

MEASUREMENT AND INTERPRETATION OF INFRARED AND RAMAN SPECTRA OF VANADYL ACETYLACETONATE*

Blanka VLČKOVÁ^a, Bohuslav STRAUCH^b and Milan HORÁK^c

^a *Department of Physical Chemistry,*

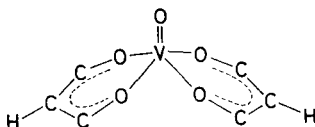
^b *Department of Inorganic Chemistry, Charles University, 128 40 Prague 2 and*

^c *The J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, 118 40 Prague 1*

Received May 6th, 1986

Infrared and Raman spectra of oxobis (2,4-pentandionate) vanadium complex have been studied. A reduction of the number of spectral bands observed in the IR and Raman spectra compared to the theoretical number of normal modes expected for a complex molecule is attributed to the isolation effect of the heavy central metal atom. A simplified model involving the skeleton of the complex and one coordinated ligand has been employed for an empirical interpretation of the vibrational spectra. An exact agreement between the number of modes predicted theoretically on the basis of the simplified model and the number of bands observed experimentally has been obtained.

Among the large variety of vanadyl complexes, oxobis (2,4-pentandionate) vanadium complex** (Scheme 1) is of interest to chemists as an efficient catalyst. Vibrational spectroscopic studies have proved to be an important tool for revealing the relationship between the structure and the



SCHEME 1

reactivity of catalytic active species. However, in the case of $\text{VO}(\text{acac})_2$, only two IR spectroscopic studies directed to a detailed assignment of vibrational modes have been published^{1,2}. Nakamoto¹ has reported a solid state IR spectrum of $\text{VO}(\text{acac})_2$ in the 1600 to 400 cm^{-1} region together with the $\text{V}=\text{O}$ (vanadyl) and $\text{V}-\text{O}$ force constants obtained by a perturbation method of calculation. Polarization IR measurements of oriented $\text{VO}(\text{acac})_2$ molecules in stretched polyethylene and polypropylene films in the 1600 to 400 cm^{-1} region have been carried out by Jonáš and Nordén.² Up to now, no investigation of Raman spectra of the $\text{VO}(\text{acac})_2$ complex has been undertaken.

* Taken in part from the *Thesis* of the author (B. V.), Charles University Prague 1984.

** Henceforth referred to as $\text{VO}(\text{acac})_2$.

In our previous paper concerning the interpretation of the complete IR and Raman spectra of planar Cu(II) and Pd(II) bis(2,4-pentandionate) complexes³, an unexpected mutual independence of the two ligands of a complex molecule has been explained by the isolation effect of the heavy central metal atom. A detailed interpretation of the vibrational spectrum of the square pyramidal⁴ VO(acac)₂ complex based on both IR and Raman spectra thus becomes attractive for comparison of vibrational behaviour of planar bis(acetylacetonate) complexes^{5,6} with that of a nonplanar species. To this purpose, a comprehensive study of solid state Raman and far IR spectra of the VO(acac)₂ complex and its deuterated analogue together with a study of both IR and Raman spectra of the complex in solution have been carried out.

EXPERIMENTAL

Samples of VO(acac)₂ and VO(acac-*d*)₂ were prepared according to the method described in ref.⁷. Acetylacetonate-*d*₂ prepared on the basis of a published method⁸ was used for a synthesis of the deuterated complex.

Infrared spectra were recorded on a Perkin-Elmer 684 spectrometer equipped with a PE 3600 data station. A mixture of indene (98.4%), camphor (0.8%) and cyclohexanone (0.8%) was used for a wavenumber calibration of the spectrometer. Solid samples in the 4 000 to 350 cm⁻¹ region were measured as thin-layer Nujol and perchloro-1,3-butadiene mulls between KBr and NaCl windows, resp. Samples of thin-layer Nujol mulls between polyethylene windows were prepared for far IR measurements in the 500–200 cm⁻¹ region. IR spectra of bromoform and of a saturated solution of VO(acac)₂ in bromoform were obtained in a 0.05 mm KBr liquid cell.

