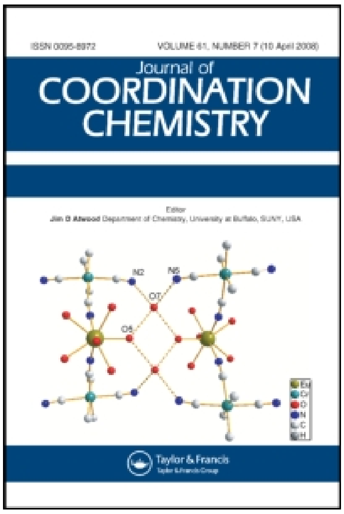

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# SPECTRAL PROPERTIES OF SOME OXOVANADIUM(IV) ß-DIKETONATES

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# SPECTRAL PROPERTIES OF SOME OXOVANADIUM(IV) ß-DIKETONATES

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*(Received November 27, 1985)*

The vibrational and electronic spectra of fifteen oxovanadium(IV) $\beta$-diketonates have been investigated. Although all the complexes are five-coordinate, substitution at $\alpha$- and $\beta$-positions in these $\beta$-diketonates give rise to some measurable effects. The spectral behaviour of VO(pybd)$_2$ and VO(tfpybd)$_2$ suggests that the pyridyl group might be interacting very weakly with the metal centre but without exerting any noticeable changes in stereochemistry.

**Keywords:** Diketones, vanadium (IV), spectra, stereochemistry, properties

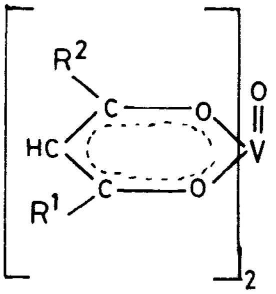
## INTRODUCTION

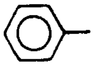
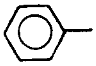
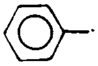
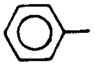
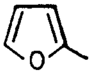
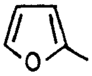
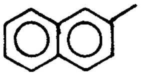
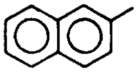
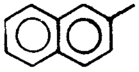
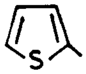
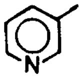
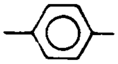
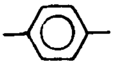
Oxovanadium(IV) has enjoyed a considerable attention from researchers[1,2] because of its unique configuration (d$^1$), high nuclear spin (7/2) and isotopic purity. Among the oxovandium(IV) complexes, oxovanadium(IV) $\beta$-diketonates have received reasonable attention.[3-6] Recently we reported[7] the magnetic properties of a series of oxovanadium(IV) $\beta$-diketonates and found that the substitution of heterocyclic rings in a $\beta$-diketone exerts a small but noticeable effect on magnetic moments down to liquid nitrogen temperature. Besides this fact it was observed that fluoromethyl substitution in a particular $\beta$-diketonate gives an effective magnetic moment independent of temperature. The e.s.r. study[8] of some of these complexes showed that they exhibited the normal eight-line spectrum characteristic of oxovanadium(IV) except in the case of VO(tfpybd)$_2$ which displayed some line-broadening in chloroform in which it was found to be tetrameric.

In this study we report the spectral properties of the $\beta$-diketonates[7,8], **I**, with the view to highlighting the effect of substitution and solvent dependence on their stereochemistry.

## EXPERIMENTAL

The preparation of the complexes has been reported elsewhere.[7] The i.r. spectra were recorded on a Perkin-Elmer 457 spectrometer in the range 250-4000 cm$^{-1}$ using pressed KBr discs. The calibration of the instrument was checked against a polystyrene film and is believed to be accurate to within $\pm 2$ cm$^{-1}$. The diffuse reflectance and solution spectra of the complexes in the range 10.0-32.0 kK were recorded on a Unicam SP 500 spectrophotometer except in some cases where the reflectance spectra were recorded on a Unicam SP 700 spectrophotometer with an SP 735 diffuse reflectance attachment in the range 5.0-50.0 kK.



