

MEASUREMENT AND INTERPRETATION OF INFRARED AND RAMAN SPECTRA OF BIS(2,4-PENTANDIONATE)COMPLEXES OF Cu(II) AND Pd(II)*

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

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

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

Received January 27th, 1984

Infrared and Raman spectra of Cu(II) bis(2,4-pentandionate) and Pd(II) bis(2,4-pentandionate) complexes have been measured and interpreted. The coincidence of numerous bands in the IR and Raman spectra has been explained by the isolation effect of the heavy central metal atom which prevents the vibrational interaction of the two ligands in the chelate molecule with each other. An 11-particle model consisting of all the atoms of one ligand (both CH₃ groups are taken as the point masses), a central metal atom and two oxygen atoms of the other ligand has been proved to be most adequate for the empirical interpretation of the spectra.

For more than twenty years, the wide range of catalytic activities of bis(2,4-pentandionate) complexes of transition metals has stimulated an effort to elucidate the relationship between the structure and the reactivity of these complexes. Spectroscopic methods have proved to be a valuable tool for this purpose.

Several investigators¹⁻⁶ have measured and interpreted infrared (IR) spectra of bis(2,4-pentandionate) copper(II) and bis(2,4-pentandionate) palladium(II) complexes.** Up to now, solid state IR data covering the 4 000 to 50 cm⁻¹ region have been reported. The NCA calculations have been carried out by Nakamoto and Martell¹ (the half molecule model) and by Mikami and coworkers² (the IR active modes of the whole molecule model). Junge and Musso³ studied the spectra of isotope substituted analogues of both complexes (H/D, ¹⁶O/¹⁸O, ¹²C/¹³C) as well as the polarized IR spectrum of Cu(acac)₂ in the 1 650 to 400 cm⁻¹ region. Their assignment of the bands in the 1 600 to 1 500 cm⁻¹ region contradicts that in ref.^{1,2}.

The principal drawback of all the previous interpretations of vibrational spectra of Cu(acac)₂ and Pd(acac)₂ was the lack of Raman (Ra) data. Regarding the fact that the molecules of both complexes are centrosymmetrical (Cu(acac)₂ — C_{2h} in solid state⁷, D_{2h} in gas phase⁸; Pd(acac)₂ D_{2h} in solid state⁹) both IR and Raman spectra are necessary for a vibrational analysis. No Raman spectrum of Cu(acac)₂ has been reported up to now. The solid state Raman spectrum of Pd(acac)₂ has been reported⁴, however, a possibility of the sample decomposition during the measurement had to be taken into account.

* Taken in part from the Thesis of B. V., Charles University Prague, 1984. Present address: Dept. of Physical Chemistry, Charles University, 128 40 Prague.

** Henceforth referred to as Cu(acac)₂ and Pd(acac)₂, resp.

The aim of this paper was to obtain Raman spectra of both $\text{Cu}(\text{acac})_2$ and $\text{Pd}(\text{acac})_2$ along with the Raman polarization data in order to carry out a vibrational analysis of these complexes which would be based on complete experimental data. To this purpose also the IR and the Raman spectra of 3-C deuteriated analogues of $\text{Cu}(\text{acac})_2$ and $\text{Pd}(\text{acac})_2^*$ were measured. The spectra of a compound in solution are important for revealing the influence of intermolecular interactions in the unit cell on the spectra of polycrystalline samples. Due to the lack of these data for $\text{Cu}(\text{acac})_2$ and $\text{Pd}(\text{acac})_2$ complexes we extended our investigation to IR and Raman spectra of the samples in solution.

EXPERIMENTAL

Samples of $\text{Cu}(\text{acac})_2$ and $\text{Pd}(\text{acac})_2$ were prepared according to the methods described in refs^{10,11} Acetylacetone- d_2 prepared according to a published method¹² was used for the synthesis of the deuteriated species. $\text{Cu}(\text{acac}-d)_2$ was obtained by the reaction of 3.5 g of anhydrous CuSO_4 in D_2O with acetylacetone- d_2 (5 ml) at $\text{pH} = 6.5-7$ (addition of 15 ml 15% solution of anhydrous Na_2CO_3 in D_2O), yield 65%. $\text{Pd}(\text{acac}-d)_2$ was prepared by a modified procedure¹³ (using a solution of KOD (potassium deuteriooxide) in D_2O prepared by dissolution of potassium in D_2O in an argon atmosphere).

