53042-43-6; $PdCl(CO_2Me)(PPh_3)_2$, 50763-37-6; $PdCl(COCO_2Me)(PPh_3)_2$, 50589-28-1; $PdCl(COCO_2Et)(PPh_3)_2$, 50589-29-2; $PdCl(COCO_2Me)(PMePh_2)_2$, 53042-37-8; $PdCl(CO_2Me)(PEt_3)_2$, 53042-41-4; $PdCl(COCO_2Me)(PEt_3)_2$, 53042-42-5; $PtCl(CO_2Me)(PPh_3)_2$, 20524-02-1; $Pd(PPh_3)_4$, 14221-01-3; $Pt(PPh_3)_4$, 14221-02-4; *trans*-$PdCl_2(PPh_3)_2$, 28966-81-6; *trans*-$PdCl_2(PEt_3)_2$, 15642-19-0; $Pt(PMePh_2)_4$, 27121-53-5; $Pd(PMePh_2)_4$, 24981-80-4; $Pd(PEt_3)_4$, 52230-29-2; $ClCO_2Me$, 79-22-1; $ClCOCO_2Me$, 5781-53-3; $ClCOCO_2Et$, 4755-77-5.

References and Notes

(1) M. Graziani, P. Uguagliati, and G. Carturan, *J. Organometal. Chem.*, **27**, 275 (1971).
(2) P. Fitton, M. P. Johnson, and J. E. McKeon, *Chem. Commun.*, 6 (1968).
(3) W. Beck and K. V. Werner, *Chem. Ber.*, **104**, 2901 (1971); K. V. Werner and W. Beck, *ibid.*, **105**, 3947 (1972).
(4) M. Hidai, M. Kokura, and Y. Uchida, *J. Organometal. Chem.*, **52**, 431 (1973).
(5) D. M. Fenton and P. J. Steinwand, *J. Org. Chem.*, **39**, 701 (1974).
(6) L. Malatesta and C. Cariello, *J. Chem. Soc.*, 2323 (1958).
(7) A. J. Mukhedkar, M. Green, and F. G. A. Stone, *J. Chem. Soc. A.*, 3023 (1969).
(8) B. L. Shaw, *Proc. Chem. Soc., London*, 247 (1960).
(9) H. C. Clark, K. R. Dixon, and W. J. Jacobs, *J. Amer. Chem. Soc.*, **91**, 1346 (1969).
(10) C. D. Cook and G. S. Jauhal, *Can. J. Chem.*, **45**, 301 (1967).
(11) P. Haake and S. H. Mastin, *J. Amer. Chem. Soc.*, **93**, 6823 (1971).
(12) W. Beck, M. Bauder, G. La Monnica, S. Cenini, and R. Ugo, *J. Chem. Soc. A*, 113 (1971).
(13) D. M. Barlex and R. D. W. Kemmitt, *J. Chem. Soc., Dalton Trans.*, 1436 (1972).
(14) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 5075 (1962).
(15) J. Fayos, E. Dobrzynski, R. J. Angelici, and J. Clardy, *J. Organometal. Chem.*, **59**, C33 (1973).
(16) J. M. Jenkins and B. L. Shaw, *J. Chem. Soc. A*, 770 (1966).
(17) C. R. Green and R. J. Angelici, *Inorg. Chem.*, **11**, 2095 (1972).
(18) K. Hagen and K. Hedberg, *J. Amer. Chem. Soc.*, **95**, 4796 (1973).
(19) J. K. Wilmshurst and J. F. Horwood, *J. Mol. Spectrosc.*, **21**, 48 (1966); H. J. Maria and S. P. McGlynn, *ibid.*, **42**, 177 (1972).
(20) R. J. Angelici, *Accounts Chem. Res.*, **5**, 335 (1972).

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Infrared Spectra and Bonding of Metal Complexes of Platinum-Carbon Bonded Acetylacetone Complexes

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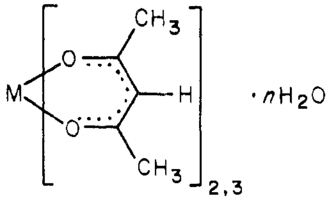
Infrared spectra of $K[PtCl(acac)_2]$ and its metal complexes $M[PtCl(acac)_2]_n$ ($M = (VO)^{II}$, Co(II), Ni(II), Cu(II), Zn(II), Pd(II) for $n = 2$; M = Fe(III) for $n = 3$) and $NiBr_2(acacH)_2$ have been measured and assigned. The metal isotope technique has been utilized to assign the M–O(keto-acac) stretching bands. Comparisons of infrared spectra between $Ni[PtCl(acac)_2]_2$, $[PtCl(acac)_2]^-$, and $NiBr_2(acacH)_2$ reveal that the C=O groups of $Ni[PtCl(acac)_2]_2$ retain the keto character even after coordination to the Ni atom and that its Ni–O(keto-acac) bonds are much weaker than those of enol-acac complexes. Similar results have been obtained for other metal complexes.

