Journal of the Less-Common Metals, *128* (1987) 281 - 296

PREPARATION, CHARACTERIZATION AND REACTIONS OF VANADIUM(IV) β-DIKETONATE COMPLEXES

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(Received August 7, 1986)

Summary

The β-diketone complexes of vanadium(IV), $VO(dik)_2$ (where dik ≡ btfac, tfac, ttfac, acac, bzac and bzbz) have been prepared either by the reaction of vanadium pentoxide with the appropriate ligand in toluene under reflux for 24 h or by the reaction of a warm aqueous or ethanolic solution of vanadium sulphate with the ligand. The oxovanadium(IV) complexes react with sulphur oxide dichloride and dibromide and phosphorus pentachloride to form dihalovanadium(IV) diketonate complexes. These compounds have been characterized by elemental analysis, melting point measurements, IR and Raman spectra, magnetic susceptibility measurements, electron spin resonance (ESR) and mass spectral studies and X-ray powder diffraction.

1. Introduction

The chemistry of vanadium(IV) is dominated by the stable VO^{2+} ion which forms a wide variety of complexes. The VO^{2+} ion remains intact during many reactions of these compounds [1]. Although a large number of chelating oxovanadium(IV) complexes are known [2 - 10], because of their low reactivity oxovanadium(VI) diketonates are not the most appropriate source for complexes of other oxidation states, since they are hardly oxidized or reduced by means of chemical reagents [2]. No octahedral complexes of the simple vanadium(IV) ion in which vanadium is not attached to a double bonded oxygen atom have been reported.

The $VCl_2(dik)_2$ complexes have been prepared by the direct reaction of diketone with VCl_4 in anhydrous benzene or dichloromethane or hexane [11]. Recently it was found that the direct reaction of oxovanadium(IV) β-diketonate with sulphur oxide dichloride and dibromide resulted in the formation of trans dihalovanadium(IV) β-diketonate complexes [2, 4, 12 - 14]. In this paper we report the preparation and characterization of a number of oxovanadium(IV) and dihalovanadium(IV) β-diketonate complexes.

0022-5088/86/$3.50

2. Experimental details

The dihalovanadium(IV) β-diketonate complexes were prepared and handled in a dinitrogen atmosphere.

2.1. *Materials*

$VOSO_4 \cdot xH_2O$ (BDH), V_2O_5 (BDH), B_2S_3 (Alfa), Sb_2S_3 (Alfa), $SOCl_2$ (BDH), $SOBr_2$ (Aldrich), $CH_3COCH_2COCH_3$ (BDH), $CH_3COCH_2COC_6H_5$ (Aldrich), $C_6H_5COCH_2COC_6H_5$ (BDH), $CF_3COCH_2COCH_3$ (BDH), $CF_3COCH_2COC_6H_5$ (Aldrich), $C_4H_3SCOCH_2COCF_3$ (BDH), PCl_5 (BDH), CH_2Cl_2 (BDH), $(CH_2CO)_2NCl$ (BDH), $(CH_2CO)_2NBr$ (BDH) and C_6H_6 (BDH) were purified and dried by standard methods.

2.2. *Analytical determination*

Analysis of vanadium, carbon, hydrogen, chlorine, bromine, fluorine and sulphur were carried out in the Microanalytical Laboratory, Chemistry Department, Manchester University by Mr M Hart (see Table 1).

2.3. *Preparation of compounds*

2.3.1. *Preparation of oxovanadium(IV) β-diketonate complexes*

β-Diketonate complexes of oxovanadium(IV) were prepared by the following routes.

(a) Vanadium pentoxide was refluxed with the stoichiometric amount (2:9 mol ratio) of β-diketone in toluene for 24 - 30 h. The blue or green suspension was filtered from the hot solution and on cooling the filtrate of blue or green crystals was isolated.

(b) A solution of the β-diketone in ethanol was added dropwise with continuous agitation to the stoichiometric amount (2:1 mol ratio) of vanadium sulphate in ethanol or water over a period of 30 min. The mixture was agitated continuously for an additional 15 min, and after all the β-diketone had been used, the green microcrystals of the complex were filtered. The aqueous filtrate was neutralized with aqueous sodium carbonate solution and an additional amount of complex was separated.

2.3.2. *Preparation of $VX_2(dik)_2$*

The β-diketone complexes of dihalovanadium(IV) were prepared by the following routes.

(a) To a benzene or toluene suspension of β-diketone complexes of oxovanadium(IV), the stoichiometric amount (1:1.1 mol ratio) of sulphur oxide dichloride or dibromide in toluene was slowly added dropwise with continuous agitation over a period of 5 - 6 h at 40 - 60 °C in a dinitrogen atmosphere. The black product was filtered off and vacuum dried.

(b) A solution of PCl_5 in benzene or dichloromethane was added dropwise with continuous agitation to the stoichiometric amount (1:1.1 mol ratio) of oxovanadium(VI) complexes in benzene at 40 °C over a period of six hours. At the end of this period the black dichlorovanadium(IV) complex was filtered off and vacuum dried.

