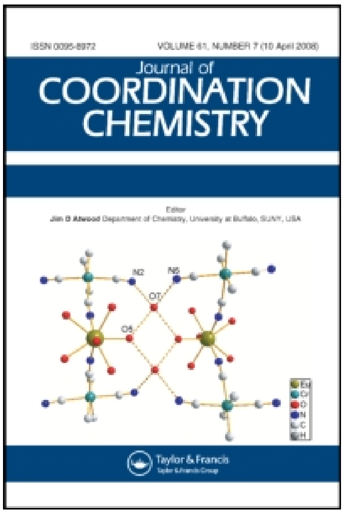

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ELECTRON SPIN RESONANCE STUDY OF SUBSTITUENT EFFECTS IN OXOVANADIUM(IV) β-DIKETONATES

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ELECTRON SPIN RESONANCE STUDY OF SUBSTITUENT EFFECTS IN OXOVANADIUM(IV) β-DIKETONATES

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The ESR spectra of seventeen oxovanadium(IV) β-diketonates in chloroform solution have been examined in order to study the effect of various substituents. Bis[4,4,4-trifluoro-1-(3-pyridyl)-1,3-butanedionato]oxovanadium(IV) which is tetrameric in chloroform solution gave an ESR spectrum suggestive of a species with a long rotation correlation time. Both 3-chloro and 3-methyl substituents increase the in-plane ligand field in $VO(3\text{-Clacac})_2$ and $VO(3\text{-CH}_3acac)_2$ while p-methoxyphenyl substituent which has the highest possible mesomeric interaction among the substituents gave the lowest isotropic splitting factor.

INTRODUCTION

Among the oxovandium(IV) β-diketonates, bis(pentane-2, 4-dionato)oxovanadium(IV), $VO(acac)_2$, have received the greatest attention[1–7] and most often can be thought of as prototypes for other β-ketoenolate complexes. $VO(acac)_2$ has been used in the study of paramagnetic relaxation in liquid-crystal solution[4] and in the study of anisotropic and spin-rotational effects.[3] ESR studies of $VO(hxfacac)_2$[5] and $VO(tfacac)_2$[7] have been reported, while $VO(bzac)_2$, $VO(3\text{-phacac})_2$, $VO(dbm)_2$ and $VO(dnm)_2$ (dinaphthoylmethane anion) have been used in the study of molecular ordering in liquid-crystal solution.[4] While the substituent effects in oxovanadium complexes of β-ketimines have been well studied,[8–9] little has been reported on the ESR study of substituent effects in oxovanadium(IV) complexes of β-diketones. We have undertaken the present study as a part of our programme of physicochemical studies of metal β-diketonates and for a better understanding of the nature of bonding in oxovanadium(IV) complex of β-diketones.

EXPERIMENTAL

The ligands: 2,4-Pentanedione(Hacac), 2,4-Hexanedione(Hhxd), 1-Phenyl-1,3-butanedione (Hphbd), 1,3-Diphenyl-1,3-propanedione (Hdbm), 1,3-Bis(*P*-Methoxyphenyl)-1,3-propanedione (Hmdbm), 1,3-Di-(2-Naphthyl)-1,3-propanedione (Hdnm), 1,1,1-Trifluoro-2,4-hexanedione (Htfhxd), 1,1,1-Trifluoro-5,5-dimethyl-2,4-hexanedione (Htfdpm), 4,4,4-Trifluoro-1-phenyl-1,3-butanedione (Htfphbd), 4,4,4-Trifluoro-1-(2-naphthyl)-1,3-butanedione (Htfnbd), 4,4,4-Trifluoro-1-(2-furyl)-1,3-butanedione (Htffbd), 1-(2-Furyl)-1,3-butanedione (Hfbd), 4,4,4-Trifluoro-1-(2-thienyl)-1,3-butanedione(Htffbd), 1-(2-Thienyl)-1,3-butanedione(Htbd), 4,4,4-Trifluoro-1-(3-pyridyl)-1,3-butanedione(Htfpybd), 1-(3-Pyridyl)-1,3-butanedione (Hpybd), 3-Chloro-2,4-pentanedione (3-ClacacH), and 3-Methyl-2,4-pentanedione (3-CH_3acacH), except Hpybd, 3-ClacacH and, 3-CH_3acacH were purchased from Eastman Organic Chemicals and were used without further purification. The ligands Hpybd,[10] 3-ClacacH[11] and 3-CH_3acacH[12] were prepared by procedures published in the literature.