Introduction

The versatility of acetylacetone (acacH) as a coordinating ligand is well recognized.[1-3] An extensive infrared study has been made on the O-bonded enol-acac complexes (structure I) which are most common among many acetylacetonato complexes.[4] The C-bonded acetylacetonato complex, $K[PtCl(acac)_2]$, was first prepared by Werner.[5] However, its structure and bonding were not known until X-ray analysis[6] revealed the structure II which contains one O-bonded enol- and one C-bonded keto-acac group. We have previously studied the infrared spectra of this and other C-bonded acac complexes.[7,8]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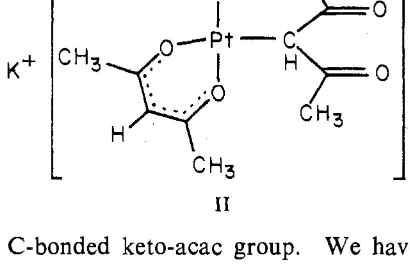
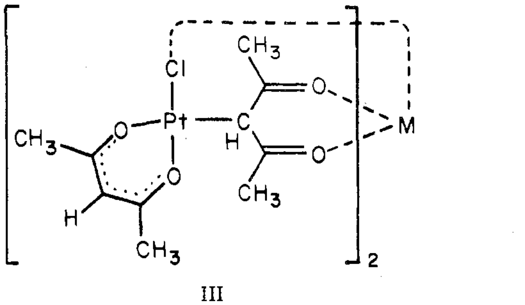

II

Lewis and Oldham[9] have shown that the above complex anion (structure II) can form neutral complexes of the type (structure III) with a number of divalent metals including the VO^{2+} and UO_2^{2+} ions. They studied the infrared spectra, electronic spectra, and magnetic susceptibility of these complexes and concluded that the majority of them take a six-coordinate octahedral structure in which two chlorine atoms occupy the fifth and sixth positions of the coordination sphere of the metal (M) and that one of the acac groups in $[PtCl(acac)_2]^-$ coordinates to the metal in the keto form.


III

In order to obtain more information about the nature of bonding between the metal and the C-bonded acac anion (structure II), we have carried out detailed vibrational analyses on a series of metal complexes of structure III. This paper reports the infrared spectra of $M[PtCl(acac)_2]_2$ where M is Co(II), Ni(II), Cu(II), Zn(II), Pd(II), and $(VO)^{II}$, and $Fe[PtCl(acac)_2]_3$. We have shown previously[10] that the

Table I. Vibrational Frequencies and Band Assignments of $\mathrm{Ni[PtCl(acac)_2]_2}$, $\mathrm{K[PtCl(acac)_2]}$, and $\mathrm{Ni(acac)_2 \cdot 2H_2O}$ ($\mathrm{cm^{-1}}$)[a]

$\mathrm{Ni[PtCl(acac)_2]_2}$	$\mathrm{K[PtCl(acac)_2]}$	$\mathrm{Ni(acac)_2 \cdot 2H_2O}$	Assignment[b]
1646 s	1699 s		$\nu(\mathrm{C{=}O})$
	1657 m		$\nu(\mathrm{C{=}O})$
1564 s	1570 s	1610 s	$\nu(\mathrm{C \overset{\cdots}{-} O})$
	1547 m		Combination?
1526 s	1523 s	1610 s	$\nu(\mathrm{C \overset{\cdots}{-} C})$
		1520 s	
1430 sh	1420 sh	1464 s	$\delta_d(\mathrm{R})$
1390 s	1392 s	1410 s	$\nu(\mathrm{C \overset{\cdots}{-} O})$
1365 sh	1362 sh	1367 s	$\delta_s(\mathrm{R})$
	1335 m		$\nu(\mathrm{C{-}C}) + \delta(\mathrm{C{-}R{-}}$
1278 m	1279 m		$\nu(\mathrm{C \overset{\cdots}{-} C})$
		1264 s	$\nu(\mathrm{C \overset{\cdots}{-} C}) + \nu(\mathrm{C{-}R})$
1190 m	1200 sh	1199 m	$\delta(\mathrm{C{-}H})$
1223 m	1188 s		$\nu(\mathrm{C{-}C})$
1190 m	1171 s		$\delta(\mathrm{Pt{-}C{-}H}) + \nu(\mathrm{C{-}R})$
1034 m	1055 m		$\rho_r(\mathrm{R})$
1026 m	1024 m	1022 s	$\rho_r(\mathrm{R})$
	1008 m		$\rho_r(\mathrm{R})$
	978 w		$\nu(\mathrm{C{-}R})$
940 m	942 w	932 m	$\nu(\mathrm{C{-}R})$
910 w	935 w		$\nu(\mathrm{C{-}R})$
890 w	880 w		$\nu(\mathrm{C{-}R})$
	864 w		$\delta(\mathrm{C{-}C{-}C}) + \nu(\mathrm{C{-}C}) + \nu(\mathrm{C{-}R})$
783 m	780 m	769 s	$\pi(\mathrm{C{-}H})$
680 sh	688 m		$\nu(\mathrm{Pt{-}O}) + \nu(\mathrm{C{-}R})$ + ring def
		677 m	$\nu(\mathrm{C{-}R})$ + ring def + $\nu(\mathrm{Ni{-}O})$
668 m	660 w		$\delta(\mathrm{C{=}O}) + \nu(\mathrm{Pt{-}C}) + \nu(\mathrm{C{-}R})$
		660 m	$\pi(\mathrm{RCCO})$
649 m	638 s		$\nu(\mathrm{Pt{-}O})$
		590 m	Ring + $\nu(\mathrm{Ni{-}O})$
590 m			Ring
558 w	572 w		$\nu(\mathrm{Pt{-}C})$
	527 m		$\delta(\mathrm{C{-}R})$
462 m	457 m		$\nu(\mathrm{Pt{-}O})$
438 w	436 w		Ring
		430 m	$\nu(\mathrm{Ni{-}O}) + \nu(\mathrm{C{-}R})$
385 w	379 m		$\delta(\mathrm{C{=}O})$
331 m	342 m		$\nu(\mathrm{Pt{-}Cl})$
312 w	297 w		$\delta(\mathrm{C{-}R}) + \delta(\mathrm{C{=}O})$
279 m			$\nu(\mathrm{Ni{-}O{=}C})$
		277 m	$\nu(\mathrm{Ni{-}O})$
	275 w		$\delta(\mathrm{C{-}R})$
266 m			$\nu(\mathrm{Ni{-}O{=}C})$
		260 m	$\nu(\mathrm{Ni{-}OH_2})$
242 m	237 m		Ring def
226 m			$\rho_t(\mathrm{Pt{-}CH}) + \nu(\mathrm{Ni{-}O{=}C})$
	215 m		$\rho_t(\mathrm{Pt{-}CH})$
		223 s	π(ring)
		195 sh	π(ring)
128 m			$\nu(\mathrm{Ni \cdots Cl{-}Pt})$?