Raman spectra were taken with a JEOL JRS-S1 spectrometer. The 488.0 nm laser line of a Coherent Radiation Model CR2 argon ion laser was employed for excitation. The power of the laser beam at the sample ranged from 40 to 50 mW. Spectra were taken using spectral slit width of 6.8 cm⁻¹. Argon plasma lines were used for the wavenumber calibration of the spectra. The rotating sample technique was employed for the measurement of solid VO(acac)₂ and VO(acac-*d*)₂ samples. Polarization measurement of the saturated solution of VO(acac)₂ in freshly distilled chloroform Uvasol grade, Merck were carried out with an analyser.

RESULTS

The solid state far IR spectra of VO(acac)₂ and VO(acac-*d*)₂ complexes in the 500 to 200 cm⁻¹ region are shown on Fig. 1. Figs 2 and 3 demonstrate the Raman spectra of VO(acac)₂ and of its deuterated analogue in the 0–1 700 cm⁻¹ region. The IR and Raman frequencies of both complexes in solid state are given in Table I (IR 4 000–200 cm⁻¹, Ra 0–4 000 cm⁻¹). The IR spectrum in the 1 600–400 cm⁻¹ region agrees with that reported in ref.² except of the absence of the 1 476 cm⁻¹ band which has not been reported in ref.¹, either. Both the IR and Raman spectra of the VO(acac)₂ complex are in the frequency region > 700 cm⁻¹ strikingly similar to those of Cu(acac)₂ and Pd(acac)₂ complexes. Most of the bands both in the skeletal and the ligand vibrations region in the IR spectrum of the complex have their counterparts in the Raman spectrum which is in accordance with the fact that

the molecule (belonging to C_{2v} point group⁴) has no center of symmetry. The most intensive band in the Raman spectrum, the $\nu(\text{V}=\text{O})$ (vanadyl) at 990 cm^{-1} , has a very intensive IR counterpart at 995 cm^{-1} , which is a typical feature of vibrational spectra of vanadyl complexes.

The changes in the spectra of the $\text{VO}(\text{acac})_2$ complex caused by H/D substitution in the 3-C position of both acetylacetonate ligands are identical with those observed for $\text{Cu}(\text{acac})_2\text{-Cu}(\text{acac-}d)_2$ and $\text{Pd}(\text{acac})_2\text{-Pd}(\text{acac-}d)_2$. The deuteration shifts $3\,092\text{ cm}^{-1} \rightarrow 2\,280\text{ cm}^{-1}$ and $797, 788\text{ cm}^{-1} \rightarrow 604, 595\text{ cm}^{-1}$ demonstrate that the bands in question belong to pure C—H vibrations. The H/D shift of the $1\,188\text{ cm}^{-1}$ band results into a doublet, the appearance of which can be attributed to Fermi resonance analogically to the case of planar acetylacetonates and their deuteriated analogues³. The deuteration shift of the $\beta(\text{C}-\text{CH}_3)$ band to lower frequencies ($425\text{ cm}^{-1} \rightarrow 418\text{ cm}^{-1}$) observed also in the spectra of planar acetylacetonates indicates a vibrational coupling between the $\beta(\text{C}-\text{CH}_3)$ (B_2) and $\beta(\text{C}-\text{H})$ (B_2) modes.

For a determination of the effect of crystal packing on vibrational spectra of a $\text{VO}(\text{acac})_2$ molecule, the IR and Raman spectra of a polycrystalline sample have been compared with those of a saturated solution of the complex in bromoform and chloroform (Tables II, III). Only a few changes in vibrational spectra of the $\text{VO}(\text{acac})_2$ complex have been observed upon dissolution. Instead of an IR doublet at $797, 788\text{ cm}^{-1}$ observed in solid state, a single band at 790 cm^{-1} has been found in the solution IR spectrum. The band in question is attributed to the $\gamma(\text{C}-\text{H})$ mode. The band at $1\,357\text{ cm}^{-1}$ and the shoulder at $1\,344\text{ cm}^{-1}$ in the solid state IR spectrum belonging to the $\delta_s(\text{CH}_3)$ mode have not been found in the solution IR spec-