Raman spectra were taken with a JEOL JRS-S1 spectrometer. A Coherent Radiation Model CR2 argon ion laser provided the exciting radiation. The exciting lines used were 488.0 and 514.5 nm, resp. The power of the laser beam at the sample ranged from 50 to 80 mW. The spectra were taken using the spectral slit widths of $6-7 \text{ cm}^{-1}$. Argon plasma lines were used for the wavenumber calibration of the spectra. Polarization measurements were carried out with an analyser. The solid state spectra of $\text{Cu}(\text{acac})_2$ and $\text{Cu}(\text{acac}-d)_2$ were measured by a stationary sample technique in sealed glass capillary tubes ($\Phi \sim 1 \text{ mm}$) while for $\text{Pd}(\text{acac})_2$ and $\text{Pd}(\text{acac}-d)_2$ samples, the rotating sample technique was employed (using RS-RC 01 JEOL rotating unit). Freshly distilled UVASOL grade chloroform (MERCK) was used for preparation of saturated solutions of $\text{Cu}(\text{acac})_2$ and $\text{Pd}(\text{acac})_2$. Spectral purity of the solvent was checked by taking its IR and Raman spectra under the conditions used for the solution measurements. The spectrum of the $\text{Cu}(\text{acac})_2$ solution was measured in a sealed capillary tube ($\Phi \sim 2 \text{ mm}$), that of the $\text{Pd}(\text{acac})_2$ solution in a rotating liquid cell.

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 the wavenumber calibration of the spectrometer. The solid samples were measured as thin-layer Nujol and perchloro-1,3-butadiene mulls between KBr, NaCl, and polyethylene windows, resp. Spectra of saturated solutions of $\text{Cu}(\text{acac})_2$ and $\text{Pd}(\text{acac})_2$ in chloroform and bromoform (UVASOL grade, Merck) were obtained in the KBr liquid cells. The spectra of solutions were averaged by a computer and the spectra of the solvents were subtracted.

Additional measurements were carried out for a verification of the Raman spectra by one of the authors (B. V.) in the laboratory of Prof. R. J. H. Clark, University College London, Great Britain. The spectra were measured on a Spex 14018 R 6 spectrometer in conjugation with Coherent Radiation CR 12 argon and CR 52 krypton ion lasers. The lines at 488.0 (Ar^+) and 482.5 nm (Kr^+) were used for excitation rotating samples technique being employed.

* Referred to as $\text{Cu}(\text{acac}-d)_2$ and $\text{Pd}(\text{acac}-d)_2$.

RESULTS

The solid state Raman spectra of $\text{Cu}(\text{acac})_2$ and $\text{Pd}(\text{acac})_2$ in the 0 to $1\,700\text{ cm}^{-1}$ region are shown in Fig. 1 and 2, resp. The Raman spectrum of $\text{Pd}(\text{acac})_2$ obtained by rotating sample technique has been found to agree to that in ref.⁴ as far as only the very strong bands are concerned. The additional measurement (see Experimental) has confirmed the results presented in this paper. The difference between the two Raman spectra in question has its origin in a sample decomposition during the

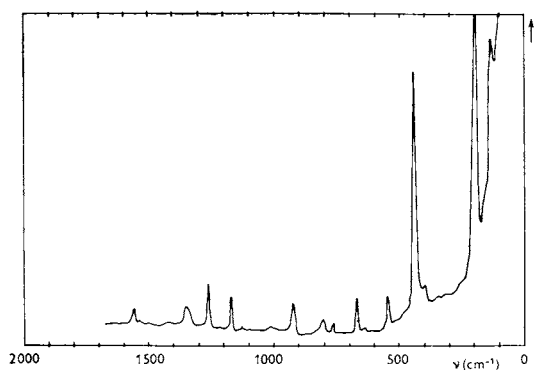


FIG. 1

Raman spectrum of $\text{Cu}(\text{acac})_2$ in solid state (excitation 488.0 nm , power 70 mW , slit 6.8 cm^{-1} , pulse counting $2 \cdot 10^3\text{ counts/s}$)