[a] Intensity abbreviations: s, strong; m, medium; w, weak; sh, shoulder. [b] R denotes the $\mathrm{CH_3}$ group.

Table II. Observed Frequencies, Isotopic Shifts, and Band Assignments for $\mathrm{Ni[PtCl(acac)_2]_2}$ and $\mathrm{Ni(acac)_2 \cdot 2H_2O}$ ($\mathrm{cm^{-1}}$)

$\mathrm{Ni[PtCl(acac)_2]_2}$		$\mathrm{Ni(acac)_2 \cdot 2H_2O}$	Assignment
^{58}Ni	Shift[a]		
		430	$\nu(\mathrm{Ni{-}O})$
384.0	1.2		$\delta(\mathrm{C{=}O})$
331.0	0.0		$\nu(\mathrm{Pt{-}Cl})$
312.0	0.0		$\delta(\mathrm{C{-}R}) + \delta(\mathrm{C{=}O})$
279.0	1.7		$\nu(\mathrm{Ni{-}O{=}C})$
		277	$\nu(\mathrm{Ni{-}O})$
267.0	5.0		$\nu(\mathrm{Ni{-}O{=}C})$
		260	$\nu(\mathrm{Ni{-}OH_2})$
242.0	0.0		Ring def
227.0	1.8		$\rho_t(\mathrm{Pt{-}CH}) + \nu(\mathrm{Ni{-}O{=}C})$
		223	π(ring)
		195	π(ring)
128.8	1.8		$\nu(\mathrm{Ni \cdots Cl{-}Pt})$?

[a] $\tilde{\nu}(^{58}\mathrm{Ni}) - \tilde{\nu}(^{62}\mathrm{Ni})$.

Table III. Observed Frequencies, Isotopic Shifts, and Band Assignments for $\mathrm{Cu[PtCl(acac)_2]_2}$ and $\mathrm{Cu(acac)_2}$ ($\mathrm{cm^{-1}}$)

$\mathrm{Cu[PtCl(acac)_2]_2}$		$\mathrm{Cu(acac)_2}$	Assignment
^{63}Cu	Shift[a]		
		457	$\nu(\mathrm{Cu{-}O})$
389.0	0.0		$\delta(\mathrm{C{=}O})$
333.0	0.0		$\nu(\mathrm{Pt{-}Cl})$
311.8	0.5		$\delta(\mathrm{C{-}R}) + \delta(\mathrm{C{=}O})$
		289	$\nu(\mathrm{Cu{-}O})$
283.0	2.0		$\nu(\mathrm{Cu{-}O{=}C})$
269.0	1.0		$\nu(\mathrm{Cu{-}O{=}C})$
		265	$\delta(\mathrm{C{-}R}) + \nu(\mathrm{Cu{-}O})$
241.0	0.0		Ring def
221.0	0.0		$\rho_t(\mathrm{Pt{-}CH})$
		217	π(ring)
168.0	0.0	168	π(ring)
120.0?	?		$\nu(\mathrm{Cu \cdots Cl{-}Pt})$?

[a] $\tilde{\nu}(^{63}\mathrm{Cu}) - \tilde{\nu}(^{65}\mathrm{Cu})$.

Table IV. Observed Frequencies, Isotopic Shifts, and Band Assignments for $\mathrm{Zn[PtCl(acac)_2]_2}$ and $\mathrm{Zn(acac)_2 \cdot H_2O}$ ($\mathrm{cm^{-1}}$)

$\mathrm{Zn[PtCl(acac)_2]_2}$		$\mathrm{Zn(acac)_2 \cdot H_2O}$	Assignment
^{64}Zn	Shift[a]		
		423	$\nu(\mathrm{Zn{-}O})$
396.0	0.0		$\delta(\mathrm{C{=}O})$
375.0	0.0	385	Ring def
328.0	0.0		$\nu(\mathrm{Pt{-}Cl})$
311.0	0.0		$\delta(\mathrm{C{-}R}) + \delta(\mathrm{C{=}O})$
		270	$\delta(\mathrm{C{-}R}) + \nu(\mathrm{Zn{-}O})$
267.0	0.0		$\delta(\mathrm{C{-}R})$
		240	$\nu(\mathrm{Zn{-}O})$
233.0	5.0		$\nu(\mathrm{Zn{-}O{=}C})$
		209	π(ring) or $\nu(\mathrm{Zn{-}OH_2})$
170.0	0.0	173	π(ring)
122.0	1.0		$\nu(\mathrm{Zn \cdots Cl{-}Pt})$?