| Compound | R$^1$ | R$^2$ | Abbreviation |
|---|---|---|---|
| 1 |  | CH$_3$ | VO(bzac)$_2$ |
| 2 |  | CF$_3$ | VO(tfbzac)$_2$ |
| 3 |  |  | VO(dbm)$_2$ |
| 4 | CH$_3$CH$_2$ | CH$_3$ | VO(hxd)$_2$ |
| 5 | CH$_3$ CH$_2$ | CF$_3$ | VO(tfhxd)$_2$ |
| 6 |  | CH$_3$ | VO(fbd)$_2$ |
| 7 |  | CF$_3$ | VO(tffbd)$_2$ |
| 8 |  |  | VO(dnpd)$_2$ |
| 9 |  | CF$_3$ | VO(tfnpd)$_2$ |
| 10 |  | CH$_3$ | VO(tbd)$_2$ |
| 11 |  | CF$_3$ | VO(tftbd)$_2$ |
| 12 |  | CH$_3$ | VO(pybd)$_2$ |
| 13 |  | CF$_3$ | VO(tfpybd)$_2$ |
| 14 | CH$_3$O | CH$_3$O | VO(mdbm)$_2$ |
| 15 | CF$_3$ | C(CH$_3$)$_3$ | VO(tfmhxd)$_2$ |

I

## RESULTS AND DISCUSSION

### *Infrared spectra*

The major assignments are given in Table I. It is now generally agreed[9–11] that the band at 1560–1620 $cm^{-1}$ is attributable to the $\nu_{as}$(C===O) frequencies whereas the band at 1510–1580 $cm^{-1}$ is due to $\nu_{as}$(C===C) frequencies. The bands between 1300 and 1400 $cm^{-1}$ and between 1200 and 1250 $cm^{-1}$ are assigned to $\nu_s$(C===O) and $\nu_s$(C===C) respectively.[10,11] The former band couples slightly to the C–H bonding mode. It is also observed that fluorination of the methyl group raises C===O and C===C stretching modes in those cases where the ligands are fluorinated except in (5) where no change is observed in $\nu_{as}$(C===C). These changes are due to the strong negative inductive effect of the trifluoromethyl group which strengthens the C===O and C===C bonds. Moreover, phenyl substitution in $M(acac)_3$ shifts C===C stretches to higher frequencies and C===O to lower frequencies due to the mesomeric interactions of the phenyl group with the pseudo-aromatic metal chelate ring.[12] Our results indicate that the asymmetric stretches for C===O and C===C are practically unaffected by the introduction of the second phenyl ring (3) when compared with (1), whereas $\nu_s$(C===O) for (1) is greater than in (3) while the second phenyl is replaced by naphthyl (8), $\nu_{as}$(C===O) and $\nu_s$(C===O) and $\nu_s$(C===C) increase. However, $\nu_{as}$(C===O) and $\nu_s$ (C===C) are lower in furyl and thienyl derivatives whereas in the pyridyl cases $\nu_{as}$(C===O) is higher. On the other hand, $\nu_s$(C===O) and $\nu_s$(C===C) are higher in furyl, thienyl and pyridyl complexes than in the phenyl. Thus it seems that aromatic (phenyl and heterocyclic) substitution shifts the symmetric stretches for both C===C and C===O to higher energy whereas the asymmetric stretches tend to respond to changes in the aromatic substituents. The factors responsible for such an observation could be electronegativity, mesomeric and inductive effects depending on the position of the heteroatom in the aromatic ring.

The $\nu$(V=O) frequencies are normal[13] for five-coordinate square-pyramidal complexes. Generally the fluorinated $\beta$-diketonates have lower frequencies than the nonfluorinated complexes except, unexpectedly, in the pyridyl complexes where $\nu$(V=O) for the non-fluorinated species is higher. The general lowering of $\nu$(V=O) is expected because of the fluorine atoms. The highest frequency recorded for (14) might be due to the electron-releasing methoxy group attached (at the *para* position) to the substituent. The unusual behaviour of (12) and (13) suggests that the hetero-*N* atom may be participating in bonding with the metal atom.[14] The $\nu$(V=O) frequency suggests that the V----N interaction in the complexes is weak. The interaction is much weaker in (13) because the presence of $CF_3$ seems to reduce the electron-density on the pyridyl-*N* atom in preference to perturbing the V=O bond; consequently the V----N interaction is weaker and hence $\nu$(V=O) is greater. The proposed structure for the pyridyl complexes is given in Figure 1.

### *Electronic spectra*

The electronic spectral data are presented in Table II. Except for (1) and (2), which gave three bands in the region 10–22 kK in the reflectance spectra, all the complexes gave four d–d transitions, in both the solid state and in chloroform solution, suggesting no fundamental structural changes in either medium. However, in pyridine solutions only (3), (4) and (5) gave four bands; (12), (13) and (15) gave three bands while the other complexes gave two bands.