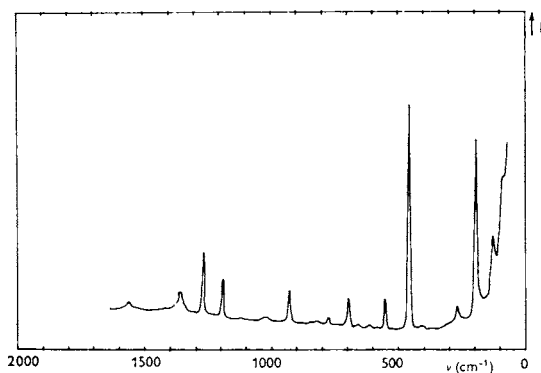


FIG. 2

Raman spectrum of $\text{Pd}(\text{acac})_2$ in solid state (excitation 488.0 nm , power 80 mW , slit 6.8 cm^{-1} , pulse counting $1 \cdot 10^4\text{ counts/s}$, rotating sample technique with $1\,500\text{ r.p.m.}$)

measurement by the stationary sample technique used in ref.⁴. The frequencies and other characteristics of the bands observed in IR and Raman spectra of both $\text{Cu}(\text{acac})_2$ and $\text{Pd}(\text{acac})_2$ complexes and their deuteriated derivatives are listed in Table I and II. Due to the strong resemblance of both Raman and IR spectra of $\text{Cu}(\text{acac})_2$ and $\text{Pd}(\text{acac})_2$ as well as of $\text{Cu}(\text{acac-d})_2$ and $\text{Pd}(\text{acac-d})_2$, a common vibrational analysis has been carried out for both the complexes studied.

The influence of the crystal packing upon the vibrational spectra of $\text{Cu}(\text{acac})_2$ and $\text{Pd}(\text{acac})_2$ has been determined by a comparison of the solid state and the solution spectra. As the only result of this effect, the splitting of the $\gamma(\text{C-H})$ band in the solid state spectra of both complexes into a doublet ($784, 781 \text{ cm}^{-1}$ for $\text{Cu}(\text{acac})_2$, $785, 779 \text{ cm}^{-1}$ for $\text{Pd}(\text{acac})_2$) has been observed while only a single band of remarkably lower relative intensity has been found in solution.

The frequency shifts of the bands observed in the $1\,600$ to $1\,400 \text{ cm}^{-1}$ region in the IR spectra have their origin in the solvent effect. The band at $1\,415 \text{ cm}^{-1}$ in the solid state spectrum of $\text{Cu}(\text{acac})_2$ exhibits a shift of -18 cm^{-1} (-23 cm^{-1}) in the chloroform (bromoform) solution. The same effect has been observed for $\text{Pd}(\text{acac})_2$: the band at $1\,397 \text{ cm}^{-1}$ shows the shift of -17 cm^{-1} (-20 cm^{-1}). In the case of $\text{Pd}(\text{acac})_2$, the band at $1\,568 \text{ cm}^{-1}$ exhibits a similar shift of -11 cm^{-1} (-17 cm^{-1}), too. All the bands discussed belong to the modes involving the main contribution of the $\text{C}\equiv\text{O}$ bond stretching and the shifts observed in solution can be attributed to the interaction of the lone electron pairs on the oxygen atoms with the hydrogen atoms in the solvent molecules. This kind of interaction has been mentioned in connection with the manifestation of the solvent effect in the UV electronic spectra of these compounds¹⁴, too. The frequency increase of the $\nu(\text{CuO}_4)$ mode from 455 cm^{-1} (solid state) to 461 cm^{-1} (chloroform solution) can be attributed to a strengthening of the $\text{Cu}-\text{O}$ bond resulting from the break of the intermolecular interaction between the central copper atom and the 3-carbon atom of the neighbouring molecule⁷ upon dissolution.

The relatively small and easily understandable differences between the solid state and solution spectra of both complexes prove that their vibrational spectra both in solid state and in solution can be related with the symmetry of an isolated molecule (D_{2h}). Therefore the Raman polarization data obtained for most of the Raman bands in the solution spectra can be used for the assignment of the totally symmetric modes both in solid state and in solution spectra (Table I, II).

DISCUSSION

Planar centrosymmetrical molecules of $\text{Cu}(\text{acac})_2$ and $\text{Pd}(\text{acac})_2$ complexes are of the D_{2h} symmetry. If the CH_3 groups are taken as the point masses, the molecule represents a 17-particle problem, for which 45 normal modes $8A_g + 2B_{1g} + 4B_{2g} + 7B_{3g}$ (Ra active) + $8B_{1u} + 8B_{2u} + 5B_{3u}$ (IR active) + $3A_u$ (inactive) are predict-

ed. Compared to the theoretical analysis, the IR and Raman spectra observed are surprisingly simple.