[a] $\tilde{\nu}(^{64}\mathrm{Zn}) - \tilde{\nu}(^{68}\mathrm{Zn})$.

metal–ligand vibrations can be assigned definitively by using the metal isotope method. We have, therefore, assigned the M–O stretching vibrations of these complexes by using isotope pairs such as (^{54}Fe, ^{56}Fe), (^{58}Ni, ^{62}Ni), (^{63}Cu, ^{65}Cu), and (^{64}Zn, ^{68}Zn).

Experimental Section

Preparation of Compounds. $\mathrm{K[PtCl(acac)_2]}$ was prepared according to the method used by Behnke and Nakamoto.[8] A similar method was used for the preparation of $\mathrm{K[PtBr(acac)_2]}$. The purity of these compounds was checked by comparing their infrared spectra with published data.[8,11] The metal complexes $\mathrm{M[PtCl(acac)_2]}_n$ (n = 2 or 3) and $\mathrm{Ni[PtBr(acac)_2]_2}$ were prepared by mixing the aqueous solution of $\mathrm{K[PtX(acac)_2]}$ (X = Cl and Br) with that of respective metal halides. The precipitates were filtered, washed with water, and dried *in vacuo*.[9] The purity of the final products was checked by elemental analysis and infrared spectra.

Metal complexes containing metal isotopes were prepared on a milligram scale by using metal isotopes purchased from Oak Ridge National Laboratory. The purity of metal isotopes was as follows: ^{54}Fe, 98.19%; ^{56}Fe, 90.73%; ^{58}Ni, 99.98%; ^{62}Ni, 99.02%; ^{63}Cu, 99.62%; ^{65}Cu, 99.70%; ^{64}Zn, 99.42%; ^{68}Zn, 98.46%. In order to aid infrared assignments of the $\mathrm{M[PtCl(acac)_2]}_n$ type complexes, the following O-bonded chelate complexes were prepared and their infrared spectra were measured: $\mathrm{VO(acac)_2}$,[12a] $\mathrm{Co(acac)_2 \cdot 2H_2O}$,[12b] $\mathrm{Ni(acac)_2 \cdot 2H_2O}$,[13] $\mathrm{Cu(acac)_2}$,[14] $\mathrm{Zn(acac)_2 \cdot H_2O}$,[12c] $\mathrm{Pd(acac)_2}$,[15] and $\mathrm{Fe(acac)_3}$.[13] $\mathrm{NiBr_2(acacH)_2}$ in which the keto form of acetylacetone coordinates to the metal was prepared by the method of Nakamura, *et al.*[16]

Spectral Measurements. Infrared spectra were measured on a Beckman IR 12 (4000–250 $\mathrm{cm^{-1}}$) and a Hitachi Perkin-Elmer FIS-3 (400–33 $\mathrm{cm^{-1}}$) far-infrared spectrophotometer. The KBr pellet technique (4000–300 $\mathrm{cm^{-1}}$) and the Nujol mull technique with polyethylene plates (400–33 $\mathrm{cm^{-1}}$) were used for all compounds. The spectra of metal isotope compounds below 400 $\mathrm{cm^{-1}}$ were measured on an expanded scale with a scanning speed of 2–4 $\mathrm{cm^{-1}}$/min. The

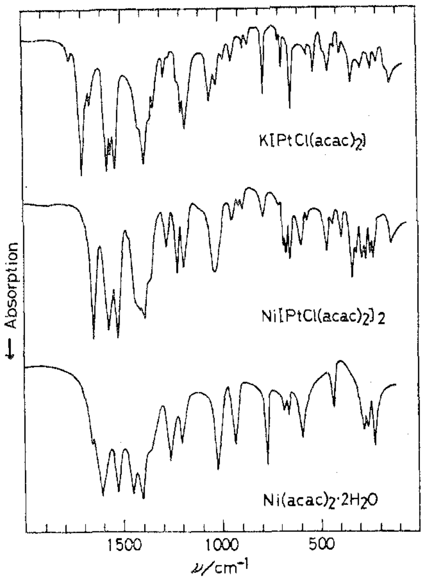


Figure 1. Infrared spectra of K[PtCl(acac)$_2$], Ni[PtCl(acac)$_2$]$_2$, and Ni(acac)$_2$·2H$_2$O.

accuracy of frequency reading was ±0.5 cm^{-1}. Reproducibility of the spectra was checked by multiple scans over the desired frequency range. The frequency was calibrated by using polystyrene film and water vapor.

Results and Discussion

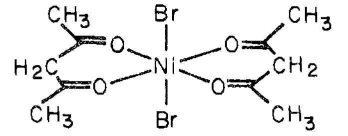
Previously, we assigned the infrared spectra of the C-bonded acac complex Na$_2$[Pt(acac)$_2$Cl$_2$]^7 and O-bonded acac complex K[Pt(acac)Cl$_2$]^{17} based on the results of normal-coordinate analyses. It was shown that the spectrum of K[PtCl(acac)$_2$] which contains both C- and O-bonded acac groups could be interpreted as a superposition of the spectra of the two compounds mentioned above.^{8} In this paper, the results of these previous investigations were used to assign the infrared spectra of M[PtCl(acac)$_2$]$_n$ type complexes.