TABLE 1

Physical properties and analytical data of β-diketonate complexes of vanadium(IV)

Complexes	*Colour*	*Melting point* (°C)	*Analysis*									
			Calculated (%)					*Found (%)*				
			V	C	H	X[a]	S	V	C	H	X[a]	S
VO(acac)$_2$	blue	168d	19.21	45.25	5.27			19.1	45.2	5.4		
VO(Clacac)$_2$	pale green	246	15.27	39.93	3.59	21.25		15.3	36.05	3.60	21.0	
VO(Bracac)$_2$	pale green	198	12.05	28.37	2.83	37.82		12.9	29.3	2.9	36.9	
VCl$_2$(acac)$_2$	black		13.11	30.84	3.08	37.82		12.6	31.8	4.2	36.9	
VBr$_2$(acac)$_2$	black		12.47	29.34	3.42	39.12		12.6	28.8	3.6	38.8	
VO(bzac)$_2$	green	280d	13.08	61.64	4.6			13.1	61.3	4.6		
VCl$_2$(bzac)$_2$	black	120	11.46	54.02	4.06	15.9		11.9	54.3	4.02	15.7	
VBr$_2$(bzac)$_2$	black		9.57	45.03	3.38	30.02		10.1	46.1	3.55	31.2	
VO(bzbz)$_2$	green	260	9.9	70.11	4.28			9.5	70.6	4.4		
VBr$_2$(bzbz)$_2$	black		7.76	54.79	3.34	24.35		8.1	53.6	3.6	25.2	
VO(btfac)$_2$	yellowish-green	278	10.26	48.29	2.41	22.94		10.1	48.2	2.4	21.9	
VO(tfac)$_2$	green	218d	13.67	32.17	2.14	30.56		13.7	31.5	1.9	29.35	
VO(ttfac)$_2$	yellow-orange	210d	10.01	37.69	1.57	22.38	12.56	9.5	36.9	1.5	21.4	12.4

[a] X ≡ F, Cl, Br.

2.3.3. *Reaction of $VCl_2(acac)_2$ with Sb_2O_3*

$VCl_2(acac)_2$ was dissolved in boiling *o*-xylene and the stoichiometric amount (3:1 mol ratio) of Sb_2O_3 was added and allowed to react with $VCl_2(acac)_2$ under reflux for 24 h. The black precipitate was filtered off and all the *o*-xylene solvent distilled off from the green filtrate. The blue $VO(acac)_2$ which was contaminated with some white crystals of $SbCl_3$ was placed in the reaction tube and purified by sublimation.

2.3.4. *Reaction of $VCl_2(acac)_2$ with X_2S_3*

Several attempts were made to prepare $VS(acac)_2$ by the reaction of $VCl_2(acac)_2$ with antimony sulphide or boron sulphide either in a range of solvents or in a sealed reaction tube. In all cases the resultant product was a mixture of different compounds which were difficult to isolate. $V(acac)_3$ was the only well-known compound obtained in most of the reactions.

2.4. *Physical measurement*

2.4.1. *IR spectra*

IR spectra were recorded using a Perkin–Elmer model 577 (4000 - 200 cm^{-1}) instrument. Nujol mulls were prepared in a dry-box.

2.4.2. *Raman spectra*

Raman spectra were recorded using a Spex 1403 double spectrophotometer instrument. Samples were prepared in a dry-box.

2.4.3. *X-ray powder photographs*

Photographs were obtained using a Debye–Scherrer camera with a diameter of 5.37 cm. In all cases Cu Kα radiation was used.

2.4.4. *Magnetic susceptibility measurements*

Magnetic susceptibility measurements on the solid complexes were made at room temperature (293 K) by the Gouy method using $Hg[Co(NCS)_4]$ as the calibrating agent ($\chi_g = 16.4 \times 10^{-6}$ c.g.s. units).

2.4.5. *Melting points*

The melting points of these complexes were determined using a Gallenkamp melting-point apparatus.

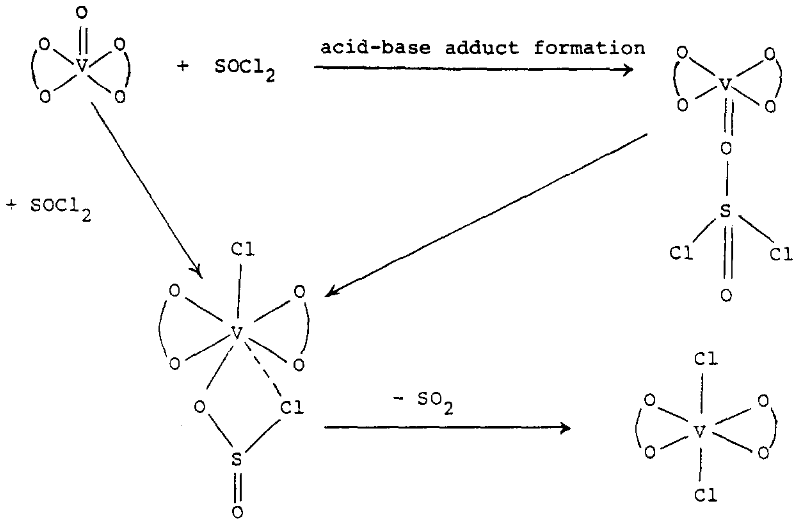
3. Results and discussion

$VO(btfac)_2$ was prepared by the reaction of benzoyltrifluoro acetylacetone with vanadium sulphate in aqueous or ethanolic solution followed by neutralization with sodium bicarbonate. The other oxovanadium(IV) complexes were prepared either by the reported methods [5, 9] or by simplified converted methods. Dihalovanadium(IV) complexes were prepared by the reaction of $VO(dik)_2$ with sulphur oxide dihalides or phosphorus pentachloride in benzene or toluene at 40 - 60 °C by the following reactions where X ≡ Cl or Br and dik ≡ acac, bzac and bzbz:

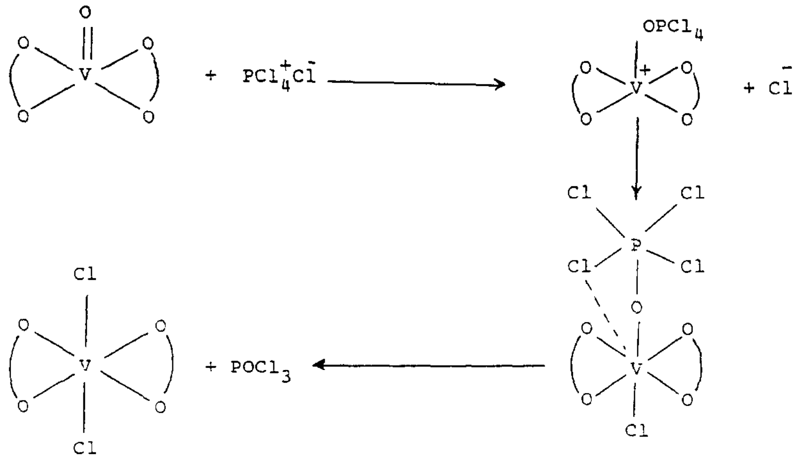
$$VO(dik)_2 + SOX_2 \longrightarrow VX_2(dik)_2 + SO_2$$

$$VO(dik)_2 + PCl_5 \longrightarrow VCl_2(dik)_2 + POCl_3$$

The suggested mechanism for the deoxygeneration of oxovanadium(IV) complexes by sulphur oxide dihalides and phosphorus pentachloride may be represented by Schemes 1 and 2. These mechanisms have already been reported for the deoxygeneration of $VO(Sal\text{-}N\text{-}R)_2$ [2, 4].



Scheme 1.

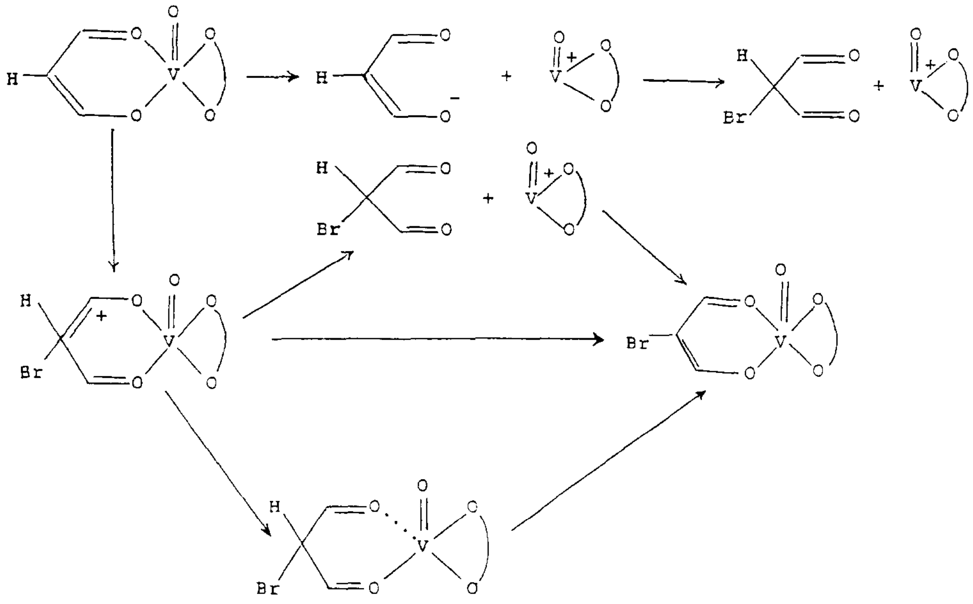


Scheme 2.

These halovanadium(IV) complexes, especially bromo complexes, are quite sensitive to oxygen and hydrolysis which result in the formation of the starting oxovanadium(IV) complexes. All of these complexes are black and soluble in the usual organic solvents.

The reaction of vanadylacetylacetonate with N-bromosuccinimide and N-chlorosuccinimide produces bromo- or chloro-chelates.

The suggested mechanism for ring halogenation may be represented by (i) initial ring cleavage and the halogenation and ring formation; (ii) halogenation of the ring itself giving rise to an intermediate which is stabilized by partial or complete ring cleavage or (iii) halogenation with the ring remaining intact throughout the transformation.



Scheme 3.

The mechanism shown in Scheme 3 has already been reported by Kluiber [15] for ring bromination of a number of β-dicarbonylchelates.

IR spectra provide valuable information regarding the nature of the carbonyl group attached to the metal atoms. The assignments that are important are those for ν(C=O), ν(C=C) and ν(M=O). There has been some confusion in the literature regarding the position of ν(C=O) and ν(C=C) in the IR spectra studies of β-diketone complexes. Bellamy and Branch [16] initially attributed the 1580 and 1520 cm^{-1} bands to the C=O and C=C stretching modes respectively. These assignments were reversed by Nakamoto *et al.* [17, 18] on the basis of force constant calculations. The above account shows that whereas Bellamy *et al.* [16, 19] and other workers [20 - 31] assigned the higher region band (1570 - 1600 cm^{-1}) to C=O stretching and the lower bands occurring around 1525 cm^{-1} to C=C stretching modes, Nakamoto *et al.* [18, 32 - 34] reversed the above assignment and attributed the higher frequency band to C⩵C and the lower frequency band to the C⩵O stretching vibration.