TABLE I
IR and Raman bands of $M(\text{acac})_2$ ($M = \text{Cu, Pd}$) complexes (cm^{-1})

$\text{Cu}(\text{acac})_2$		$\text{Pd}(\text{acac})_2$		Assignment ^b
IR	Ra	IR	Ra	
3 077 w	3 079 w	—	3 075 w	$\nu(\text{C—H})$
2 997 w	3 000 vw	—	3 000 w	$\nu(\text{CH}_3)_{\text{as}}$
2 974 w	—	—	—	$\nu(\text{CH}_3)_{\text{as}}$
2 923 w	2 924 w-m	2 922 m-s	2 919 m-s	$\nu(\text{CH}_3)_{\text{s}}$
1 578 vs	1 580 w(p)	1 568 vs	1 570 w	$\nu(\text{C}=\text{O})_{\text{s}}$
1 552 vs	—	1 548 vs	—	$2\gamma(\text{C—H})$
1 530 vs	1 526 w	1 523 vs	—	$\nu(\text{C}=\text{C}=\text{C})_{\text{as}}$
1 460 sh	—	1 458 sh	—	$\delta(\text{CH}_3)_{\text{as}}$
1 430 sh	—	1 435 sh	—	$\delta(\text{CH}_3)_{\text{as}}$
1 445 s(br)	—	1 397 s(br)	—	$\nu(\text{C}=\text{O})_{\text{as}}$
1 355 m-s	1 365 w(p)	1 355 s	1 365 m	$\delta(\text{CH}_3)_{\text{s}}$
1 277 m-s	1 279 m(p)	1 271 s	1 271 m-s	$\nu(\text{C}=\text{C}=\text{C})_{\text{s}}$
1 191 w-m	1 189 m(dp)	1 198 w-m	1 195 m-s	$\beta(\text{C—H})$
1 021 m-s	1 025 vw	1 020 m-s	1 025 w	$\rho(\text{CH}_3)$
938 m	939 m(p)	935 m-s	935 m	$\nu(\text{C—CH}_3)$
—	825 w	—	825 w	$\nu(\text{C—CH}_3)$
784, 781 s	781 w	785, 779 s	780 w	$\gamma(\text{C—H})$
685 w-m	686 m(p)	697 m	703 m	$\beta(\text{ring})$
653 m	654 vw	677 w-m	—	$\gamma(\text{ring})$
612 w-m	—	659 m-s	—	$\beta(\text{ring})$
—	560 m(dp)	—	555 m	$\nu(\text{MO}_4)$
455 s	—	465 s	—	$\nu(\text{MO}_4)$
—	447 s(p)	—	457 vs	$\nu(\text{MO}_4)$
432 w-m	—	444 w	—	$\beta(\text{C—CH}_3)$
—	408 w(dp)	—	410 w	$\gamma(\text{C—CH}_3)$
289 m-s	—	296 m-s	—	$\nu(\text{MO}_4)$
267 w	271 w	265 s	270 w-m	$\beta(\text{C—CH}_3)$
—	—	220 vw	—	$\beta(\text{MO}_4)$
218 s	—	—	—	$\gamma(\text{C—CH}_3)$
—	203 vs(p)	—	197 s	$\beta(\text{MO}_4)$
—	128 sh	—	127 sh	$\gamma(\text{ring})$
—	68 sh	—	60 sh	$\gamma(\text{MO}_4)$

^b As in Table II.

TABLE II
IR and Raman bands of $M(\text{acac-d})_2$ ($M = \text{Cu, Pd}$) complexes (cm^{-1})