Ni[PtCl(acac)$_2$]$_2$. Figure 1 compares the infrared spectra of Ni[PtCl(acac)$_2$]$_2$, K[PtCl(acac)$_2$], and Ni(acac)$_2$·2H$_2$O. In general, the bands due to the O-bonded acac of K[PtCl(acac)$_2$] do not shift appreciably whereas those due to the C-bonded acac group show marked shifts upon complex formation with Ni. The C-bonded acac group of K[PtCl(acac)$_2$] exhibits two C═O stretching bands at 1699 and 1657 cm^{-1}. Upon complex formation with Ni(II), these bands are shifted to 1646 cm^{-1}. [Theoretically, two bands are expected to appear in this region. However, the other band was not observed as a separate band because it is too close to the 1646-cm^{-1} band (see ref 16)]. However, this frequency is still much higher than the C$\overset{\cdots}{-}$O stretching frequencies (1610 and 1410 cm^{-1}) of Ni(acac)$_2$·2H$_2$O in which acac is in the enol form. Thus, the CO bonds of the C-bonded acac group in Ni[PtCl(acac)$_2$]$_2$ retain their keto C═O bond character although their bond order is somewhat decreased by complex formation with Ni(II).

Nine bands between 1600 and 1100 cm^{-1} of Ni[PtCl(acac)$_2$]$_2$ can be assigned easily by comparing their frequencies with those of K[PtCl(acac)$_2$].^{8} It was noted that two C–C stretching bands of the latter at 1335 and 1188 cm^{-1} (C-bonded acac group) are shifted to higher frequencies upon complex formation with Ni(II) (the band corresponding to the 1335 cm^{-1} band is hidden under the 1390-cm^{-1} band in the Ni(II) complex). This result suggests that the C–C bond order is increased slightly as a result of the chelate ring formation with Ni(II). A number of bands are observed between 1100 and 600 cm^{-1}. Most of these bands are due to the methyl or O-bonded acac group vibrations and do not show appreciable shifts by complex formation with Ni(II).

We have shown previously^{18} that O-bonded chelate complexes of the type M(acac)$_{2,3}$·nH$_2$O exhibit two M–O stretching bands in the 460–430- and 360–290-cm^{-1} regions, one of which is coupled with the C–CH$_3$ bending and other is pure. Ni[PtCl(acac)$_2$]$_2$ exhibits four bands between 600 and 400 cm^{-1}, none of which are metal isotope sensitive. Therefore, these bands cannot be assigned to the Ni–O stretching or any other mode involving the motion of the Ni atom. As is shown in Figure 2 and Table II, the Ni(II) complex shows five metal isotope sensitive bands below 400 cm^{-1}. The bands at 384.0, 331.0, 312.0, 242.0, and 227.0 cm^{-1} of the ^{58}Ni complex can be assigned as shown in Table I based on previous assignments on K[PtCl(acac)$_2$]. The band at 331.0 cm^{-1} is the Pt–Cl stretching since it disappears in Ni[PtBr(acac)$_2$]$_2$. Instead, the latter exhibits its Pt–Br stretching at 244 cm^{-1}.

Previously, Nakamura, *et al.*,^{16} synthesized a novel complex NiBr$_2$(acacH)$_2$ in which the neutral acetylacetone (keto form) is bonded to the metal through the oxygen atoms. Subsequent X-ray analysis^{19} on this compound revealed the octahedral structure IV. Nakamura, *et al.*,^{16} tentatively assigned the



IV

Ni–O stretching at 237 cm^{-1} and the Ni–Br stretching at 178 cm^{-1}. In order to confirm these assignments, we prepared ^{58}NiBr$_2$(acacH)$_2$ and its ^{62}Ni analog and compared their spectra in the low-frequency region. The results indicated that three bands at 264 ($\Delta\nu = 4$), 239 ($\Delta\nu = 5$), and 179 cm^{-1} ($\Delta\nu = 2$ cm^{-1}) ($\Delta\nu$ is isotopic shift) are isotope sensitive. The last band can be assigned to the Ni–Br stretching mode since the octahedral Ni–Br stretching frequencies are below 200 cm^{-1}.^{20} Then, the former two bands at 264 and 239 cm^{-1} must be assigned to the Ni–O stretching modes. As mentioned above, Ni[PtCl(acac)$_2$]$_2$ exhibits two bands at 279 and 266 cm^{-1} which are metal isotope sensitive. These bands are not present in K[PtCl(acac)$_2$]. Since these frequencies are close to those of Ni–O stretching bands of NiBr$_2$(acacH)$_2$, it is most reasonable to assign them to the Ni–O stretching modes of Ni[PtCl(acac)$_2$]$_2$. This result indicates that the Ni–O bonds of these two compounds are similar and that the C═O bonds of both compounds are of keto type. The slight higher frequency shifts of the Ni–O stretching bands and the lower frequency shifts of the C═O stretching bands of Ni[PtCl(acac)$_2$]$_2$ relative to NiBr$_2$(acacH)$_2$ (the C═O stretching band of this compound is at 1693 cm^{-1})^{16} suggest, however that the π electrons are slightly more delocalized in the Ni–acac chelate ring of the former than in that of the latter compound. As is shown in Table II, Ni[PtCl(acac)$_2$]$_2$ exhibits two bands at 227 and 128.8 cm^{-1} which are metal isotope sensitive. These vibrations must involve the substantial motion of the Ni atom. We tentatively assigned them to other vibrations listed in Table II.