The problem remained unresolved until Pinchas *et al.* [35] measured the IR spectra of ^{18}O-labelled Cr^{III} and Mn^{III} acetylacetonates and observed that the band occurring around 1570 cm^{-1} was significantly affected by ^{18}O labelling and was shifted by 12 cm^{-1} to a lower frequency, whereas the band at 1515 cm^{-1} was not appreciably affected by changing $C{=}^{16}O$ to $C{=}^{18}O$. This appeared to indicate that the band at 1570 cm^{-1} must be associated with the vibration mode characteristic of C⩵O and the one at 1515 cm^{-1} must be a pure C⩵C band, contrary to the observation of Nakamoto *et al.* [18, 32 - 34] and in agreement with the conclusion of earlier workers [20 - 31].

Later Behnke and Nakamoto [36, 37] concluded that their assignment for ν(C⩵O) and ν(C⩵C) for acetylacetonate of a number of metals [38] on the basis of normal coordinate analysis were in error and therefore they reinvestigated their IR studies for platinum complexes using the modified Urey–Bradley force-field treatment. Behnke and Nakamoto [36, 37], on the basis of the observed and calculated data, assigned the band at about 1560 cm^{-1} to almost pure C⩵O stretching and that at 1540 cm^{-1} to the C⩵C stretching mode coupled slightly with the C—H in plane bending mode. As a result of deuteration, this coupling disappeared completely because the C—H in plane bending frequency is significantly too small to couple with the C⩵C stretching mode, and this decoupling causes the shift of the band from 1540 to 1500 cm^{-1}.

Liang *et al.* [39] studied the IR spectra of a variety of adducts of β-diketonates of europium^{III} and supported the corrected assignment of Pinchas *et al.* [35] and those of Behnke and Nakamoto [36, 37], and the bands at 1600 and 1515 cm^{-1} observed for $Eu(acac)_3 \cdot 2H_2O$ were assigned to C⩵O and C⩵C stretching modes respectively. It was observed that the replacement of methyl by trifluoromethyl, strengthened the C⩵O and C⩵C bands and weakened the M—O bands. The former two bands are therefore shifted to higher frequencies and the latter to lower frequencies. This observation is in agreement with those made earlier by Nakamoto *et al.* [17] in the case of copper and nickel analogues.

Joshi and Pathak [40, 41] examined the IR spectra of a large number of fluorinated metal β-diketonates and observed a strengthening of the C⩵O and C⩵C bond owing to the strong negative (I—) inductive effect of the CF_3 groups; this causes marked shifts of C⩵O and C⩵C stretching bands to higher frequencies. Ferrao and Healy [42] investigated the IR spectra of a number of thenoyltrifluoroacetylacetonate complexes and the bands at about 1600 and 1535 cm^{-1} were assigned to C⩵O and C⩵C stretching vibrations respectively. Fay and Pinnavaia [43] measured the IR spectra of complexes of the type $M(acac)_2X_2$ (M ≡ Ti, Zr; X ≡ Cl, Br), $M(acac)_3X$ (M ≡ Zr, Hf; X ≡ Cl, Br) and $M(acac)_4$ (M ≡ Zr, Hf, Ce, Th) and the carbonyl bands for all of these complexes occurred in the chelated region (1570 - 1592

cm^{-1}) and on this basis six-, seven- and eight-coordination have been assumed for dihalide, monohalide acetylacetonate and tetrakis (acetylacetonate) respectively. Probably the most characteristic feature of oxovanadium(IV) complexes is the very strong sharp V=O stretching frequency observed [44] at 985 ± 50 cm^{-1} corresponding to a V=O force constant of $K = 7.0 \pm 0.7$ mol $Å^{-1}$. The ν(V=O) stretching vibration in the gaseous state at 160 °C of $VO(tfac)_2$ is reported to be at 1025 cm^{-1} [45].

Martinez *et al.* [46] have assigned an intense band at 1575 - 1530 cm^{-1} to the combined vibrational stretching mode of C=C and C=O bands in the IR spectra of $VO(acac)_2$ and its substituted pyridine adducts. The same worker also reported that terminal (V=O) in $VO(acac)_2$ is displaced to higher frequencies (1000 cm^{-1}) when compared with the substituted pyridine adducts (975 - 952 cm^{-1}). This difference can be attributed to the electronic donation of pyridine to vanadium ($N \rightarrow V$) which increases the electron density in the metal d orbitals and consequently the donation from oxygen to vanadium is expected to be reduced to an extent which depends upon the donor ability of the base. As a result of these contributions there will be a lowering of the V=O bond strength and hence a lowering of the ν(V=O) stretching vibrations. These workers also reported ν(V=O) of $VO(bzac)_2$ to be at 1000 cm^{-1} [47].

Recently the thermal decomposition of some oxovanadium(IV) complexes with substituted pyridines have been studied [46 - 49]. The differential scarring calorimetry and differential thermal analysis curves of all compounds $VO(dik)_2 \cdot B$ (where dik ≡ acac, bzac, bzbz, ttfac and B is a substituted pyridine such as 3-MP, 4-MP, 3,4-DMP, 3-AP, 4-AP) showed a first endothermic process with a mass loss corresponding to the loss of molecules of base coordinated to vanadium and a further exothermic process with the resultant production of V_2O_5. It has been reported that all adducts obtained with ttfac give higher values of E_a and T_i for the process of loss of base than those obtained with other β-diketonates. This indicates that the CF_3 groups of ttfac increase the energy levels of the metal as a consequence of the inductive effect of the halogen atoms, hence the metal-base bonding is stronger.

The observed IR spectra of $VO(dik)_2$ (where dik ≡ acac, bzac, bzbz, tfac, btfac, ttfac, Clacac, Bracac) and $VX_2(dik)_2$ (where X ≡ Cl, Br and dik ≡ acac, bzac and bzbz) which are in good agreement with the above discussion, are shown in Table 2.

