[6] (V–O: 2.177(4) and 1.949(4) Å, V–N: 2.300(4) and 2.148(4) Å). An additional weakening of the V–O(β-dik) bond is effected when an electron-withdrawing substituent is introduced into the acetylacetonate ligand of compounds **1** and **2**. In the trifluoro- and hexafluoroacetylacetonato complexes (**5**, **6**, **9**, and **10**) the carbonyl band is, in fact, observed at still higher frequencies than those of **1** and **2**, with concomitant shifts of $\nu_s(VO_2)$ and $\nu_{as}(VO_2)$ to the higher-frequency region (Table 2). It is also of interest that compound **5** was not prepared by Method A. This is probably because the reaction of $VO(tfac)_2$ with 1,10-phenanthroline gave the stable *cis*-adduct $VO(tfac)_2$(phen),[5] which hindered oxidation to the *cis*-dioxo complex.

The reflectance spectra of all the dioxo complexes prepared in this paper exhibit no band assignable to the d-d transitions in the visible region, in conformity with d^0 configuration. A similar feature is also observed in the solution spectra in methanol containing a small quantity of β-diketone to prevent decomposition.

Solvolysis Products. The solvolysis products, $V_2O_4(OCH_3)_2$ (phen or bpy) and their dihydroxo counterparts, include a $V_2O_4^{2+}$-moiety in these complexes. Although many binuclear molybdenum(V) complexes containing a $Mo_2O_4^{2+}$-moiety are known,[13] scarcely no corresponding vanadium(V) complexes with $V_2O_4^{2+}$-moiety have been found. Very recently, (2,2′-bipyridine)fluorodioxovanadium(V), VO_2F(bpy) was prepared[19] and its structure was found by X-ray analysis to have one V=O(terminal) bond on each vanadium(V) atom and asymmetric oxygen bridges .[20] The IR spectrum of this compound shows three V–O stretching bands, at 954, 938, and 872 cm^{-1}, while the present dimethoxo complexes exhibit two bands in the 940—960 cm^{-1} region, together with a broad band in the 700—720 cm^{-1} region. The lower frequency of the last band might be indicative of the presence of more symmetric oxygen bridges .[21] However, these solvolysis products are unstable in air and insoluble in any solvents, thus precluding further examination.

Reduction of $VO_2(\beta$-dik)(phen or bpy) Complexes. The VO_2(acac) (phen or bpy) complexes were easily reduced by hydrogen bromide in dichloromethane to produce the vanadium(IV) species, VOBr(acac)(phen or bpy)·$2H_2O$, which show the magnetic moments of 1.75 and 1.73 B.M. per vanadium atom. The complexes are very similar in composition to the corresponding nitrophenolato complexes, $VO(OC_6H_{5-n}X_n)$-(acac)(phen or bpy) ($X=NO_2$; $n=1$—3), previously isolated by us.[22] One of the latter complexes, the 4-nitrophenolato derivative, reacted with sodium bromide to afford VOBr(acac)(phen or bpy)·$2H_2O$. The reactions of complexes **3** and **4** with hydrogen bromide also gave the corresponding benzoylacetonato vanadium(IV) complexes, **13** and **14**. The ν(V=O) bands of these bromo complexes appear in the 960—980 cm^{-1} region, just as do those of the nitrophenolato complexes which have the *cis* configuration,[22] indicating the cis arrangement of the bromide and oxo ligands.

The absorption spectra of VOBr(acac)(phen or bpy)·$2H_2O$ in dichloromethane showed two bands near 13000 and 16000 cm^{-1}, together with a shoulder around 21000 cm^{-1}. These frequencies are very close to those of the nitrophenolato complexes (12500, 17000, and 21000 cm^{-1}),[22] suggesting the octahedral monomeric structure of the bromo complexes in dichloromethane. On the contrary, the complexes behave as uni-univalent electrolytes in methanol, as evidenced by the Λ_M values of 99(phen) and 91(bpy) ohm^{-1} cm^2 mol^{-1}.

The Mixed-valence Divanadium(IV, V) Complex. Unlike the reaction with 1,10-phenanthroline in methanol leading to $VO(acac)_2(phen)\cdot 2CH_3OH$,[5] $VO(acac)_2$ reacts with 2,2′-bipyridine in the same solvent to afford green crystals with the composition of $V_2O_3(acac)_3$(bpy) (**15**). The magnetic moment of **15** was found at room temperature to be 1.70 B.M. per divanadium unit, nearly corresponding to the value for a single spin. Thus, complex **15** seems to consist of two vanadium atoms in different oxidation states, V(IV)

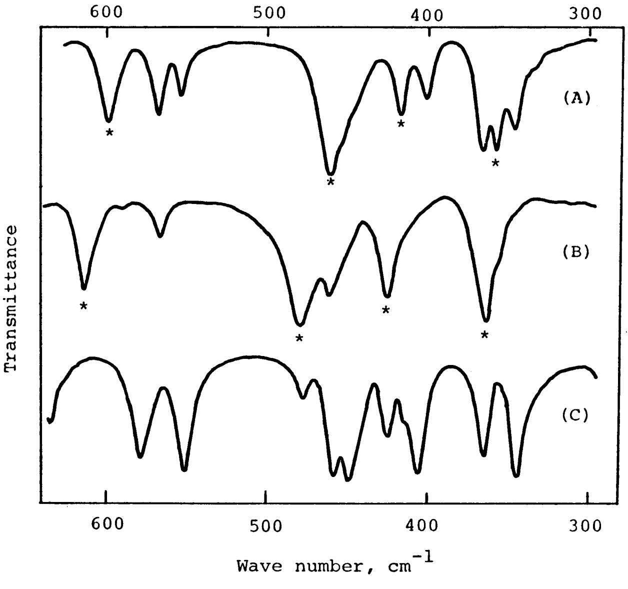
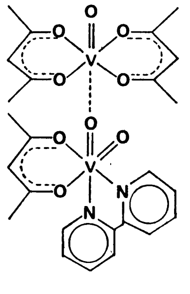


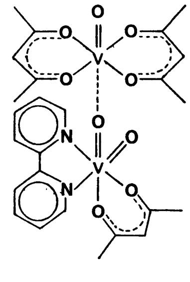
Fig. 2. The far IR spectra of $V_2O_3(acac)_3$(bpy) (A), $VO(acac)_2$ (B) and VO_2(acac)(bpy) (C) in Nujol. Asterisks denote V–O sensitive bands according to the assignment by Caira *et al.* [28].

and V(V).