Other M[PtCl(acac)$_2$]$_n$ Type Complexes. The spectra of other M[PtCl(acac)$_2$]$_n$ type complexes where M is Cu(II), Zn(II), Fe(III), Co(II), (VO)^{II}, and Pd(II) can be assigned by using a procedure similar to that used for Ni[PtCl(acac)$_2$]$_2$ previously. The M–O stretching bands of the Cu(II), Zn(II), and Fe(III) complexes have been assigned by using isotope shift data due to the ^{63}Cu–^{65}Cu, ^{64}Zn–^{68}Zn, and ^{54}Fe–^{56}Fe substitution, respectively. Figure 2 shows the far-infrared spectra of these isotopic compounds. Tables III–V list their vibrational frequencies and band assignments. These tables also include the vibrational frequencies of the corresponding O-bonded enol-acac complexes. The spectra of the Co(II),

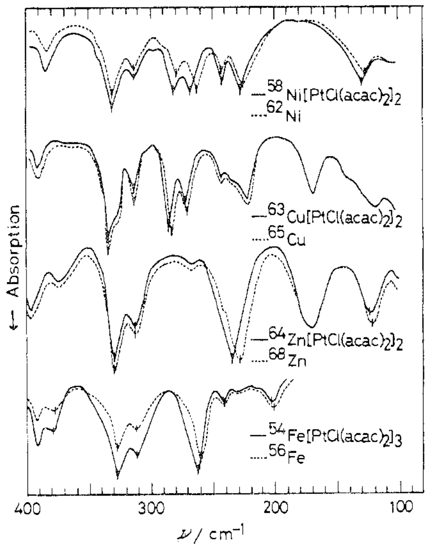


Figure 2. Far-infrared spectra of Ni$[PtCl(acac)_2]_2$, Cu$[PtCl(acac)_2]_2$, Zn$[PtCl(acac)_2]_2$, and Fe$[PtCl(acac)_2]_3$ containing metal isotopes.

Table V. Observed Frequencies, Isotopic Shifts, and Band Assignments for Fe$[PtCl(acac)_2]_3$ and Fe$(acac)_3$ (cm^{-1})

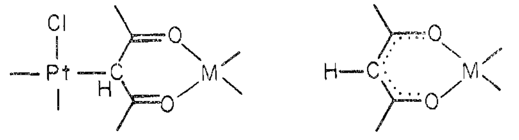
Fe$[PtCl(acac)_2]_3$			
^{54}Fe	Shift[a]	Fe$(acac)_3$	Assignment
		438	ν(Fe–O)
392.0	0.0		δ(C=O)
379.0	1.0		Ring def
327.0	0.0		ν(Pt–Cl)
311.0	0.0		δ(C–R) + δ(C=O)
		298	ν(Fe–O)
262.0	2.0		ν(Fe–O=C)
241.5	0.5		ν(Fe–O=C)
202.0	1.0	201	π(ring)

[a] $\tilde{\nu}(^{54}Fe) - \tilde{\nu}(^{56}Fe)$.

Pd(II), and (VO)^{II} complexes have been assigned by comparing their spectra with those of other metals for which metal isotope data are available. Tables VI and VII summarize the vibrational frequencies and band assignments of all the main bands observed in this work.

M–O Bonding in M$[PtCl(acac)_2]_n$ Complexes. The results obtained from our infrared studies can be summarized as follows. (1) In all M$[PtCl(acac)_2]_n$ complexes, their C=O stretching frequencies are lower than that of the $[PtCl(acac)_2]^-$ ion but much higher than the C⩦O stretching frequencies of the O-bonded (enol) complexes. (2) The C–C stretching bands of the O-bonded (keto) M–acac ring are higher than those of the free $[PtCl(acac)_2]^-$ ion. (3) The M–O(keto-acac) stretching frequencies (360–230 cm^{-1}) are lower than the M–O (enol-acac) stretching frequencies (490–240 cm^{-1}). (4) Except for M = Pd(II) and (VO)^{II}, the Pt–Cl stretching frequencies of M$[PtCl(acac)_2]_n$ are lower than that of the free $[PtCl(acac)_2]^-$ ion. The origins of these spectral changes will be discussed below.

The changes observed for the C=O, C–C, and M–O stretching bands suggest that, in the M–acac(keto) chelate ring, the C=O groups still retain their keto character although the π electrons are somewhat more delocalized than that of the $[PtCl(acac)_2]^-$ ion. Accordingly, the C–C stretching bands shift to higher frequencies upon complex formation. However, the extent of π-electron delocalization is much less than that of the M–acac (enol) chelate ring. Thus the M–O bonds in the keto coordination are weaker than those in the enol coordination, and this is reflected in the M–O stretching frequencies discussed above.



keto coordination   enol coordination

Table VI. Characteristic Frequencies and Band Assignments Observed for K$[PtCl(acac)_2]$, M$[PtCl(acac)_2]_2$, and M$(acac)_2 \cdot nH_2O$ (M = Co, N, Cu, Zn; n = 0, 1, 2) (cm^{-1})