The oxovanadium(IV) β-diketonates were prepared by the procedure described previously.[13]

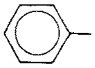
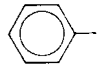
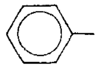
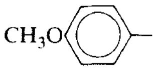
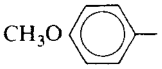
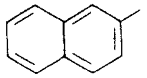
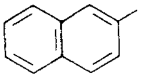
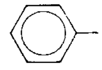
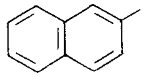
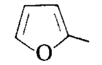
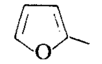
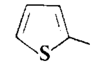
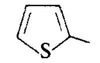
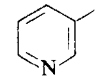
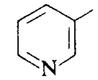
The ESR samples were degassed by the freeze-pump-thaw method. Spectra were taken within two hours of sample preparation as some complexes in solution were observed to decompose with time. Between 0.5 and 1.0×10^{-4} M solution of a vanadium complex (Table I) in purified chloroform was used in the ESR study, however, when the complex was not very soluble a saturated solution was employed. Powdered DPPH was used as a *g*-marker while the magnetic field was calibrated using the hyperfine splitting constant of vanadium in a chloroform solution of $VO(acac)_2$.[9] The *g*-values were corrected for second-order effects.[14]

RESULTS AND DISCUSSION

All the vanadyl complexes except bis[4,4,4-trifluoro-1-(3-pyridyl)-1,3-butanedionato]oxovanadium(IV)

TABLE I

ESR parameters of oxovanadium(IV) β-diketonate complexes, $VO(R_1COCR_3COR_2)_2$.

Ligand	R_1	R_2	R_3	$A_{iso}G$	g_{iso}
Hacac	CH_3	CH_3	H	106.4	1.966
Hhxd	CH_3CH_2	CH_3	H	106.0	1.965
Hphbd	CH_3		H	104.3	1.967
Hdbm			H	103.8	1.968
Hmdbm			H	103.3	1.965
Hdnm			H	Not soluble in chloroform	
Htfhxd	CH_3CH_2	CF_3	H	108.6	1.964
Htfdpm	$(CH_3)_3C$	CF_3	H	109.5	1.963
Htfphbd		CF_3	H	107.5	1.964
Htfnbd		CF_3	H	112.1	1.962
Htffbd		CF_3	H	107.3	1.965
Hfbd		CH_3	H	105.1	1.967
Htffbd		CF_3	H	108.6	1.964
Htbd		CH_3	H	105.5	1.966
Htfpybd		CF_3	H	107.3	1.965
Hpybd		CH_3	H	105.1	1.966
3-ClacacH	CH_3	CH_3	Cl	103.3	1.965
3-CH_3acacH	CH_3	CH_3	CH_3	103.8	1.965

exhibited the normal well defined eight line spectrum characteristic of vanadyl complexes.[4] $VO(tfpybd)_2$ showed a weak eight line spectrum superimposed on a broad one line spectrum (Figure 1). The linewidths of the signals became smaller at higher temperatures. While the origin of the line broadening is not well known at this time, a molecular weight determination has shown that the complex $VO(tfpydb)_2$ exists in chloroform solution as a tetramer.[13] It is conceivable that the large molecular weight of the tetramer unit could increase the rotation correlation time of the complex to such an extent as to produce an "immobilised" ESR spectrum. The decrease of linewidths of the signals with increasing temperature is consistent with the above explanation. The peculiar behaviour of this complex must be attributed partly to the trifluoromethyl substitution since the methyl analogue gave the normal ESR spectrum.