It has been well established that the ν(V=O) band of VO(acac)$_2$ at 1000 cm^{-1} is shifted to the lower-frequency region on adduct formation, and that the extent of the frequency reduction varies in the range of 20 to 60 cm^{-1} according to the variation in the bases.[23-29] The IR spectrum of the present mixed-valence complex **15** exhibits three intense bands in the ν(V=O) region of 850 to 1000 cm^{-1}. The first band, at 960 cm^{-1}, is just in the range of the ν(V=O) frequencies of the base adducts, and the other two, at 930 and 883 cm^{-1} are very close to the ν_s(VO$_2$) and ν_{as}(VO$_2$) frequencies of VO$_2$(acac)(bpy) (**2**) derived earlier in this paper. Hence, a simple adduct of VO(acac)$_2$ and **2** with one of the oxo ligands in **2** intervening between two vanadium atoms may be presumed for complex **15** ((I) or (II)):



(I)



(II)

In Fig. 2, the IR spectrum of **15** in the lower-frequency region is shown, together with those of VO(acac)$_2$ and **2** for comparison. The spectrum of **15** (Spectrum A) is very similar to a superposition of those for the latter two (Spectra B and C), supporting the proposed structure of **15**. Four bands, at 611, 488, 425, and 367 cm^{-1} of VO(acac)$_2$ previously assigned by Caira *et al.*[28] to the V–O sensitive modes, are lowered to 600, ≈460, 420, and 360 cm^{-1} respectively in complex **15**. Such a lowering without splitting of those bands has also been noted for the *trans* adducts of VO(acac)$_2$ with substituted pyridines[28] and substituted pyridine *N*-oxides.[29] Thus, these data again support the idea that complex **15** is a *trans* adduct of VO(acac)$_2$ with **2**. In fact, complex **15** could be synthesized by an equimolar reaction of VO(acac)$_2$ and VO$_2$(acac)(bpy) in methanol containing excess acetylacetone. However, it is not possible at the present stage of investigation to discriminate the above two possible structures.

Table 3. The reflectance (in solid) and absorption (in methanol) spectra of V$_2$O$_3$ (acac)$_3$(bpy) and VO(acac)$_2$ (ν_{max}, 10^3 cm^{-1})

Compound	Reflectance spectra	Absorption spectra[a]
V$_2$O$_3$(acac)$_3$(bpy)	13.0	12.7 (45)[b]
	17.2	
	22.7	22.7 (1670)[b]
VO(acac)$_2$	14.6	13.0 (40)
	16.8	17.3 (16)
	25.0	25.0 (91)

a) ε values in parentheses.
b) In the presence of acetylacetone (0.503 M).

In Table 3 the reflectance and solution spectral data of **15** are shown, together with those of VO(acac)$_2$. As has been described earlier, VO$_2$(acac)(bpy) exhibits no d-d band in the visible region. Hence, it is likely that the two bands in the reflectance spectrum of complex **15** at 13000 and 17200 cm^{-1}, along with a shoulder at around 22700 cm^{-1}, were brought about by the shift of the absorption bands of VO(acac)$_2$ at 14600 and 16800 cm^{-1} and a shoulder 25000 cm^{-1} respectively. Such shifts of the first and second bands of VO(acac)$_2$ to the lower and higher frequencies respectively are caused by the attainment of the octahedral environment around the vanadium(IV) ion on adduct formation.[30] If a dilute solution of **15** in methanol containing a small quantity of acetylacetone is left standing, VO$_2$(acac)(bpy) is deposited from the mixture. These results may indicate that complex **15** dissociates in this solvent to VO(acac)$_2$ and VO$_2$(acac)(bpy). The absorption spectrum of **15** in methanol containing acetylacetone in a large excess to prevent the decomposition of the complex exhibits two bands, at 22700 (ε=1670) and 12700 (ε=45) cm^{-1}, as is shown in Table 3. Because of the low solubility of **15** in this solution, a 10 cm-cell was used for the measurement of the low intensity band. The former band corresponds essentially to the absorption band at 22200 cm^{-1} (ε=1690) of VO$_2$(acac)(bpy) in methanol containing acetylacetone in a large excess, while the latter corresponds to the first band of VO(acac)$_2$ in the same solvent. The other bands of VO(acac)$_2$ are masked by the tails of the strong ligand bands of VO$_2$(acac)(bpy).

Another support for the presence of the VO$_2$(acac)(bpy) species in methanol was obtained polarographically. The current-voltage curves of **15** and VO$_2$(acac)(bpy) in methanol containing acetylacetone in 6.6 × 10^{-3} M were recorded using tetrabutylammonium perchlorate as a supporting electrolyte. In addition to the similarity of both the wave-shape and the wave-height, the half-wave potential of −0.02 V *vs.* SCE obtained for **15** is very close to that of −0.03 V *vs.* SCE for VO$_2$(acac)(bpy), indicating the presence of VO$_2$(acac)(bpy) in the solution.

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