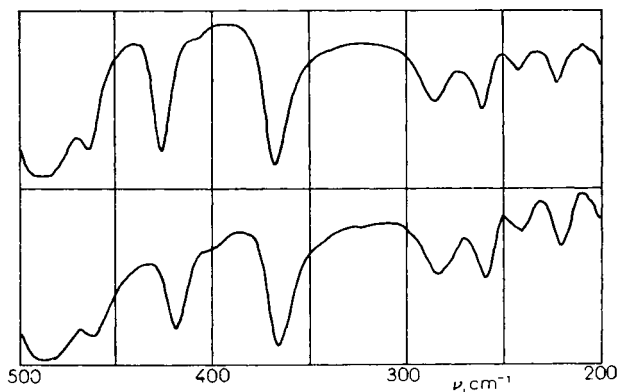


FIG. 1
Far IR spectrum of $\text{VO}(\text{acac})_2$ and $\text{VO}(\text{acac-}d)_2$ complexes in solid state

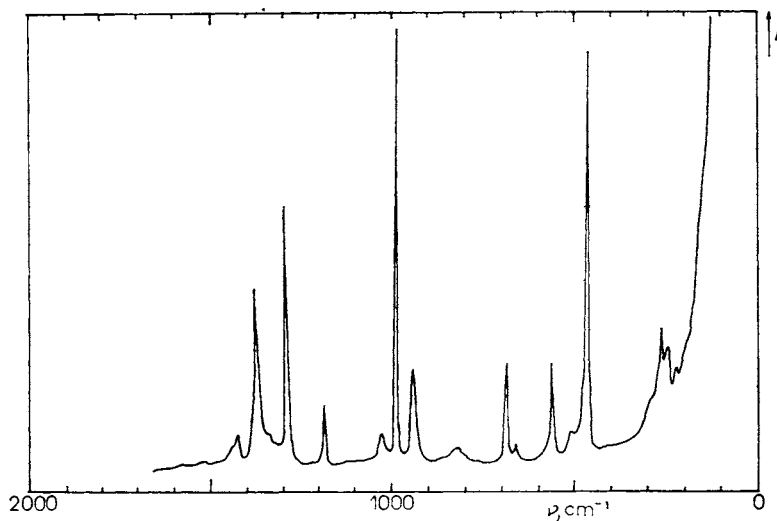


FIG. 2

Raman spectrum of $\text{VO}(\text{acac})_2$ in solid state (excitation 488.0 nm, power 40 mW, slit 6.8 cm^{-1} , pulse counting 10^3 counts/s, rotating sample technique)

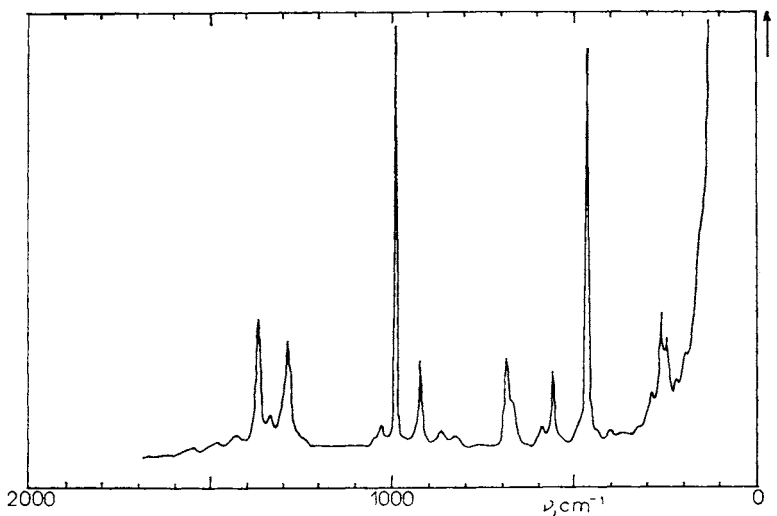


FIG. 3

Raman spectrum of $\text{VO}(\text{acac-}d)_2$ in solid state (excitation 488.0 nm, power 50 mW, slit 6.8 cm^{-1} , pulse counting $2 \cdot 10^3$ counts/s, rotating sample technique)

TABLE I
IR and Raman bands of VO(acac)₂ and VO(acac-d)₂ complexes (values of wavenumbers in cm⁻¹)