The observed medium absorption at 1190 cm^{-1} in the IR and 1186 cm^{-1} in the Raman spectra of $VO(acac)_2$ has been assigned to the ν(C—H) vibration which on ring halogenation is completely removed. The strong absorptions at 710 and 704 cm^{-1} in the IR spectra of $VO(Clacac)_2$ and $VO(Bracac)_2$ respectively are assigned to carbon–halogen vibrations.

In metal β-diketonates in which coordination to the metals occurs via oxygen atoms, the chelate ring is planar and the π electron density partially delocalized over the chelate ring. From the mass spectral studies of metal acetylacetonates, McDonald and Shannon [50] postulated valency changes

TABLE 2

IR and Raman spectra of vanadium(IV) β-diketonate complexes

	C=O	C=C	V=C		V−X		μ_{eff}
	IR (cm^{-1})	IR (cm^{-1})	IR (cm^{-1})	Raman (cm^{-1})	IR (cm^{-1})	Raman (cm^{-1})	(μ_B)
$VO(acac)_2$	1593		1004	991			1.70
$VO(Clacac)_2$	1586	1530	912	904			1.76
$VO(Bracac)_2$	1568	1542	918	909			1.74
$VCl_2(acac)_2$	1524	1510			361	358w	1.74
$VBr_2(acac)_2$	1530	1515			325	272	1.87
$VO(bzac)_2$	1596	1530	1005	995			1.73
$VCl_2(bzac)_2$	1520	1510			363	312	1.74
$VBr_2(bzac)_2$	1597	1535			321	340	1.82
$VO(bzbz)_2$	1593	1524	1000	991			1.70
$VBr_2(bzbz)_2$	1596	1525			319		1.85
$VO(btfac)_2$	1616	1578	899	895			1.84
$VO(tfac)_2$	1620	1546	937	931			1.72
$VO(ttfac)_2$	1600	1542	902	899			1.78

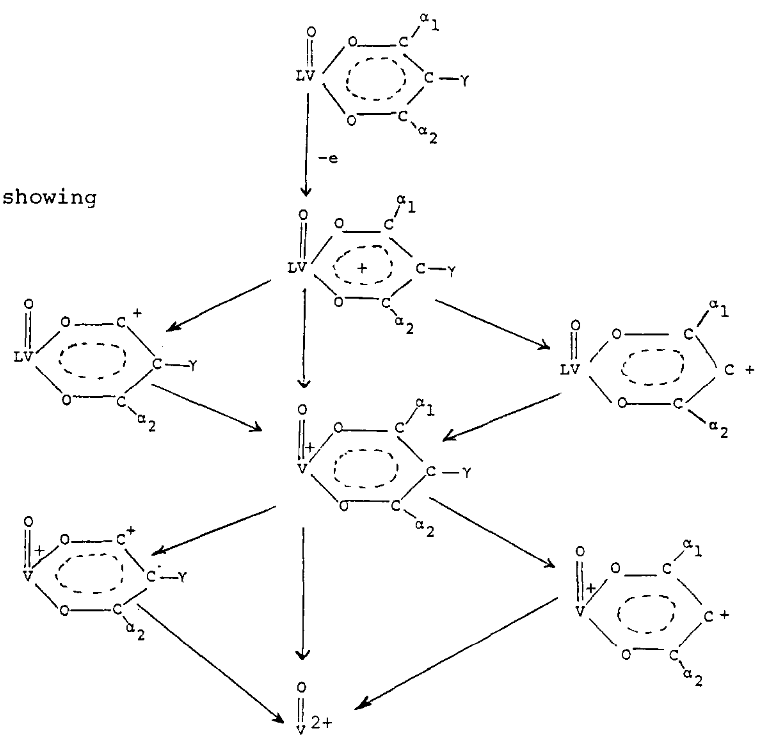
w, weak.

in the metal to account for the observed mass spectra of several acetylacetonates, and correlated these with the occurrence or non-occurrence of valency changes within the established chemistry of the metal. Bancroft *et al.* [51] have discussed the results of mass spectral studies and concluded that these are consistent with the loss of an electron from an orbital localized mainly on the ligand. Changes in the appearance potentials for a number of substituted acetylacetonates could be correlated with the bonding properties of various substituents to a ring which has aromatic character. The peaks observed in mass spectral studies of vanadium(IV) diketonates represent fragments which include the loss of one complete ligand, two complete ligands or the loss of an α or γ group on the carbon ring as shown in Scheme 4 (L = diketone). Similar schemes have been reported [51] for L_3M^{III} where L is a number of β-diketones.

The mass spectral studies on oxovanadium(IV) and dihalovanadium(IV) β-diketonate complexes show the following mass peaks.

3.1. $VO(acac)_2$

$VO(OCMeCHMeCO)_2$, 265(66.8); VO(OCMeCHMeCO)(OCCHMeCO), 250(26.1); VO(OCMeCHMeCO)(OCCMeCO), 249(5.1); VO(OCMeCHMeCO)-(OCCHO); VO(OCCHMeCO)(OCMeCHCO), 223(8.1); VO(OCMeCMeCO)-(OCCHO), 222(5); VO(OCMeCHCO)(OO); VO(OCMeO)(OCCHO); VO-(OCMeCHO)(OCO), 183(43.2); VO(OCMeCCO)(O); VO(OCMeO)(OCC), 166(97.3); VO(OCMeCHCO)(O); VO(OCCH)(OCMeO), 167(21.7); VO(OCMeCCO)(O); VO(OC)(OCMeC), 150(13.2); $VO(OC)_2$, 123(13); VO, 67(33.1).