It therefore seems that all the complexes have $C_{2v}$ symmetry in the solid and in chloroform solution. Under $C_{2v}$ symmetry four transitions are expected, with $e_{\pi}^{*}(d_{xy}, d_{xz})$[15] splitting.[16] However, it is well documented that in most oxovanadium(IV) complexes these four bands are not normally observed at room temperature except in

TABLE I
Relevant vibrational frequencies (cm$^{-1}$)[a] of the oxovanadium(IV) complexes

| Compound | $\nu_{as}$(C===O) | $\nu_{as}$(C===C) | $\nu_s$(C===O) | $\nu_s$(C===C) | $\nu$(V=O) | V–O sensitive modes | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| VO(bzac)$_2$ | 1585s | 1518vs, br | 1370s<br>1308m | 1208m | 999 | 591m | 568vs | | 454vs | 381s |
| VO(tfbzac)$_2$ | 1600s | 1574m | 1323m)<br>1294m) | 1255m | 949m, 896s | 600m | 554m | | | 380m |
| VO(dbm)$_2$ | 1568s | 1522vs | 1366s<br>1320s | 1230s | 998vs, 947m | 586vs | 551m | | 468m | 375s |
| VO(hxd)$_2$ | 1573vs, br | 1531vs, br | 1398s<br>1368w, sh | 1258m | 1000vs, 963m | 616m | | 480vs | 423w | 367m |
| VO(tfhxd) | 1612vs | 1530s | 1356m | 1280s | 921vs | 598s | 531m | | 446s | 375m<br>310w |
| VO(fbd)$_2$ | 1582sh | 1515vs | 1389m<br>1366s | 1230m | 997vs, 962m | 612vs<br>590m | | | 448s | 377m<br>357w |
| VO(tffbd)$_2$ | 1590w)<br>1575vs) | 1540m | 1387s<br>1312vs | 1266s | 950s, 917s | 595m | 525w | | 440w | 382m |
| VO(dnpd)$_2$ | 1605m | 1528vs | 1389s | 1240m | 987m, 970wm | 619m | 552m | 474m | 435w | 372m |
| VO(tbd)$_2$ | 1588sh | 1530vs, br | 1382m)<br>1348m) | 1236m | 1000s, 964m | 619w<br>588m | 550m | | 442m | 375m |
| VO(tftbd)$_2$ | 1600s) | 1545s<br>1580vs) | 1355s<br>1321vs | 1260m<br>1236m | 901s | 602m | 550w | | 420w | 380m |
| VO(pybd)$_2$ | 1588s | 1510s | 1380vs<br>1325wm | 1296s | 960vs, 858s | 612m | 554s | | 437vs | 350s |
| VO(tfpybd)$_2$ | 1602vs, br<br>1566m | 1535s | 1335w<br>1308vs | 1258s | 980vs | 596s | 555s<br>523m | | 470w | 340s |
| VO(mdbm)$_2$ | 1600s)<br>1584w)$^{vs}$ | 1530vs, br | 1365s<br>1324m | 1262s<br>1230s | 1027vs, 989s | 562m | 537m<br>515m | | 484m | 375s |
| VO(tfmhxd)$_2$ | 1619w)<br>1596vs)$^{vs}$ | 1546m<br>1520m | 1307vs | 1254s<br>1228wm | 940vs | 605s | 537m | 499m | 457w | 378m |

[a] $\nu_{as}$, $\nu_s$ = asymmetric and symmetric stretching frequencies respectively. vs = very strong, s = strong, m = medium, wm = weak medium, w = weak, br = broad.