Cu(acac-d) ₂		Pd(acac-d) ₂		Assignment ^b
IR	Ra	IR	Ra	
2 993 w	—	3 008 w	3 010 vw	$\nu(\text{CH}_3)_{\text{as}}$
2 974 w	—	—	2 965 w	$\nu(\text{CH}_3)_{\text{as}}$
2 923 w	2 920 w	2 923 w	2 924 s	$\nu(\text{CH}_3)_{\text{s}}$
2 269 w	2 270 w	2 269 w	2 270 m-w	$\nu(\text{C—D})$
1 568 vs	1 575 m	1 555 vs	1 560 m-w	$\nu(\text{C}=\text{O})_{\text{s}}$
1 502 vs	—	1 490 vs	—	$\nu(\text{C}=\text{C}=\text{C})_{\text{as}}$
1 480 sh	—	1 465 sh	—	$\delta(\text{CH}_3)_{\text{as}}$
1 430 sh	—	1 430 sh	—	$\delta(\text{CH}_3)_{\text{as}}$
1 415 s	—	1 392 s	—	$\nu(\text{C}=\text{O})_{\text{as}}$
1 352 s	1 368 m	1 355 s	1 365 m	$\delta(\text{CH}_3)_{\text{s}}$
1 273 m-s	1 278 m	1 270 m-s	1 272 m-s	$\nu(\text{C}=\text{C}=\text{C})_{\text{s}}$
1 158 w	—	1 158 w	—	$2\nu(\text{C—D})$
1 019 m-s	1 020 w	1 020 m	1 020 w	$\rho(\text{CH}_3)$
939 m	940 w	939 m	—	$\nu(\text{C—CH}_3)$
918 m-w	921 m	915 m	911 m	$\beta(\text{C—D})^a$
865 w	860 m-w	878 w	873 w	$\beta(\text{C—D})^a$
—	828 m	—	825 w	$\nu(\text{C—CH}_3)$
682 m-w	683 m	697 m	698 m	$\beta(\text{ring})$
655 m-s	656 m-w	676 sh	—	$\gamma(\text{ring})$
610 m	—	665 m-s	660 w	$\beta(\text{ring})$
584, 581 m-s	575 w	587, 581 m-s	575 w	$\gamma(\text{C—D})$
—	560 m	—	555 m	$\nu(\text{MO}_4)$
455 s	—	465 s	—	$\nu(\text{MO}_4)$
—	446 s	—	461 vs	$\nu(\text{MO}_4)$
425 m-w	—	435 m-w	—	$\beta(\text{C—CH}_3)$
—	404 vw	—	409 vw	$\gamma(\text{C—CH}_3)$
288 m-s	—	294 m	—	$\nu(\text{MO}_4)$
266 w	260 vw	263 m-s	271 m-w	$\beta(\text{C—CH}_3)$
215 s	—	263 m-s	—	$\gamma(\text{C—CH}_3)$
—	—	220 w	—	$\beta(\text{MO}_4)$
—	199 vs	—	197 s	$\beta(\text{MO}_4)$
—	122 m-w	—	124 m-s	$\gamma(\text{ring})$
—	90 sh	—	90 sh	$\gamma(\text{MO}_4) (?)$
—	70 sh	—	40 sh	

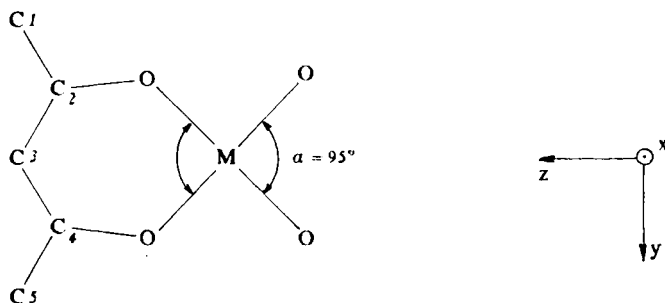
^a Splitting by FR; ^b ν stretching mode, β in-plane bending mode, γ out-of-plane bending mode, ρ rocking mode.

For a $M(\text{acac})_2$ molecule, in which the two ligands of C_{2v} symmetry are coordinated centrosymmetrically to the central metal atom, two vibrational modes result theoretically for each mode of a single ligand. A particular mode of one ligand can be coupled with the same mode of the other ligand either "in-phase" or "out-of-phase", one of the resulting modes being symmetric with respect to the centre ("g", R_a active), the other one antisymmetric ("u", IR active or inactive). The frequency difference between the mutually corresponding IR and Raman bands is assumed to reflect the extent of the vibrational coupling between the two ligands. Experimental data (Table I, II) show that the IR and Raman frequencies are nearly coincident for most of the ligand vibrations which testifies to a very weak vibrational interaction of the two ligands. The restriction of such an interaction in the $M(\text{acac})_2$ molecules can be explained by the isolation effect of the "heavy" metal atom. The relatively large mass of the metal atom compared to that of the atoms forming the skeleton of the ligand together with a relatively weak bonding between the central atom and the oxygen atoms of the ligand prevents the vibrational coupling between the ligands. This phenomenon has been described, *e.g.*, in vibrational spectra of organosilicon compounds¹⁵, nevertheless, it has never been taken into account for the interpretation of the spectra of metal chelates.

There is an alternative explanation of the frequency coincidence of IR and Raman bands which results from the geometry of the complexes. Small frequency differences between the "in-phase" and "out-of-phase modes" are known to appear in the spectra of "inversely" oriented mutually coupled oscillators, this being also the case of $M(\text{acac})_2$ molecules. Nevertheless, the former explanation seems to be more likely than the latter, as the nearly complete independence of vibrational spectra of different rings in the same molecule has already been mentioned for both bis and tris-(acetylacetonate) complexes¹⁶. This statement was the result of the study of high resolution spectra of a series of asymmetrically substituted chelates¹⁷.