Partial scheme showing
some suggested
fragmentation.

L = diketone

Scheme 4.

3.2. *VO(Clacac)$_2$*

VO(OCMeC^{35}ClMeCO)$_2$, 333(14.2); VO(OCMeC^{35}ClMeCO)(OCMeC^{37}ClMeCO), 335(9.3); VO(OCMeC^{37}ClMeCO)$_2$, 337(1.5); VO(OCMeC^{35}ClMeCO)(OCCH$_2$CMeCO), 297(3.4); VO(OCMeC^{37}CMeCO)(OCCH$_2$CMeCO), 299(1.8); VO(OCMeCO)(OCMeC^{35}ClMeCO), 271(2.2); VO(OCMeC^{35}ClMeCO)(OCCHCO), 269(6.4); VO(OCCHMeCO)$_2$, 253(3.1); VO(OCCCCO)$_2^2$, 227(2); VO(OCCCO)(OCCHMeCO), 221(23.3); VO(OCMeC^{35}ClMeCO), 200(7.6); VO(OCC^{35}ClMeCO), 185(2.6); VO, 67(19.6).

3.3. *VO(Bracac)$_2$*

VO(OCMeCBrMeCO)$_2$, 423(4.3); VO(OCMeCBrMeCO)(OCMeCMeOC), 343(1.7); VO(OCMeCBrMeCO)(OCCCO), 313(1.6); VO(OCCH$_2$CBrCH$_2$CO)(OCCCO), 311(3.8); VO(OCCHCBrCHCO)(OCCCO), 309(7.8); VO(OCCCBrCCO)(OCCOO), 307(4.1); VO(OCMeCMeCO)$_2$, 263(1.7); VO(OCCH$_2$CMeCO)(OCCCO), 231(2); VO(OCCH$_2$CCHCO)(OCCCO), 229(2.1); VO(OCCHCCHCO)(OCCCO), 228(1.4); VO(OCCHO)(OCMeO), 183(1.1); VO(OCCO)(OCMeO), 166(2.1); VO(OCCHC)(OC), 148(1.9); VO(OCCHO), 120(1.4); VO, 67(23.3).

3.4. VCl$_2$(acac)$_2$

V^{35}Cl(OCMeCHMeCO)$_3$, 383(0.3); V(OCMeCHMeCO)$_3$, 348(12.4); VCl(OCMeCHMeCO)$_2$, 284(5.9); VO(OCMeCHMeCO)$_2$, 265(57.2); VO(OCMeCHMeCO)(OCMeCHCO), 250(26.4); V(OCMeCHMeCO)$_2$, 249(57.1); V(OCMeCHMeCO)(OCMeCMeCO), 248(1.9); VO(OCMeCHMeCO)(OCCHO); VO(OCCHMeCO)(OCMeCHO), 223(6.9); VO(OCMeCHMeCO)(OCCO); VO(OCCHMeCO)(OCMeCO), 222(4.7); VO(OCMeCHCO)(OO); VO(OCMeO)(OCCHO); VO(OCMeCHO)(OCO), 183(38.8); VO(OCMeCHCO), 167(21.2); VO(OCMeCCO); VO(OCMeO)(OCC), 166(9.1); VO(OCCH$_2$CO)(OO); VO(OCCH$_2$O)(OCC), 165(6.6); VO(OCMeCCC)(O); VO(OCMeC)(OC), 150(12.4); VO(OCMeCHCO)(O); VO(OCMeCHOC), 151(7.5); V(OCCH$_2$CCO)(O); VO(OCCH$_2$C(OC), 149(5); VO(CCCHCCO)(O); VO(OCCHC)(OC), 148(7.1); VO(OC)$_2$, 123(9.6); VO(OC), 195(9.6); VO, 67(22.4).

3.5. VBr$_2$(acac)$_2$

VBr$_2$(OCMeCHMeCO)$_3$, 508(0.3); VBr$_2$(OCMeCHMeCO)(OCMeCMeCO)$_2$, 506(0.8); VBr(OCMeCHMeCO)(OCMeCMeCO)$_2$, 426(2.3); VO(OCMeCHMeCO)$_3$, 348(4.6); VBr(OCMeCHMeCO)$_2$, 329(3.3); VBr(OCMeCHMeCO)(OCMeCMeO), 328(2.3); VBr(OCMeCMeCO)$_2$, 327(3.3); VO(OCMeCHMeCO)$_2$, 265(12.7); V(OCMeCHMeCO)$_2$, 249(43.6); VO(OCMeCHMeCO)(OCMeCHCO), 250(9.8); VO(OCMeCHO)(OO); VO(OCMeO)(OCCHO); VO(OCMeCHO)(OCO), 183(12); VO(OCMeCHCO), 167(8.8); VO(OCMeCCC)(O); VO(OCMeO)(OCC), 166(37.7); VO(OCMeCHCO)(O); VO(OCCMeCH)(OC), 151(3.2); VO(OCMeCCO); VO(OCMeC)(OC), 150(5.9); VO(OCCH$_2$CCO); VO(OCCH$_2$C)(OC), 149(4.4); VO(OCCHCCO); VO(OCCHC)(OC), 148(3.5); VO(OC)$_2$, 123(4); VO, 67(17.4).