VO(acac) ₂		VO(acac-d) ₂		Assignment ^a
IR	R	IR	R	
	3 092 vw	2 280 w	2 280 m-w	$\nu(\text{C}-\text{H}/\text{C}-\text{D})$
3 000 w	3 005 w	2 999 w	3 003 w	$\nu(\text{CH}_3)_{\text{as}}$
2 971 w	2 978 w	2 971 w	2 978 w	$\nu(\text{CH}_3)_{\text{as}}$
2 921 w	2 927 s	2 918 w	2 926 s	$\nu(\text{CH}_3)_{\text{s}}$
1 587 sh	—	1 581 sh	—	} $\nu(\text{C}=\text{O})$
1 562 vs	1 560 vw	1 564 sh	1 565 vw	
1 554 sh	—	1 550 vs	—	
1 526 vs	1 525 w	1 493 vs	1 490 w	$\nu(\text{C}=\text{C}=\text{C})$
1 420 s, br	1 440 m-w, br	1 420 s, br	1 440 w, br	$\delta(\text{CH}_3)_{\text{as}}$
1 375 s, br	1 380 s(p)?	1 372 s	1 375 s	$\nu(\text{C}=\text{O})$
1 357 s	koinc.	1 351 s	koinc.	$\delta(\text{CH}_3)$
1 344 sh	1 340 sh	—	—	} $\nu(\text{C}=\text{C}=\text{C})_{\text{s}}$
1 287 s	1 289 s(p)	1 287 m-s	1 290 s	
1 188 w	1 188 w	926 m	922 m	
			865 w	} $\beta(\text{C}-\text{H}/\text{C}-\text{D})$
1 020 m-s	1 032 m-w	1 021 m	1 032 w	
995 vs	990 vs(p)	995 s	989 vs	$\nu(\text{V}=\text{O})$
945 sh, m	945 m	940 m-s	—	} $\nu(\text{C}-\text{CH}_3)$
936 m				
—	825 w	—	825 w	$\nu(\text{C}-\text{CH}_3)$
797, 788 m	—	595, 604 m	590 w	$\gamma(\text{C}-\text{H}/\text{C}-\text{D})$
686 m	688 m(p)	684 m	688 m	$\delta(\text{ring})$
657 m-w	660 w	664 m-w	670 sh	$\delta(\text{ring})$
608 m	—	604 m ^a	—	$\delta(\text{ring})$
560 vw	560 m	562 vw	560 m	$\nu(\text{VO}_4)$
486 s	480 sh	485 s	480 sh	$\nu(\text{VO}_4)$
463 sh	462 vs(p)	460 sh	461 vs	$\nu(\text{VO}_4)$
425 m-w	—	418 m-w	—	$\beta(\text{C}-\text{CH}_3)$
408 vw	405 w	400 vw	400 w	$\beta(\text{C}-\text{CH}_3)$
368 m		366 m		$\delta(\text{O}-\text{V}=\text{O})$
286 w	290 w	285 w	285 w	} bands of
262 m-w	260 m	260 w	258 m	
243 vw	242 m	241 vw	240 m	$\nu(\text{VO}_4)$
223 w	220 w	221 w	218 w	$\delta(\text{O}-\text{V}=\text{O})$
200 m	195 w	200 w	190 w	} $\beta(\text{C}-\text{CH}_3)$
	112 sh		115 sh	
	95 sh		100 sh	
			55 sh	modes

^a ν stretching mode, β in-plane bending mode, γ out-of-plane bending mode, ρ rocking mode, δ deformation mode.

trum. Both these effects have been observed in the case of $\text{Cu}(\text{acac})_2$ and $\text{Pd}(\text{acac})_2$, too³. The latter effect is quite common in the case of compounds consisting of the CH_3 — groups attached to an aromatic cycle and has its origin in a free rotation of the CH_3 — groups in solution. Another change connected with the dissolution of the complex is a slight upward shift of the $\nu(\text{V}=\text{O})$ frequency observed both in the IR and Raman spectra (Tables II, III). Similar values of the $\nu(\text{V}=\text{O})$ IR frequencies are reported⁹ for several other solvents: chloroform $1\,004\text{ cm}^{-1}$, carbon disulfide and acetone $1\,007\text{ cm}^{-1}$, benzene $1\,008\text{ cm}^{-1}$.

