

Infrared and Nuclear Magnetic Resonance Studies on
Metal Complexes of 3-Substituted 2,4-PentanedionesYukito Murakami,* Katsuyuki Nakamura, Hiroaki Uchida,
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Received April 27, 1968

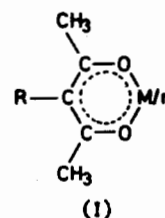
In an effort to understand the nature of chelate rings of 2,4-pentanedione complexes, infrared and nmr spectra of some divalent and trivalent metal complexes of 3-substituted 2,4-pentanediones, where phenyl, *p*-bromophenyl, *p*-cyanophenyl, *p*-nitrophenyl, benzyl and *p*-nitrobenzyl were these substituents, have been investigated. The introduction of any of these substituents to the 2,4-pentanedione complexes resulted in the lower frequency shift of C=O stretching vibration and the higher frequency shift of M—O stretching. Thus, these substituents tend to increase the strength of coordinate bond, and the relative strength of M—O bonds follows the sequence: $Cu^{II} < Pd^{II}$; $Fe^{III} < Cr^{III} < Co^{III}$. Three structural formula have been put forward to elucidate the nature of chelate rings of various metal complexes. The relatively minor effect of a phenyl group, which is comparable with a benzyl group, is probably due to the twist of a phenyl ring from the plane of a chelate ring. Nmr spectra have not provided much useful information.

Introduction

In recent years, the infrared spectral method has been much applied to the metal chelate systems of 2,4-pentanediones for the elucidation of the nature of these chelate rings and coordinate bonds.¹⁻⁸ The normal coordinate treatment of these metal chelates has been much successful in the analysis of their vibrational spectra and become reliable basis for the assignment of those characteristic bands.^{1,2} In addition, the isotope techniques, where 2,4-pentanedione complexes labeled with deuterium, oxygen (¹⁸O) and carbon (¹³C) isotopes were used, have provided much valuable information for the assignments of absorption bands in the NaCl region and for the valence-tautomerism involved in the chelate rings.^{7,8} Meanwhile, the

infrared study has been extended to the far infrared region, where the metal-ligand stretching vibration is expected to appear, and the normal coordinate analysis^{9,10} has been shown even more efficient in cooperation with deuterium^{9,10} and oxygen (¹⁸O)¹¹ isotope techniques.

In connection with the previous study on the electronic spectra of some trivalent metal complexes of 3-phenyl- and 3-benzyl-2,4-pentanedione,¹² the present investigation deals with the infrared spectra of metal complexes of 2,4-pentanediones (I), which carry phenyl,



R = C₆H₅, *p*-BrC₆H₄, *p*-CNC₆H₄, *p*-NO₂C₆H₄, C₆H₅CH₂,
p-NO₂C₆H₄CH₂

M = Be^{II}, Cu^{II}, Pd^{II}; Al^{III}, Cr^{III}, Fe^{III}, Co^{III}

p-substituted phenyl, benzyl or *p*-substituted benzyl group at the 3-position, in the 4000-200 cm⁻¹ region. The assignments of vibrational bands have been performed by referring to the results of normal coordinate calculation on the 2,4-pentanedione complexes and to some empirical data.^{7,11,13} The nmr measurements have also been added to understand the nature of these chelate rings.

Experimental Section

Preparation of Metal Complexes. The preparative procedures for the divalent and trivalent metal com-

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Table I. Analyses of the metal complexes of 3-substituted 2,4-pentanediones