Frequency differences observed between the corresponding IR and Raman bands of both $\text{Cu}(\text{acac})_2$ and $\text{Pd}(\text{acac})_2$ are within the range of experimental error. This difference being neglected and both the IR and the corresponding Raman band being attributed to a particular mode of one coordinated ligand of the local symmetry C_{2v} , the number of bands predicted theoretically for one coordinated ligand and the number of bands observed in the IR and Raman spectra and attributed to the ligand is exactly the same, *i.e.*, 18. This induces an idea that the interpretation of vibrational spectra of $M(\text{acac})_2$ complexes could be reduced to the analysis of a "half molecule model". Unfortunately, this approach (used in *ref.*¹ for NCA) can be adopted as far as only the ligand vibrations are concerned, as it fails in the description of the modes of the MO_4 skeleton. Our attempts to find a more suitable simplified model¹⁸ resulted in the 11-particle model of $M(\text{acac})_2$ molecules which is suggested in this paper. The model consists of the skeleton of one ligand (both CH_3 groups are taken as the point masses), of the central metal atom and of the two

oxygen donor atoms of the other ligand (Scheme 1).



SCHEME 1

The model unit is of C_{2v} symmetry and the 27 vibrational modes belong to the following representations: $10A_1 + 3A_2 + 5B_1 + 9B_2$. The description of modes which follows from the theoretical analysis of the 11-particle model is given in Table III together with the assignment of the characteristic frequencies of $\text{Cu}(\text{acac})_2$, $\text{Pd}(\text{acac})_2$ and their deuteriated analogues to the modes of the 11-particle model. A comparison of the data in Table III with the complete list of IR and Raman frequencies observed (Table I, II), shows that by means of the 11-particle model all the bands observed in the IR and Raman spectra of both $\text{Cu}(\text{acac})_2$ and $\text{Pd}(\text{acac})_2$ as well as of their deuteriated analogues (except for those of CH_3 groups and overtones) have been assigned.

The 11-particle unit generates 27 vibrations, 11 of which belong to stretching modes and 16 to bending ones. The contributions of particular bonds and groups of atoms are further discussed in detail.

The hydrogen atom attached to the central 3-C atom of the ligand gives rise to three vibrations: stretching (A_1), in-plane bending (B_2) and out-of-plane bending (B_1). Their assignment was done in a straightforward manner by a comparison of the spectra of the complexes with those of their deuteriated analogues. The doublet appearing in the spectra of deuteriated analogues may have its origin in the Fermi resonance of the $\beta(\text{C}-\text{D})$ vibrational level (B_2) with the 455 cm^{-1} (465 cm^{-1}) (A_1) + 425 cm^{-1} (435 cm^{-1}) (B_2) combination level.

If the CH_3 groups are taken as the point masses, their contribution is reduced only to six vibrations. These are the "in-phase" and the "out-of-phase" coupled pairs of stretching, in-plane bending and out-of-plane bending modes. The stretching and the in-plane bending modes are of the symmetry A_1 ("in-phase") and B_2 ("out-of-phase") while the out-of-plane bending modes are of the symmetry A_2 and B_1 . The bands at 940 cm^{-1} (Raman polarized) (A_1) and 825 cm^{-1} (B_2) are attributed

to the two stretching modes. The bands of the bending modes are localized in the 450 to 200 cm^{-1} region (Table III).

For the skeleton of the ligand consisting of five atoms $\text{—O}=\text{C}=\text{C}=\text{C}=\text{O—}$, the following vibrational modes are expected (referred to as "ring" vibrations in Table III): four stretching modes ($2A_1 + 2B_2$), two in-plane bending modes ($A_1 + B_2$)

TABLE III
Fundamental frequencies (cm^{-1}) of $\text{M}(\text{acac})_2$ and $\text{M}(\text{acac-d})_2$ complexes ($\text{M} = \text{Cu, Pd}$)