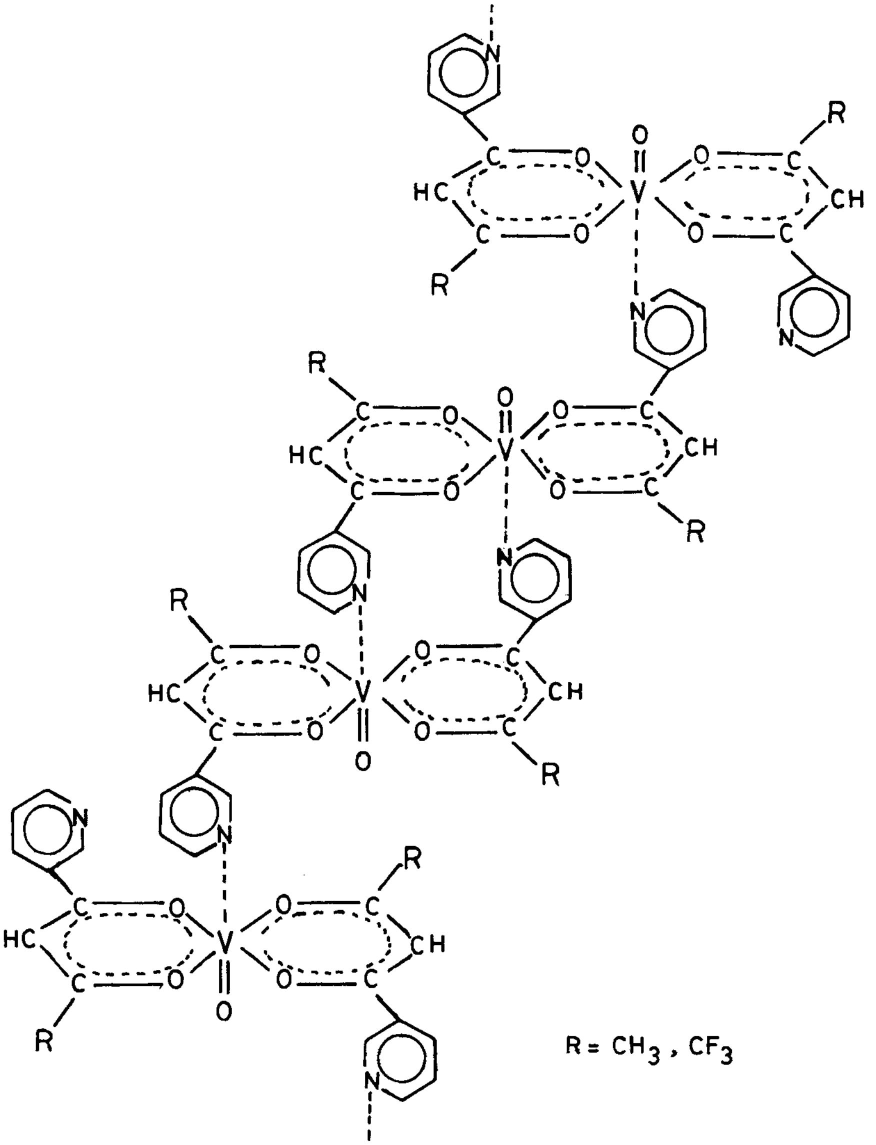


FIGURE 1 Proposed structure for VO(pybd)$_2$ and VO(tfpybd)$_2$.

some low-symmetry complexes.[17] In a few six-coordinate complexes[18,19] two bands have been reported. Apart from the splitting of the $e_\pi^*$ level the possibility of the inversion of the $e_\pi^*$ and $b_1^*(d_{x^2-y^2})$ levels has been reported.[13,19–21] For the purposes of interpreting our data, therefore, we have adopted the energy levels proposed by Selbin *et al.*,[13] incorporating the modification of Kuska and Yang[15] on the splitting of the $e_\pi^*$ level. In those cases where two bands are observed in pyridine solution, the second band occurred below 17 kK which we consider somewhat low to be assigned to band III, and therefore it is not clear whether those complexes can be regarded as octahedral in pyridine solution. It could be that band III is obscured by the adjoining charge-transfer

TABLE II
Electronic spectra of the oxovanadium(IV) complexes.[a]