3.6. VO(bzac)$_2$

VO(OCPhCHMeCO)$_2$, 389(100); VO(OCpHCHMeCO)$_3$, 534(2.9); V(OCPhCHMeCO)$_2$, 373(10.4); VO(OCPhCCCO)(OCPhCHO); VO(OCPhCHMeCO)(OCPhCH), 346(1.5); VO(OCPhCHMeCO)(OCMeCH), 284(2.9); VO(OCPhCHMeCO)(OCMe), 271(5.9); VO(OCPhCHMeCO), 228(53.3), VO(OCPhCHMeC); VO(CPhCHMeCO); V(OCPhCHMeCO), 212(4.8); VO(OCPhCH), 185(4.1); VO(OCCCMeO), 150(28.3); VO, 67(2.8).

3.7. VCl$_2$(bzac)$_2$

V^{35}Cl(OCPhCHMeCO)(OCPhCMeCO), 568(0.3); V(OCPhCHMeCO)$_3$, 543(1.2); V^{35}Cl(OCPhCHMeCO)$_2$, 408(1.5); V^{37}Cl(OCPhCHMeCO)$_2$, 410(0.5); V(OCPhCHMeCO)$_2$, 373(2.7); VO(OCPhCHMeCO)$_2$, 389(15); VO(OCPhCMeCO)(OCMeC), 282(1.6); VO(OCPhCHMeCO), 228(9.8); VO(OCMeCCO), 150(4); VO, 67(3.9).

3.8. VBr$_2$(bzbz)$_2$

V(OCPhCHPhCO)$_3$, 720(0.4); VBr(OCPhCHPhCO)(OCPhCPhCO), 576(0.3); VO(OCPhCHPhCO)$_2$, 513(30.8); V(OCPhCHPhCO)$_2$, 497(1.2); VBr$_2$-

(OCPhCHPhCO), 434(13.1); $\mathrm{VBr_2(OCPhCPhCO)}$, 433(1.2); $\mathrm{VBr_2(OCCCHPhCO)}$, 369(8.1); VBr(OCPhCHPhCO), 354(5.8); VBr(OCPhCPhCO), 353(2.2); VO(OCPhCHPhCO)(O); V(OCPhCHPhCO)(OO), 306(12.6); VO(OCPhCHPhCO), 290(5.4); VBr(OCCCHPhCO), 289(1.1); VO(OCCCHPhCO), 225(8.1); VO(OCCHPhCO), 213(2.2); VO(OCCPhCO), 212(2.6); $\mathrm{VO(OCCC_2HCO)}$, 160(1.5); VO, 67(10.7).

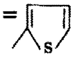
3.9. $\mathrm{VO(btfac)_2}$

$\mathrm{VO(OCPhCHCF_3CO)_2}$, 497(34.9); $\mathrm{V(OCPhCHCF_3CO)_2}$, 481(1); $\mathrm{VO(OCPhCHCF_3CO)(OCPhCHCO)}$, 428(1.2); $\mathrm{VO(OCPhC)_2}$, 301(19.2); VO(OCPhCH)(OCPhC), 302(2); VO(OCPhCHCO)(OCCHCO); $\mathrm{VO(OCPhCHCF_3CO)}$, 282(5.1); VO(OCPhCO)(OCO), 232(7.2); VO(OCPhCOC), 212(4.8); VO(OCPhCOO); VO(OCPhO)(OC), 216(4.4); VO(OCPh)(O); VO(OCPhO), 188(3.5); VO(OCCHCHO), 149(8.2); VO(OCCCCO), 147(7.2); VO(OCCCHCH), 133(2.8); V, 51(7.3).

3.10. $\mathrm{VO(tfac)_2}$

$\mathrm{VO(OCMeCHCF_3CO)_2}$, 373(34.9); $\mathrm{V(OCMeCHCF_3CO)_2}$, 357(0.11); $\mathrm{V(OCMeCHCF_3CO)_3}$, 510(0.8); $\mathrm{VO(OCMeCHCF_3CO)(OCMeCHCO)}$, 304(10.1); VO(OCMeCHCFCO)(OCCHO), 239(36.9); VO(OCMeCCFCO)(OCCO), 237(1.1); VO(OCMeCHCO)(OCMeCHO), 223(2.8); VO(OCMeCCO)(OCMeCO), 221(1.2); VO(OCMeCHCO)(OCCHCO); $\mathrm{VO(OCMeCHCF_3CO)}$, 220(19.3); VO(OCMeC)(OCMeCC), 189(6.6); VO(OCMeCHO(OO), 171(1.2); VO(OCMeO)(OCC), 170(23.9); VO(OCMeCCO), 150(8.7), VO(OCOOC), 139(2.9); VO, 67(11.6).

3.11. $\mathrm{VO(ttfac)_2}$

$\mathrm{VO(OCTCHCF_3CO)_2}$, 509(62); $\mathrm{VO(OCTCF_3CO)(OCTCHCO)}$, 440(2.7); $\mathrm{VO(OCTCHCF_3)_2}$, 371(2.7); $\mathrm{VO(OCHCF_3CO)(OCF_3CO)}$, 306(1.4); VO(OCTCHO)(OCCHCO); $\mathrm{VO(OCTCHCF_3CO)}$, 288(1.4); VO(OCTO)(OCO), 238(14.7); VO(OCCHCO)(OCCCHCHO), 218(8.8); VO(OCTO), 194(10.6); $\mathrm{VO(OCO)_2}$, 155(18.9); VO(OCCCO), 135(6); VO, 67(1.8); T =  = $\mathrm{C_4H_3S}$.