Sym.	No	$\text{M}(\text{acac})_2$		$\text{M}(\text{acac-d})_2$		Assignment
		$\text{M} = \text{Cu}$	$\text{M} = \text{Pd}$	$\text{M} = \text{Cu}$	$\text{M} = \text{Pd}$	
A_1	1	3 078	3 075	2 270	2 270	$\nu(\text{C—H/C—D})$
	2	1 579	1 569	1 572	1 558	$\nu(\text{ring})$
	3	1 278	1 271	1 276	1 271	$\nu(\text{ring})$
	4	939	935	940	939	$\nu(\text{C—Me})$
	5	686	700	683	698	$\beta(\text{ring})$
	6	455	465	455	465	$\nu(\text{MO}_4)$
	7	447	457	446	461	$\nu(\text{MO}_4)$
	8	269	268	266	267	$\beta(\text{C—Me})$
	9	203	197	199	197	$\beta(\text{MO}_4)$
	10	187 ^a	220	—	220	$\beta(\text{MO}_4)$
B_2	11	1 528	1 523	1 502	1 490	$\nu(\text{ring})$
	12	1 415	1 397	1 415	1 392	$\nu(\text{ring})$
	13	1 190	1 197	920, 863 ^b	913, 876 ^b	$\beta(\text{C—H/C—D})$
	14	825	825	828	825	$\nu(\text{C—Me})$
	15	612	660	610	663	$\beta(\text{ring})$
	16	560	555	560	555	$\nu(\text{MO}_4)$
	17	432	444	425	435	$\beta(\text{C—Me})$
	18	289	296	286	294	$\nu(\text{MO}_4)$
	19	84 ^a	94 ^a	90	90	$\beta(\text{MO}_4)$
B_1	20	781	781	580	580	$\gamma(\text{C—H/C—D})$
	21	654	677	656	676	$\gamma(\text{ring})$
	22	218	268	215	267	$\gamma(\text{C—Me})$
	23	167 ^a	174 ^a	—	—	$\gamma(\text{ring})$
	24	47 ^a	53 ^a	—	—	$\gamma(\text{MO}_4)$
A_2	25	408	410	404	409	$\gamma(\text{C—Me})$
	26	128	127	122	124	$\gamma(\text{ring})$
	27	68	60	70	40	$\gamma(\text{MO}_4)$

^a Taken from ref.²; ^b splitting by FR (see text).

and three out-of-plane bending modes ($2B_1 + A_2$). The assignment of the particular stretching modes has previously been a subject of controversy¹⁻³. As follows from Raman polarization measurements, the bands at $1\,580\text{ cm}^{-1}$ and $1\,280\text{ cm}^{-1}$ belong to A_1 modes. The former exhibits the main contribution of the $\text{C}\equiv\text{O}$ bond stretching whereas the latter is assigned to the $\nu(\text{C}\equiv\text{C}\equiv\text{C})$ mode. The bands at $1\,415\text{ cm}^{-1}$ ($\text{Cu}(\text{acac})_2$), $1\,397\text{ cm}^{-1}$ ($\text{Pd}(\text{acac})_2$) and at $1\,520\text{ cm}^{-1}$ (for both complexes) belong to the antisymmetric stretching modes (B_2), the former band exhibiting both the solvent and metal dependences which follow from the significant contribution of the $\text{C}\equiv\text{O}$ bond stretching. The bands of both symmetric (A_1) and antisymmetric (B_2) in-plane bending modes appear in the 700 to 600 cm^{-1} region, these of the three out-of-plane modes in the 200 to 100 cm^{-1} region.

The description of the modes of the central part of the complex molecule (formally taken as MO_4) by the 11-particle model requires a special attention. The advantage is that all the four oxygen atoms coordinated to the metal atom are involved in this model. Thus the vibrational modes of the 11-particle unit include all the modes expected for the MO_4 skeleton. It has been previously pointed out⁴ that the vibrations of the MO_4 skeleton can be assigned on the basis of the D_{2h} local symmetry of the MO_4 (chelated) unit. For the MO_4 unit, nine modes are expected, four of them being stretching, three in-plane bending and two out-of-plane bending. In that case the nine modes of this unit belong to the following representations: $2A_g + B_{3g}$ (Raman active), $2B_{1u} + 2B_{2u} + B_{3u}$ (IR active), and A_u (inactive). The IR active modes have been assigned by Mikami and coworkers². In this paper, the most intense polarized bands at 450 cm^{-1} and at 200 cm^{-1} in the Raman spectra of $\text{Cu}(\text{acac})_2$ and $\text{Pd}(\text{acac})_2$ are assigned to the totally symmetric stretching and bending mode, resp. The depolarized Raman band at 560 cm^{-1} is attributed to the antisymmetric stretching mode. In the 11-particle model which includes only one complete ligand and is of the C_{2v} symmetry, the symmetry of these vibrations drops to the representations of the C_{2v} point group. Thus, e.g., A_g and B_{1u} modes can no more be distinguished as they both belong to the representation A_1 . These symmetry changes follow exactly the correlation between the D_{2h} and C_{2v} point groups. The modes of the MO_4 skeleton belong now to the representations $4A_1 + A_2 + B_1 + 3B_2$ whereas their assignment remains the same and is given in detail in Table III.