K[PtCl-(acac)$_2$]		Co[PtCl-(acac)$_2$]$_2$		Co(acac)$_2$·2H$_2$O		Ni[PtCl-(acac)$_2$]$_2$		Ni(acac)$_2$·2H$_2$O		Cu[PtCl-(acac)$_2$]$_2$		Cu(acac)$_2$		Zn[PtCl-(acac)$_2$]$_2$		Zn(acac)$_2$·H$_2$O		Assignment
1699	1657	1647				1646				1630				1647				ν(C=O)
1570	1392	1578	1390	1617	1406	1564	1390	1610	1410	1574	1390	1580	1419	1580	1390	1605	1400	ν(C⩦O)
1523	1279	1530	1281	1617	1266	1526	1278	1610	1264	1528	1280	1531	1278	1530	1285	1605	1265	ν(C⩦C)
1335	1188	*a*	1225			*a*	1223			*a*	1232			*a*	1224			ν(C–C)
1200		1192		1205		1190		1199		1195		1190		1195		1195		δ(C–H)
780		786		771		783		769		780		781		787		772		π(C–H)
638	457	650	461			649	462			649	457			650	461			ν(Pt–O)
				425	261			430	277			457	289			423	240	ν(M–O)
		270	264			279	266			283	269			233				ν(M–O=C)
572		*b*				558				580				*b*				ν(Pt–C)
342		331				331				333				328				ν(Pt–Cl)

[a] This band overlaps with a lower ν(C⩦O) band near 1390 cm^{-1}. [b] This band overlaps with a ring deformation band.

Table VII. Characteristic Frequencies and Band Assignments Observed for M$[PtCl(acac)_2]_{2,3}$ and M$(acac)_{2,3}$ (M = VO, Pd, Fe) (cm^{-1})

VO$[PtCl(acac)_2]_2$		VO$(acac)_2$		Pd$[PtCl(acac)_2]_2$		Pd$(acac)_2$		Fe$[PtCl(acac)_2]_3$		Fe$(acac)_3$		Assignment
1615				1592				1640				ν(C=O)
1570	1388	1560	1423	1570	1384	1570	1400	1570	1390	1572	1392	ν(C⩦O)
1526	1290	1532	1290	1527	1279	1530	1275	1530	1280	1530	1278	ν(C⩦C)
a	1240			*a*	1242			*a*	1225			ν(C–C)
1192		1190		1201		1201		1191		1190		δ(C–H)
783		800		781		788		810	788	805	775	π(C–H)
990		1000										ν(V=O)
653	452			650	458			650	462			ν(Pt–O)
		488	365			468	296			438	298	ν(M–O)
355				309	297			260	242			ν(M–O=C)
				565				*b*				ν(Pt–C)
346				345				327				ν(Pt–Cl)

[a] This band overlaps with a lower ν(C⩦O) band near 1390 cm^{-1}. [b] This band overlaps with a ring deformation band.

The magnitude of the C=O stretching frequency shift ($\Delta\tilde{\nu}$) upon complex formation depends upon the metal involved. Using the 1699-cm^{-1} band of the $[PtCl(acac)_2]^-$ ion as the standard, we obtain the following order of the metals as a function of $\Delta\tilde{\nu}$ (the numbers in parentheses are $\Delta\tilde{\nu}$ in cm^{-1}): Pd(II) (107) >> $(VO)^{II}$ (84) > Cu(II) (69) > Fe(III) (59) > Ni(II) (53) ~ Co(II) (52), Zn(II) (52). This order is surprisingly similar to that of the stability constants (log K_1K_2) of the enol–acac complexes involving these metals:[18a] Pd(II) (27.1) >> $(VO)^{II}$ (15.79) > Cu(II) (14.93) > Ni(II) (10.38) > Co(II) (9.51) > Zn(II) (8.81). As pointed out previously, a more quantitative comparison must be made between the force constant and the enthalpy of formation rather than between the frequency and the stability constant.[18a] Only the Pd(II) complex, however, has a planar structure, as will be shown later, and, hence, the largest shift ($\Delta\tilde{\nu}$ = 107 cm^{-1}) of the C=O stretching band is probable. Except for the five-coordinate $(VO)^{II}$ complex the order of all other octahedrally coordinated metals as a function of $\Delta\tilde{\nu}$ (Co(II) < Ni(II) < Cu(II) > Zn(II)) seems to reflect the trend of the crystal field stabilization energy. Such a trend is also the general case for the stability of the first-row transition metal complexes.[21]

If we arrange the metals in the order of the M–O(keto) stretching frequencies (in parentheses), we have $(VO)^{II}$ (355), > Pd(II) (309, 297) > Cu(II) (283, 269) > Ni(II) (279, 266) > Co(II) (270, 264) > Zn(II) (233). Different from the C=O stretching frequencies in the high-frequency region, the M—O stretching frequencies are sensitive to the mass of the metal and the structure of the complex. Thus, the reversal of the order between $(VO)^{II}$ and Pd(II) may be accounted for by these factors. The Fe(III) complex was not included in the above series by the same reason. Otherwise, both C=O and M—O stretching frequencies indicate that the strength of the M—O bond follows the stability order of these divalent metals.