Existence of an intermolecular interaction between the $\text{VO}(\text{acac})_2$ molecules in solid state as the most probable explanation of the differences between the solid state and solution spectra has been checked using ORTEP, a Fortran Thermal–Ellipsoid plot program for crystal structure illustration¹⁰ and structural data⁴. No reasonable specific bonding interaction between the atoms of the neighbouring $\text{VO}(\text{acac})_2$ molecules has been found. Alternative explanation of the changes in the spectra while going from solid state to solution is suggested: The splitting of the $\gamma(\text{C}—\text{H})$ band in the solid state spectrum results probably because of two types

TABLE II

Comparison of IR spectral bands of $\text{VO}(\text{acac})_2$ in solid state and in solution in the $1\,600$ to 700 cm^{-1} region

Solid state ν, cm^{-1}	Bromoform solution ν, cm^{-1}	Assignment ^a
1 587 sh		$2\gamma(\text{C}—\text{H})?$
1 562 sh, vs	1 560 sh	} $\nu(\text{C}—\text{O})$
1 554 vs	1 553	
1 526 vs	1 528	$\nu(\text{C}—\text{C}—\text{C})$
1 420 s, br	1 426	$\delta(\text{CH}_3)_{\text{as}}$
1 375 s, br	1 370	$\nu(\text{C}—\text{O})$
1 357 s	—	} $\delta(\text{CH}_3)_s$
1 344 sh	—	
1 287 s	1 284	$\nu(\text{C}—\text{C}—\text{C})$
1 188 w	—	$\beta(\text{C}—\text{H})$
1 020 m—s	1 022	$\rho(\text{CH}_3)$
995 vs	1 000	$\nu(\text{V}=\text{O})$
945 sh, m	943 sh	} $\nu(\text{C}—\text{CH}_3)$
936 m	935	
797 m—s	790	} $\gamma(\text{C}—\text{H})$
788 m		

^a ν stretching mode, β in-plane bending mode, γ out-of-plane bending mode, ρ rocking mode, δ deformation mode.

of orientation of the $\text{VO}(\text{acac})_2$ molecules in the structure of the complex⁴, one being the inverse of the other. The strenghtening of the $\text{V}=\text{O}$ bond deduced from the increase of $\nu(\text{V}=\text{O})$ in solution may originate from a change of the geometry of the complex towards planarity of the $\text{acac}-\text{V}-\text{acac}$ unit due to the occupation of the free sixth coordination position by a solvent molecule. In the case of $\text{VO}(\text{acac})_2$, such type of solvation is highly probable as no other type of solute – solvent interaction has been observed; *e.g.*, no shifts of the $\nu(\text{C}\equiv\text{O})$ bands attributed to the interaction of lone electron pairs of the oxygen atoms with the hydrogen atoms of the solvents and observed in the case of $\text{Cu}(\text{acac})_2$ and $\text{Pd}(\text{acac})_2$ have appeared in the solution spectra of $\text{VO}(\text{acac})_2$.

Due to the lack of any specific intermolecular bonding in solid state, the interpretation of the solid state IR and Raman spectra of the $\text{VO}(\text{acac})_2$ complex can be based on the C_{2v} point group symmetry of an isolated $\text{VO}(\text{acac})_2$ molecule.

DISCUSSION

Considering the $-\text{CH}_3$ groups as point masses, the molecule of $\text{VO}(\text{acac})_2$ possesses the C_{2v} symmetry and represents an 18-particle problem for which 48 vibrations

TABLE III
Comparison of Raman spectra of $\text{VO}(\text{acac})_2$ in solid state and in solution in the $400-1400\text{ cm}^{-1}$ region

Solid state ν, cm^{-1}	Chloroform solution ν, cm^{-1}	Assignment ^a
462 vs	465 vs, p	$\nu(\text{VO}_4)$
480 sh	486 sh	$\nu(\text{VO}_4)$
560 m	—	$\nu(\text{VO}_4)$
660 w	—	$\delta(\text{ring})$
688 m	—	$\delta(\text{ring})$
825 w	—	$\nu(\text{C}-\text{CH}_3)$
945 m	948 m, p	$\nu(\text{C}-\text{CH}_3)$
990 vs	1 004 vs, p	$\nu(\text{V}=\text{O})$
1 032 m—w	1 030 m—s, dp	$\rho(\text{CH}_3)$
1 188 w	1 190 m, dp	$\beta(\text{C}-\text{H})$
1 289 s	1 292 vs, p	$\nu(\text{C}\equiv\text{C}\equiv\text{C})_s$
1 340 sh	1 362 m, dp	$\nu(\text{C}\equiv\text{O})$
1 380 s	1 377 m, p	$\delta(\text{CH}_3)_s$