3-Substituent	Complex	Analyses, %					
		C		H		N	
		Found	Calcd.	Found	Calcd.	Found	Calcd.
Phenyl	Be(C ₁₁ H ₁₁ O ₂) ₂	73.21	73.52	6.32	6.17	—	—
	Cu(C ₁₁ H ₁₁ O ₂) ₂	63.63	63.83	5.49	5.36	—	—
	Pd(C ₁₁ H ₁₁ O ₂) ₂	58.18	57.85	5.08	4.85	—	—
	Al(C ₁₁ H ₁₁ O ₂) ₃	71.40	71.73	6.21	6.02	—	—
	Cr(C ₁₁ H ₁₁ O ₂) ₃	68.59	68.62	5.78	5.76	—	—
	Fe(C ₁₁ H ₁₁ O ₂) ₃	67.74	68.17	5.85	5.72	—	—
	Co(C ₁₁ H ₁₁ O ₂) ₃	66.03	67.81	5.68	5.69	—	—
<i>p</i> -Bromophenyl	Be(C ₁₁ H ₁₀ O ₂ Br) ₂	51.26	51.09	4.02	3.90	—	—
	Cu(C ₁₁ H ₁₀ O ₂ Br) ₂	46.54	46.22	3.81	3.53	—	—
	Cr(C ₁₁ H ₁₀ O ₂ Br) ₃	48.42	48.67	3.76	3.71	—	—
	Fe(C ₁₁ H ₁₀ O ₂ Br) ₃	48.23	48.45	3.98	3.70	—	—
	Co(C ₁₁ H ₁₀ O ₂ Br) ₃	48.01	48.26	3.85	3.68	—	—
<i>p</i> -Cyanophenyl	Be(C ₁₂ H ₁₀ NO ₂) ₂	70.21	70.40	5.37	4.92	6.84	6.84
	Cu(C ₁₂ H ₁₀ NO ₂) ₂	62.13	62.13	4.36	4.35	6.41	6.04
	Fe(C ₁₂ H ₁₀ NO ₂) ₃	65.88	65.86	5.02	4.61	6.06	6.40
<i>p</i> -Nitrophenyl	Be(C ₁₁ H ₁₀ NO ₄) ₂	60.82	58.79	4.73	4.49	5.90	6.23
	Cu(C ₁₁ H ₁₀ NO ₄) ₂	52.19	52.43	4.17	4.00	5.83	5.56
	Fe(C ₁₁ H ₁₀ NO ₄) ₃	56.24	55.32	4.55	4.22	4.76	4.86
	Co(C ₁₁ H ₁₀ NO ₄) ₃	55.00	55.08	4.41	4.20	5.64	5.84
Benzyl	Be(C ₁₂ H ₁₃ O ₂) ₂	74.10	74.40	6.79	6.76	—	—
	Cu(C ₁₂ H ₁₃ O ₂) ₂	65.19	65.22	6.13	5.93	—	—
	Pd(C ₁₂ H ₁₃ O ₂) ₂	59.50	59.45	5.65	5.41	—	—
	Al(C ₁₂ H ₁₃ O ₂) ₃	72.61	72.71	6.75	6.61	—	—
	Cr(C ₁₂ H ₁₃ O ₂) ₃	70.06	69.78	6.35	6.34	—	—
	Fe(C ₁₂ H ₁₃ O ₂) ₃	69.38	69.34	6.58	6.30	—	—
	Co(C ₁₂ H ₁₃ O ₂) ₃	68.74	69.00	6.44	6.27	—	—
<i>p</i> -Nitrobenzyl	Be(C ₁₂ H ₁₂ NO ₄) ₂	60.34	60.37	5.29	5.06	5.92	5.87
	Cu(C ₁₂ H ₁₂ NO ₄) ₂	53.97	54.19	4.69	4.55	5.19	5.27
	Cr(C ₁₂ H ₁₂ NO ₄) ₃	57.48	57.29	4.86	4.81	5.91	5.57
	Fe(C ₁₂ H ₁₂ NO ₄) ₃	60.37	57.00	4.95	4.78	4.97	5.54

plexes of 3-substituted 2,4-pentanediones were essentially similar to those employed for the corresponding 2,4-pentanedione complexes. A part of these experimental results have been described previously.¹⁴ The results of microanalyses¹⁵ are listed in Table I.

Spectral Measurements. Infrared spectra in the region 4000-650 cm⁻¹ were recorded on a Koken Model DS-301 spectrometer equipped with sodium chloride optics. The KBr disk method was employed for the most complexes in this region, whereas the nujol mull technique was adopted for the metal complexes of 3-(*p*-nitrobenzyl)-2,4-pentanedione. A Hitachi Model EPI-L grating spectrophotometer was used to obtain the spectra in the 700-200 cm⁻¹ region. For these spectra, all the samples were measured as nujol mulls sandwiched between polyethylene film. Calibration of frequency readings was made with polystyrene film, and water vapor as well as carbon dioxide in the air.

Nmr spectra were recorded on a Varian A-60 spectrometer. Chemical shifts are reported in ppm from internal tetramethylsilane (TMS) and data are good to 0.5 cps. The spectra were calibrated by the use of chloroform signal (436 cps from TMS) as the secondary reference.

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(15) The analyses of all the metal complexes were performed at the Microanalysis Center of Kyushu University.

Results and Discussion

Infrared Spectra. The region 4000 to 2250 cm⁻¹ has been excluded from this discussion, since no significant absorptions are seen except the C—H stretching bands. Then, the infrared frequency range treated in this work is divided into six regions for the sake of discussion: 2250-1300 cm⁻¹, 1300-1050 cm⁻¹, 1050-1000 cm⁻¹, 950-900 cm⁻¹, 900-700 cm⁻¹ and 700-200 cm⁻¹. The characteristic absorption bands along with the most plausible assignments for the 3-phenyl-2,4-pentanedione complexes are summarized in Table II, while absorption peaks assigned to the C=O stretching and the M—O stretching modes for all the metal complexes treated in this work are listed in Tables III and IV, respectively. The observed bands for the metal complexes of 3-phenyl-2,4-pentanedione are shown schematically in Figure 1 in the 1600-700 cm⁻¹ region for the sake of correlation. Figures 2 and 3 illustrate the far infrared spectra for the same metal complexes in the 700-200 cm⁻¹ region.