Previously, Lewis and Oldham[9] explained the lowering of the Pt–Cl stretching frequency upon coordination by assuming that, in $M[PtCl(acac)_2]_n$, the Cl atoms may occupy the fifth and sixth sites of octahedral coordination around M through intramolecular interaction. Their magnetic studies on the Co(II) and Ni(II) complexes confirmed the octahedral coordination in these compounds. Using the Pt–Cl stretching frequency (342 cm^{-1}) of the $[PtCl(acac)_2]^-$ ion as the standard, the magnitude of the shift of this band (in parentheses) upon complex formation is $(VO)^{II}$ (4) > Pd(II) (3) > Cu(II) (−9) > Ni(II) (−11) ~ Co(II) (−11) > Zn(II) (−14) ~ Fe(III) (−15). In the cases of $(VO)^{II}$ and Pd(II), the Cl atoms are probably free from further coordination, and their Pt–Cl stretching frequencies are not lowered by complex formation. However, it is rather difficult to explain the large negative shift obtained for the Fe(III) complex based on the above theory since the fifth and sixth positions are not available for chlorine coordination in this case. On the other hand, in contrast with the cases of other metal complexes the Fe–O stretching frequency (242 cm^{-1}) in the Fe(III) complex is unusually lower compared to that (298 cm^{-1}) of $Fe(acac)_3$. This abnormal weakness of the Fe–O bond strength may be caused by the strain originated from coordination of three large ligands ($PtCl(acac)_2^-$) to a metal ion. The negative shift of the Pt–Cl stretching frequency obtained for the Fe(III) complex might also be based on the same reason.

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Registry No. $Co[PtCl(acac)_2]_2$, 15663-82-8; $Ni[PtCl(acac)_2]_2$, 15663-83-9; $Cu[PtCl(acac)_2]_2$, 15663-84-0; $Zn[PtCl(acac)_2]_2$, 53011-12-4; $VO[PtCl(acac)_2]_2$, 15630-19-0; $Pd[PtCl(acac)_2]_2$, 53011-13-5; $Fe[PtCl(acac)_2]_3$, 53092-47-0; $K[PtCl(acac)_2]$, 15258-91-0; $Co(acac)_2{\cdot}2H_2O$, 15136-94-4; $Ni(acac)_2{\cdot}2H_2O$, 14363-16-7; $Cu(acac)_2$, 13395-16-9; $Zn(acac)_2{\cdot}2H_2O$, 26151-50-8; $VO(acac)_2$, 3153-26-2; $Pd(acac)_2$, 14024-61-4; $Fe(acac)_3$, 14024-18-1; $NiBr_2(acacH)_2$, 53109-79-8; ^{58}Ni, 13981-79-8; ^{62}Ni, 13981-81-2; ^{63}Cu, 14191-84-5; ^{65}Cu, 14119-06-3; ^{64}Zn, 14378-32-6; ^{68}Zn, 14378-35-9; ^{54}Fe, 13982-24-6; ^{56}Fe, 14093-02-8.

References and Notes

(1) J. P. Fackler, Jr., *Progr. Inorg. Chem.*, **7**, 361 (1966).
(2) D. W. Thompson, *Struct. Bonding (Berlin)*, **9**, 27 (1971).
(3) D. Gibson, *Coord. Chem. Rev.*, **4**, 225 (1969).
(4) For example, see K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1970, p 247.
(5) A. Werner, *Ber. Deut. Chem. Ges.*, **34**, 2584 (1901).
(6) B. N. Figgis, J. Lewis, R. F. Long, R. Mason, R. S. Nyholm, P. J. Pauling, and G. B. Robinson, *Nature (London)*, **195**, 1278 (1962); R. Mason, G. B. Robertson, and P. J. Pauling, *J. Chem. Soc. A*, 485 (1969).
(7) G. T. Behnke and K. Nakamoto, *Inorg. Chem.*, **6**, 440 (1967).
(8) G. T. Behnke and K. Nakamoto, *Inorg. Chem.*, **7**, 330 (1968).
(9) J. Lewis and C. Oldham, *J. Chem. Soc. A*, 1456 (1966).
(10) K. Nakamoto, *Angew Chem., Int. Ed. Engl.*, **11**, 666 (1972).
(11) J. Lewis, R. F. Long, and C. Oldham, *J. Chem. Soc.*, 6740 (1965).
(12) (a) *Inorg. Syn.*, **5**, 114 (1957); (b) *ibid.*, **11**, 83 (1968); (c) *ibid.*, **10**, 75 (1967).
(13) R. G. Charles and M. A. Pawlikowski, *J. Phys. Chem.*, **62**, 440 (1958).
(14) H. F. Holtzclaw, Jr., K. W. R. Johnson, and F. W. Hengeweld, *J. Amer. Chem. Soc.*, **74**, 3776 (1952); H. F. Holtzclaw, Jr., A. H. Carlson, and J. P. Collman, *ibid.*, **78**, 1838 (1956).
(15) A. A. Grinberg and K. K. Simonova, *Zh. Prikl. Khim. (Leningrad)*, **26**, 880 (1953).
(16) Y. Nakamura, K. Isobe, H. Morita, S. Yamazaki, and S. Kawaguchi, *Inorg. Chem.*, **11**, 1573 (1972).
(17) G. T. Behnke and K. Nakamoto, *Inorg. Chem.*, **6**, 433 (1967).
(18) (a) K. Nakamoto, P. J. McCarthy, A. Ruby, and A. E. Martell, *J. Amer. Chem. Soc.*, **83**, 1066, 1272 (1961); (b) K. Nakamoto, C. Udovich, and J. Takemoto, *ibid.*, **92**, 3978 (1970).
(19) S. Koda, S. Ooi, H. Kuroya, K. Isobe, Y. Nakamura, and S. Kawaguchi, *Chem. Commun.*, 1321 (1971).
(20) Y. Saito, C. W. Schlapfer, M. Cordes, and K. Nakamoto, *Appl. Spectrosc.*, **27**, 213 (1973); C. W. Schlapfer, Y. Saito, and K. Nakamoto, *Inorg. Chim. Acta*, **6**, 284 (1972).
(21) For example, see F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," Wiley, New York, N. Y., 1967, p 80.