^a ν stretching mode, β in-plane bending mode, γ out-of-plane bending mode, ρ rocking mode, δ deformation mode.

are expected theoretically. In the C_{2v} point group, these vibrations belong to the following representations: $14A_1 + 10A_2 + 13B_1 + 11B_2$. Taking into account that according to the selection rules all the vibrational modes are Raman active, the Raman spectrum observed experimentally (28 bands) is considerably simpler than that expected theoretically. Such a reduction of spectral bands is similar to that observed in the vibrational spectra of planar $Cu(acac)_2$ and $Pd(acac)_2$, in the case of which it was accompanied, moreover, with a break of the IR/Raman complementarity rule for centrosymmetrical molecules. In our previous paper on $Cu(acac)_2$ and $Pd(acac)_2$, the phenomenon observed has been finally attributed to the "isolation effect of a heavy central metal atom", while an alternative explanation resulting entirely from the planar geometry of the complexes was also considered, but excluded as a less probable one. As the same effect of a reduction of spectral bands is now observed in the vibrational spectra of non-planar, non-centrosymmetrical $VO(acac)_2$ complex for which no alternative explanation following from the geometry of the complex comes into consideration, it is evident that both in the case of planar centrosymmetrical $Cu(acac)_2$ and $Pd(acac)_2$ and of non-planar $VO(acac)_2$ complex with no center of symmetry it is the isolation effect of a heavy central metal atom³ which causes the relative simplicity of the spectra observed. The isolation effect results in a vibrational independence of the two acetylacetonate ligands in a complex molecule, *i.e.*, the same situation arises as if the molecule of the complex consisted only of one coordinated ligand and the skeleton of the complex.

The isolation effect thus not only enables but also requires an employment of reduced molecular models which include only those parts of a molecule which effectively contribute to its vibrational spectrum. A reduced 11-particle molecular model was successfully employed for an interpretation of the vibrational spectra of $Cu(acac)_2$ and $Pd(acac)_2$.

In the case of $VO(acac)_2$, an analogous 12-particle model would belong to the C_s point group being thus of a lower symmetry than both the skeleton of the complex and the coordinated ligand the symmetry of which is C_{2v} . However, the striking similarity of the vibrational spectra of the coordinated acetylacetonate ligand in various metal acetylacetonates^{11,12} (which is now confirmed by comparison of the spectra of planar $Cu(acac)_2$ and $Pd(acac)_2$ and square pyramidal $VO(acac)_2$) suggests that the local symmetry of the coordinated ligand (C_{2v}) is relevant for the spectral bands of a coordinated ligand while the local symmetry of the skeleton (C_{2v} ; too, but with the different set of axis) determinates the spectrum of the skeleton of the complex. This suggestion, of course, implies a very weak vibrational coupling between the skeleton of the complex and the coordinated ligand. The idea of the weak vibrational coupling is confirmed by the fact that the frequencies of a coordinated ligand are independent not only on the symmetry of the skeleton of the complex but also on the mass of the central metal atom (*e.g.*, comparison of the spectra of $Cu(acac)_2$ and $Pd(acac)_2$ (Cu - at. mass 63.456; Pd - at. mass 106.4 (ref.³))

Considering the nature of the isolation effect of a heavy central metal atom and the conditions which lead to a separation of the skeletal and ligand frequencies we find that they have the same origin: a weak and relatively long metal—oxygen bonding together with a relatively large mass of the central metal atom lead to lower frequency values of the skeletal vibrations while strong, partially double bonds within the ligand together with a low mass of the atoms forming an acetylacetonate ligand (C, O, H) locate the frequencies of the coordinated ligand to the higher frequency region.

Following the foregoing considerations, a reduced 12 - particle molecular model based on the skelet—ligand frequency separation is suggested. The model consists of two separate fragments, the skeleton and one coordinated ligand to each of which, a different set of Cartesian coordinates is attributed. This model is the only one which enables to consider the effective symmetry both of the skeleton of the complex (C_{2v}) and coordinated ligand (C_{2v} , different set of axis) which, according to the previous considerations, is substantial for interpretation of the vibrational spectrum of $VO(acac)_2$.