The isotropic g-factors and hyperfine splitting constants of the vanadyl β-diketonates are shown in Table I. The g-values are generally lower than the free-electron value g_e (2.00232). This lowering of g-values is related to the spin-orbit interaction of the ground state, d_{xy}, level with low lying excited

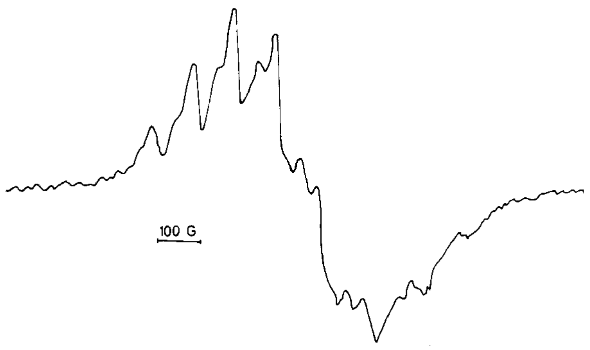
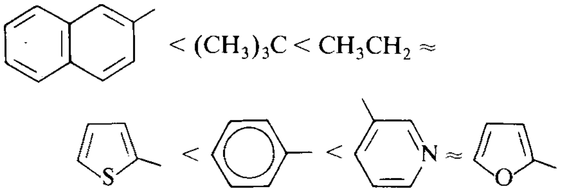


FIGURE 1 ESR spectrum obtained from chloroform solution of bis[4,4,4-trifluoro-1-(3-pyridyl)-1,3-butanedionato]oxovandium(IV) at 298 K.

states.[2,9,14] The spread in g-values (1.962–1.968) is relatively small in comparison to the variation in the isotropic hyperfine constant A_{iso} (103.3–112.1G).

A plot of g *vs* A_{isp} shows that as A_{iso} increases the g-value decreases except for complexes of Hmdbm, 3-ClacacH and 3-CH_3acacH. Complexes of 3-ClacacH and 3-CH_3acacH are the only two complexes with R_3 substituent that is not a hydrogen atom while complex of Hmdbm shows the lowest value of A_{iso} among the complexes with R_3 = H. It is significant that the p-methoxyphenyl substituent in complex VO(mdbm)$_2$ has the highest possibility of mesomeric interaction among the substituents involved in the present study.

The isotropic splitting constant A_{iso} is higher while the g-value is lower in the complex $VO(R_1COCR_3COR_2)_2$ when $R_2 = CF_3$ and R_3 = H, than in the corresponding complex where $R_2 = CH_3$ and R_3 = H irrespective of the substituent R_1 (Table I). The values of A_{iso} are higher in all trifluoromethyl substituted complexes than in VO(acac)$_2$. The magnitude of A_{iso} indicates the strength of the in-plane ligand field. The work of McGarvey[15] showed that for most vanadyl complexes the major contribution to the variation of A_{iso} is the amount of the 4s contribution to the σ bonding in the complexes. The contribution of a bonding molecular orbital which contains a metal 4s contribution to A_{iso} by a spin polarisation mechanism decreases as the molecular orbital becomes stabilised. The stability of the molecular orbital is dependent on the strength of the in-plane ligand field. The hyperfine constant, A_{iso} should increase as the in-plane ligand field decreases and vice-versa. For those ligands with trifluoromethyl substituent we have two effects to consider: $-I$ effect due to CF_3 and $+I$ effect due to R_1. The $-I$ effect is far much greater because of the very high electronegativity value of the fluorine atom. The net result is the weakening of the in-plane ligand field and a consequential increase in the value of A_{iso}. We expect that in the complex $VO(R_1COCR_3COR_2)_2$ when $R_2 = CF_3$, R_3 = H the splitting constant, A_{iso} would decrease as the $+I$ effect of R_1 increases. The values of A_{iso} in Table I, for such complexes would suggest the following order of $+I$ effect for the various substituents:



It has not been possible to estimate the contribution of steric effect to the observed trend of A_{iso}. However, steric factors are expected to have little effect on the energy levels of the vanadyl complexes.

In the other vanadyl complexes that do not have the trifluoromethyl substituent the values of A_{iso} are generally lower than the value of A_{iso} in VO(acac)$_2$ (Table I). It is to be noted that in these complexes in which R_3 = H, both R_1 and R_2 substituents have $+I$ effect. The complexes, VO(3-Clacac)$_2$, and VO(3-CH_3acac)$_2$ have very low A_{iso} values. It appears that both R_3 substituents increase the in-plane ligand field and that the mesomeric effect of the chlorine atom is more effective than its $-I$ effect. It will be necessary to study many more of the complexes with R_3 substituents to fully understand the effect of such substitution on the in-plane ligand field.

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