| Compound | Medium | Band I $b_2 \rightarrow b_1^*$ | Band II $b_2 \rightarrow e_\pi^*$ | Band III $b_2 \rightarrow a_1^*$ | Band IV C.T. | BandV C.T. | Band VI $\pi_3 \rightarrow \pi_4^*$ | Band VII $\pi \rightarrow \pi^*$ | Band VIII $\pi_3 \rightarrow \pi_5^*$ |
|---|---|---|---|---|---|---|---|---|---|
| VO(bzac)$_2$ | Solid | 14.29 | 16.12 | 21.59 | 24.59 | 27.82 | 34.18 | 38.06 | 45.21 |
| | CHCl$_3$ | 11.77 | 14.93(0.92)<br>16.53(0.94) | 22.73(1.18) | | | 30.77(3.64) | | |
| | py | 12.99(0.55) | 17.86(0.60) | | | | 30.30(3.24) | | |
| VO(tfbzac)$_2$ | Solid | 10.94 | 17.65sh | 21.65sh | | 29.76 | | 36.76br | |
| | CHCl$_3$ | 11.49sh(0.66) | 15.04(1.05)<br>16.67(1.12) | 21.28(2.16) | | | 30.30(3.70) | | |
| | py | 13.51(0.56) | 16.13sh(0.68) | | | 28.99(3.34) | | | |
| VO(dbm)$_2$ | Solid | 11.76sh | 14.76<br>16.06 | 20.82 | 24.41sh | 27.18 | 32.44 | 37.06 | 44.82 |
| | CHCl$_3$ | 11.63sh(0.44) | 14.49(0.98)<br>16.13(1.05) | 20.83sh(2.08) | | 28.57(3.80) | | | |
| | py | 11.91sh(0.30) | 13.16(0.09)<br>15.87sh(0.40) | 20.00(0.40) | | 27.78(3.20) | | | |
| VO(hxd)$_2$ | Solid | 11.77 | 14.29<br>16.67 | 19.42 | 25.76br | 29.76br | | 36.68br | 45.09 |
| | CHCl$_3$ | 11.91sh(0.48) | 14.71(0.82)<br>16.95(0.88) | 19.61(0.88) | 24.10(1.20) | 28.17sh(1.70) | | | |
| | py | 11.11sh(1.0) | 12.74(1.42)<br>16.95sh(1.30) | 22.22(1.80) | | | | | |
| VO(tfhxd)$_2$ | Solid | 11.36 | 13.25<br>16.39 | 22.22 | | | | | |
| | CHCl$_3$ | 11.70sh(0.50) | 13.51(0.88)<br>16.39(1.00) | 22.73sh(1.76) | | | | | |
| | py | 11.11sh(0.10) | 13.16(0.58)<br>16.81sh(0.58) | 21.75(2.00) | | | 31.25(3.00) | | |
| VO(fbd)$_2$ | Solid | 11.05 | 12.82<br>16.26 | 20.00 | 25.32 | | | | |
| | CHCl$_3$ | 10.73sh(0.40) | 14.29(0.78)<br>16.67(0.83) | 20.62sh(0.95) | | 29.41(3.70) | | | |
| | py | 13.07(0.53) | 16.67sh(0.56) | | | 28.57(3.40) | | | |

Table II continued overleaf

Table II continued

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| VO(tffbd)$_2$ | Solid | 11.36sh | 12.27<br>16.26 | 20.41 | 25.00 | | | | |
| | CHCl$_3$ | 11.36(0.40) | 14.29(0.92)<br>16.95(1.09) | 22.73sh(1.64) | | 28.57(3.85) | | | |
| | py | 13.33(0.58) | 16.67sh(0.80) | | | 27.78(3.52) | | | |
| VO(dnpd)$_2$ | Solid | 11.44 | 14.56<br>15.50 | 18.71sh | 23.82sh | | 30.53br | 37.12br | 45.29 |
| | CHCl$_3$ | 11.76sh(1.80) | 12.79(1.95)<br>15.75(2.00) | 21.29sh(3.00) | 26.67(3.82) | | | | |
| | py | 13.33(0.43) | 16.36sh(1.03) | | 26.67(3.60) | | | | |
| VO(tfnpd)$_2$ | Solid | 11.63 | 13.44<br>16.67 | 20.00 | 25.41 | | 31.71 | 36.24br<br>37.76br | 45.18 |
| | CHCl$_3$ | 11.77(1.60) | 13.99(1.73)<br>16.67(1.81) | | 24.57sh(3.20) | 28.99(3.92) | | | |
| | py | 13.26(0.76) | 16.39sh(1.04) | | | 28.57(3.68) | | | |
| VO(tbd)$_2$ | Solid | 10.64sh | 14.09<br>16.06 | 23.26 | 25.24sh | 27.59 | 32.35 | 36.47 | 44.94 |
| | CHCl$_3$ | 10.81sh(0.19) | 14.09(0.88)<br>16.53(0.96) | | 24.10sh(1.58) | 27.59(3.60) | | | |
| | py | 13.99(0.74) | 17.39sh(0.88) | | | 28.17(3.52) | | | |
| VO(tftbd)$_2$ | Solid | 10.89 | 14.09<br>17.70 | 19.88sh | 24.53 | 28.78 | | 37.24 | |
| | CHCl$_3$ | 10.20sh(1.20) | 13.79(1.31)<br>16.67(1.36) | 23.26sh(1.49) | | 28.57(4.40) | | | |
| | py | 13.33(0.60) | 16.39sh(0.93) | | | 27.03(3.36) | | | |
| VO(pybd)$_2$ | Solid | 11.36 | 13.70<br>17.27 | 20.84 | 25.00 | 27.29sh | 31.00sh | 36.76br<br>37.59br | 45.00 |
| | CHCl$_3$ | 11.36sh(0.04) | 13.89(0.57)<br>17.24(0.71) | 21.74sh(0.70) | | 27.03(3.19) | | | |
| | py | 12.99(0.50) | 16.67sh(0.53) | 20.00sh(1.35) | | | 31.25(3.23) | | |
| VO(tfpybd)$_2$ | Solid | 11.24 | 13.37<br>16.13 | 20.83 | 25.64 | 27.88 | 31.47br | 35.24br | 44.82 |
| | CHCl$_3$ | 11.49sh(0.69) | 13.99(0.49)<br>16.39sh(0.76) | 20.41(1.47) | | 28.57(2.98) | | | |
| | py | | 13.51(0.50) | 19.23sh(0.53) | | 29.41(3.23) | | | |