A very close similarity of the vibrational spectra of $VO(acac)_2$ to those of $Cu(acac)_2$ and $Pd(acac)_2$ in the ligand vibrations region $> 700\text{ cm}^{-1}$ enables to establish assignment of the modes of the coordinated ligand in the spectra of $VO(acac)_2$ on that carried out for $Cu(acac)_2$ and $Pd(acac)_2$ (Table I).

For the skeleton of the complex consisting of the central vanadium atom and five oxygen atoms, 12 vibrational modes are expected: $4A_1 + 2A_2 + 3B_1 + 3B_2$. Three of them, A_1 (stretching) and B_1, B_2 (bending) represent a vibrational contribution of the vanadyl ($V=O$) group. The remaining 9 vibrations, 4 stretching $A_1 + A_2 + B_1 + B_2$ and 5 deformation modes $2A_1 + A_2 + B_1 + B_2$ involve the central vanadium and four oxygen atoms of the acetylacetonate ligands.

The frequency of the $\nu(V=O)$ vanadyl (A_1) mode has been found at 995 cm^{-1} (IR) and 990 cm^{-1} (Ra, polarized), respectively. Another very strong polarized Raman band at 462 cm^{-1} , having only a weak band at 463 cm^{-1} as its IR counterpart, is attributed to the $\nu_s(VO_4)$ mode (A_1). The Raman depolarized band at 560 cm^{-1} is assigned to the $\nu_{as}(VO_4)$ (A_2) mode while a strong IR band at 486 cm^{-1} (shoulder at 480 cm^{-1} in the Raman spectrum) belongs to another $\nu_{as}(VO_4)$ (B_1) mode (Table I). The assignment of modes in the $< 300\text{ cm}^{-1}$ region is rather complicated as the frequencies of the three types of deformation modes lie in this region: $\delta(VO_4)$, $\delta(O—V—O)$ and ligand deformations. As Raman polarization data could not be obtained for this frequency region, a preresonance Raman study has been suggested to enable assignment of modes in the low frequency region. The results of this study are the subject of a following paper.

CONCLUSION

Employment of the reduced molecular model based on the skeletal–ligand modes separation provides an agreement between the theoretical number of normal modes expected (30 modes) and the number of bands observed experimentally in the IR and Raman spectra of VO(acac)₂ (30 bands). This agreement proves correctness of the reduced molecular model in which only the skeleton of the complex and one complex and one coordinated ligand are included thus determining the number of expected modes while the effective symmetry of the separate fragments skeleton–coordinated ligand determines the point group to which the representations of these modes belong.

The model appears to form a good basis for the interpretation of vibrational spectra of a variety of substituted species. Among them, the 3-C substituted derivatives which will be a subject of our following study are of special interest both from the spectroscopic and chemical point of view.

The authors are indebted to Dr J. Podlahová for the ORTEP calculation and to Dr J. Podlaha for helpful discussions.

REFERENCES

1. Nakamoto K., Morimoto Y., Martell A. E.: *J. Am. Chem. Soc.* **83**, 4533 (1961).
2. Jonáš I., Nordén B.: *Spectrochim. Acta*, **A 32**, 427 (1976).
3. Vlčková B., Strauch B., Horák M.: *This Journal* **50**, 306 (1985).
4. Dodge R. P., Templeton D. M., Zalkin A.: *J. Chem. Phys.* **35**, 55 (1961).
5. Starikova Z. A., Shugam E. A.: *Zh. Strukt. Khim.* **10**, 290 (1969).
6. Knazheva A. N., Shugam E. A., Shkolnikova L. M.: *Zh. Strukt. Khim.* **11**, 938, (1970).
7. Fernelius W. C., Bryant B. E.: *Inorg. Synt.* **5**, 113 (1957).
8. Ogoshi M., Nakamoto K.: *J. Chem. Phys.* **45**, 3113 (1966).
9. Selbin J., Manning H. R., Cessac G.: *J. Inorg. Nucl. Chem.* **25**, 1253 (1963).
10. Johnson C. K.: ORNL — 3794, 1965.
11. Young W. L. (III): *Thesis*. University of North Carolina 1964.
12. Vlčková B.: *Thesis*. Charles University, Prague 1984.

Translated by the author (B.V.).