The characteristic frequencies attributed to the hydrogen atoms of methyl groups (which have not been included into the model) are of the expected values. Bands of the stretching modes appear at $3\,000$, $2\,975$ and $2\,920\text{ cm}^{-1}$, those of bending modes at $1\,460$, $1\,430$ and $1\,360\text{ cm}^{-1}$ and of the rocking modes near $1\,020\text{ cm}^{-1}$ (Table I, II). Both the frequencies and intensities of the bands are independent on the changes within the chelate molecule (H/D, Pd/Cu substitution), therefore, the approximation of CH_3 groups to the point masses proves to be reasonable.

The appearance of overtones has been observed in IR spectra of both $\text{Cu}(\text{acac})_2$ and $\text{Pd}(\text{acac})_2$ and their deuterioderivatives. The band at $1\,550\text{ cm}^{-1}$ (solid state IR

spectra of $\text{Cu}(\text{acac})_2$ and $\text{Pd}(\text{acac})_2$, weak shoulder in solution spectra and absent in the spectra of deuteriated analogues) has been assigned to $2\gamma(\text{C—H})$. Its unusually high intensity can be attributed to the Fermi resonance between the $2\gamma(\text{C—H})$ (A_1) and $\nu(\text{ring})$ (A_1) vibrational levels. The weak band at $1\,158\text{ cm}^{-1}$ in the spectra of $\text{Cu}(\text{acac-d})_2$ and $\text{Pd}(\text{acac-d})_2$ is assigned to $2\gamma(\text{C—D})$.

The assignment of the vibrational modes of $\text{Cu}(\text{acac})_2$ and $\text{Pd}(\text{acac})_2$ proposed in this paper requires a verification by a NCA calculation, especially as far as the out-of-plane modes are concerned. The assignment of the IR and Raman bands resulting from 11-particle model has been used as the base for the NCA calculation which is in progress now.

REFERENCES

1. Nakamoto K., Martell A. E.: *J. Chem. Phys.* **32**, 588 (1960).
2. Mikami M., Nakagawa I., Shimanouchi T.: *Spectrochim. Acta A* **23**, 1037 (1967).
3. Junge H., Musso H.: *Spectrochim. Acta A* **24**, 1219 (1968).
4. Bulkin B. J., Rose R. K.: *Appl. Spectrosc.* **32**, 151 (1978).
5. Nakamoto K., Udovich C., Takemoto J.: *J. Amer. Chem. Soc.* **92**, 3973 (1970).
6. Jonáš I., Nordén B.: *Spectrochim. Acta A* **32**, 427 (1976).
7. Starikova Z. A., Shugam E. A.: *Zh. Strukt. Khim.* **10**, 290 (1969).
8. Shibata S., Sone K.: *Bull. Chem. Soc. Jap.* **29**, 852 (1956).
9. Knazheva A. N., Shugam E. A., Shkolnikova L. M.: *Zh. Strukt. Khim.* **11**, 938 (1970).
10. Jones M. M.: *J. Amer. Chem. Soc.* **81**, 3188 (1959).
11. *Gmelins Handbuch der Anorganischen Chemie*, Palladium, Lief. 1, p. 302. Verlag Chemie, Weinheim 1947.
12. Ogoshi M., Nakamoto K.: *J. Chem. Phys.* **45**, 3113 (1966).
13. Grinberg A. A., Simonova L. K.: *Zh. Prikl. Khim. (Leningrad)* **26**, 880 (1953).
14. Holm R. H., Cotton F. A.: *J. Amer. Chem. Soc.* **80**, 5658 (1958).
15. Smith A.: *Spectrochim. Acta* **16**, 87 (1960).
16. Collman J. P. in the book: *Transition Metal Chemistry* (R. L. Carlin, Ed.) Vol. 2, p. 42. Marcel Dekker, New York 1966.
17. Young (III) W. L.: *Thesis*. University of North Carolina 1964.
18. Vlčková B., Strauch B.: *Proc. XXII International Conference on Coordination Chemistry (ICCC)*, Budapest, August 23–28, 1982, p. 297.

Translated by the author (B. V.).