Table II continued overleaf

Table II continued

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| VO(mdbm)$_2$ | Solid | 10.64 | 14.29<br>16.53 | 20.83 | 24.39 | 26.67 | |
| | CHCl$_3$ | 10.99sh(1.12) | 14.49(1.44)<br>16.67(1.44) | 22.22(1.80) | | 27.03(3.56) | |
| | py | 12.82(0.52) | 16.67sh(0.88) | | | 26.32(3.70) | |
| VO(tfdmhxd)$_2$ | Solid | 11.17 | 13.33<br>16.67 | 23.26 | | 28.19 | |
| | CHCl$_3$ | 11.17sh(1.42) | 13.70(1.60)<br>16.95(1.64) | 23.81(2.08) | | | 31.25sh(3.72) |
| | py | 13.51(0.74) | 16.67(0.78) | 22.22(1.26) | | | 31.25sh(3.12) |

[a] Band maxima in kK (log $\varepsilon$); $\varepsilon$ in $M^{-1}$ $cm^{-1}$.

band or the energy of the $d_{z^2}$ level had been lowered to form a degenerate transition with the $d_{x^2-y^2}$ level, thus lowering the energy of band III.

Fluoro-substitution raises the energy of band III (in the solid) except in (10) and (11) where the substitution lowers the energy. It is practically unchanged in (12) and (13). However, in solution, and in bands I and II in the solid state no discernible trend can be perceived. It is also observed that on changing from one phenyl (1) to diphenyl (3) and then to dinaphthyl (8) substitution patterns, the positions of bands II and III shift to lower frequencies accompanied by a corresponding reduction in $\nu(V{=}O)$, thus suggesting that these phenyl substituents make the complexes more planar.[22]

In the reflectance spectra five bands are observed around 45, 36–38, 34–36, 27–31 and 24–26 kK. The spin-allowed transitions $\pi_3$–$\pi_5^*$ and $\pi_3$–$\pi_4^*$ lie in the 50 and 37–30 kK regions respectively.[20,21] Phenyl substitution lowers the frequencies of these transitions to 45 and 38 kK.[21,23] Similar effects are anticipated for pyridyl,[14] furyl[24] and thienyl substituted $\beta$-diketonates since they possess basic $\pi$ systems. The bands at about 45 and 30–38 kK may therefore be assigned to $\pi_3$–$\pi_5^*$ and $\pi_3$–$\pi_4^*$ respectively where the band at 30–37 kK arises from the primary bands of aromatic and hetero-aromatic systems while the band at about 36–38 kK which is observed only when the $\beta$-diketone contains either aromatic or heteroaromic substituents has been assigned to a $\pi$–$\pi^*$ secondary transition of the aromatic ring.[24,25] The bands at 24–28 kK are assigned to d–$\pi$ or $\pi$–d metal-ligand or ligand-metal charge-transfer bands.[26] It is generally observed that aromatic substitution tends to lower frequencies of the UV bands while fluorination increases them.

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