These complexes are paramagnetic, the μ_{eff} values being in the range 1.70 - 1.85 μ_{B}, which is quite close to the spin only value for one unpaired electron as is expected for vanadium(IV) with a d^1 electronic configuration. These approximately normal magnetic susceptibility values indicate that there is no significant interaction between neighbouring vanadium(IV) ions.

Electron spin resonance (ESR) measurements on a powdered sample of $\mathrm{VO(btfac)_2}$, $\mathrm{VO(Clacac)_2}$ and $\mathrm{VO(Bracac)_2}$ show the three signals for each sample, which on the basis of their intensities are assigned as follows: $\mathrm{VO(btfac)_2}$, $g_1 = 1.972$, $g_2 = 1.966$, $g_3 = 1.948$; $\mathrm{VO(Clacac)_2}$, $g_1 = 1.979$, $g_2 = 1.965$, $g_3 = 1.947$; $\mathrm{VO(Bracac)_2}$, $g_1 = 1.979$, $g_2 = 1.966$, $g_3 = 1.948$. These g values suggest that vanadium has a d^1 electronic configuration.

Some X-ray powder diffraction results for complexes prepared in this study are listed in Tables 3 and 4. The compounds appear to possess low

TABLE 3

X-ray powder diffraction

$VO(bzac)_2$		$VCl_2(bzac)_2$		$VBr_2(bzac)_2$		$VCl_2(acac)_2$		$VBr_2(acac)_2$	
d (Å)	Intensity	*d* (Å)	Intensity	*d* (Å)	Intensity	*d* (Å)	Intensity	*d* (Å)	Intensity
11.26	m	9.41	vs	7.86	vs	6.94	s	7.11	m
9.03	s	7.66	m	7.14	s	6.22	vs	6.29	vs
7.73	m	6.42	vs	6.78	m	5.62	m	5.75	m
6.88	m	5.39	w	5.19	w	5.34	m	5.40	m
6.33	vw	4.92	m	4.68	s	4.04	m	3.81	vw
6.01	w	4.62	s	4.37	w	3.82	m	3.69	w
5.40	s	3.97	m	4.03	w	3.51	m	3.23	w
5.22	vw	3.77	m	3.84	w	3.37	s	3.13	vw
4.87	s	3.56	m	3.63	m	3.18	w	2.88	w
4.49	m, br	3.28	m	3.31	s	2.84	vw	2.77	w
4.15	w	3.06	m	3.10	w	2.67	w	2.66	m
3.82	w, br	2.80	w, br	3.01	vw	2.57	m	2.49	w
3.55	s	2.46	w, br	2.78	w	2.47	w	2.42	vw
3.45	m	2.32	m	2.65	w	2.39	vw	2.34	vw
3.34	w	2.14	m	2.45	w	2.16	w	2.28	w
2.62	vw	2.01	vw	2.35	w	2.04	vw	2.19	w
2.31	vw	1.87	vw	2.08	w	1.97	w	2.04	vw
2.03	vw			1.71	vw	1.85	w	1.90	vw
1.99	vw					1.75	w	1.86	vw
								1.78	vw

s, strong; v, very; m, medium; w, weak; br, broad.

TABLE 4

X-ray powder diffraction

$VO(btfac)_2$		$VO(tfac)_2$		$VO(ttfac)_2$		$VO(Clacac)_2$		$VO(Bracac)_2$	
d (Å)	Intensity	*d* (Å)	Intensity	*d* (Å)	Intensity	*d* (Å)	intensity	*d* (Å)	Intensity
11.26	vs	10.92	m	11.48	vs	11.12	vs	11.36	w
8.39	m	6.97	vs	7.94	m	6.86	vs	7.25	w
6.37	m	5.40	m	6.39	vw	6.15	m	6.26	vs
5.59	m	4.42	w	5.13	m	5.23	vw	4.43	w
5.31	m	4.27	w	4.74	w	4.47	w	4.08	w
4.81	w	3.99	s	4.57	m	3.80	m	3.87	vw
4.66	m	3.77	s	4.26	s	3.61	w	3.75	m
4.36	m	3.58	s	4.00	m	3.49	s	3.54	m
4.20	w	3.35	w	3.91	s	3.31	m	3.40	s
3.93	w	3.16	v	3.61	w	3.15	vw	3.13	w
3.77	s	2.87	vw	3.46	w	3.04	vw	3.03	w
3.61	vw	2.53	w	3.20	vw	2.95	vw	2.81	w
3.45	vw	2.44	m	2.89	vw	2.83	vw	2.66	m
3.27	vw	2.29	m	2.61	vw	2.74	vw	2.55	vw
2.81	vw	2.22	m	2.40	w	2.66	w	2.41	m
2.50	vw	2.16	w	2.32	vw	2.50	vw	2.32	w
2.37	w	2.00	vw	2.26	w	2.42	w	2.20	vw
2.11	w	1.94	vw	2.14	vw	2.31	vw	2.05	vw
1.88	vw	1.76	vw	1.99	w	2.25	vw	2.00	w
		1.63	vw			1.94	w	1.89	vw
		1.58				1.81	w	1.80	w
								1.76	vw
								1.71	w
								1.67	w
								1.64	w

s, strong; v, very; m, medium; w, weak.

symmetry, but the results have not been interpreted in detail. The *d* values for VO(bzac)$_2$, which crystallized in the $P2_1/C$ system with unit cell dimensions of $a_0 = 8.103$, $b_0 = 22.599$, $C_0 = 10.505$ Å and $\beta = 106°\ 47'$, have been calculated using the program of "powder pattern" run on the CDC 7600 computer at UMRCC by Mr R. L. Beddoes. These are in good agreement with the measured *d* values.

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