The 2250-1300 cm⁻¹ region involves several distinct bands which are assigned to the C=O stretching, the C=C stretching, the CH₃ deformation and the C—CH₃ stretching modes in addition to the benzene-ring stretching vibrations. Although the assignment of vibrational bands for the 2,4-pentanedione complexes has been made on the purely empirical basis,^{16,17}

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Table II. Infrared absorption bands of the metal complexes of 3-phenyl-2,4-pentanedione

Be ^{II}	Cu ^{II}	Pd ^{II}	Al ^{III}	Cr ^{III}	Fe ^{III}	Co ^{III}	Assignments
1582 vs 1459 s	1576 vs 1490 s 1454 s	1554 vs 1490 w	1595 vs 1462 s	1575 vs 1490 w 1453 m	1573 vs 1490 w 1452 s	1570 vs 1490 w 1477 w 1451 m 1423 m	C [∞] O (+ C [∞] C) str benzene ring
1439 sh	1424 s	1428 m 1420 m	1439 m	1439 m	1437 s	1423 m	CH ₃ deg def
1383 s 1369 s 1335 m 1250 w 1179 vw 1157 vw 1073 w 1021 s	1381 s 1381 s 1315 s 1175 w 1154 w 1075 w	1360 m 1335 s 1304 m 1241 w 1176 w 1072 w	1396 s 1372 s 1330 m 1155 vw 1075 w	1373 m 1349 s 1330 m 1178 vw 1157 vw 1074 w	1363 s 1346 s 1318 s 1173 w 1158 w 1074 w	1360 m 1349 m 1315 m 1225 w 1155 w 1074 w	C [∞] O str CH ₃ sym def C [∞] C + C—CH ₃ str benzene C—H in-plane
983 w 932 m	979 w 930 w 921 w	976 w 929 w	983 w 930 w	979 w 927 m	970 w 926 w 916 m	1037 w 1018 w 1003 w 980 w 929 w	CH ₃ deg rock C—CH ₃ + C [∞] O str
749 m 705 m	764 s 710 s	768 w 721 w 706 w	770 w 707 m	778 sh 766 w 709 m	769 sh 764 w 707 m	765 w 704 m	benzene C—H out-of-plane
1042 s 856 m 845 s 684 w 660 s 617 w 553 s	682 m 664 w 635 s 618 w 541 m	693 s 618 w 556 m	683 m 665 w 625 m 608 s 560 vw 533 m	684 m 661 vw 634 s 617 s 538 w	680 w 655 w 618 w 598 s 588 s 557 vw 522 w	688 s 650 s 617 w 555 m	ring def + M—O str C—CH ₃ bend + M—O str
499 w 462 w 449 s 440 s 430 w 369 w	470 s 457 s 426 m 393 s	474 s 458 m 442 w 408 w	508 s 492 s 455 m 448 m 432 sh 425 m	466 s, br 439 s 397 m	451 s 437 s 425 s 415 sh 390 m	473 s 421 w	M—O str
283 w 245 m, br	313 m 227 s	305 w 271 m	377 m 313 w 239 w	350 s 291 w 247 w	315 s 234 m, br 220 sh	385 w 361 m	M—O str

s = strong, m = medium, and w = weak intensity; v = very, sh = shoulder, and br = broad.

Table III. The C[∞]O stretching bands (cm⁻¹) for the metal complexes of 3-substituted 2,4-pentanediones

Ligand	Be ^{II}	Cu ^{II}	Pd ^{II}	Al ^{III}	Cr ^{III}	Fe ^{III}	Co ^{III}
PAA	1582	1576	1554	1595	1575	1573	1570
BrPAA	1583	1574	—	—	1573	1570	1570
CPAA	1582	1568	—	—	—	1571	—
NPAA	1582	1575	—	—	—	1570	1570
BAA	1578	1569	1556	1595	1568	1570	1567
NBAA	1585	1571	—	—	1583	1566	—

Abbreviations are made for ligands: PAA, 3-phenyl-2,4-pentanedione; BrPAA, 3-(*p*-bromophenyl)-2,4-pentanedione; CPAA, 3-(*p*-cyanophenyl)-2,4-pentanedione; NPAA, 3-(*p*-nitrophenyl)-2,4-pentanedione; BAA, 3-benzyl-2,4-pentanedione; NBAA, 3-(*p*-nitrobenzyl)-2,4-pentanedione.

Nakamoto *et al.*^{1,2} first applied the normal coordinate treatment to these metal complexes and the strong band at higher frequency side in the 1600-1500 cm⁻¹ region was assigned to the C[∞]C stretching mode. Recently, however, Behnke and Nakamoto has made the normal coordinate analysis of dichloro(2,4-pentanedione)-platinate(II) by introducing a modified Urey-Bradley force field.⁹ In cooperation with the deuterium isotope effect on vibrational spectra of the 2,4-pentanedione-platinum complexes, they have proposed to interchange the band assignments for the C[∞]O and the C[∞]C

stretching mode. This result has been supported by investigation of the vibrational band-shift in the infrared spectra of the ¹⁸O-labeled 2,4-pentanedione complexes of chromium(III) and manganese(III),¹¹ and also of the ²H-, ¹⁸O-, and ¹³C-labeled 2,4-pentanedione complexes of copper(II).⁷ Another interchange of the band assignments made by Nakamoto and his co-worker⁹ is for the CH₃ degenerate deformation and the lower frequency C[∞]O stretching mode, and this has been supported by the infrared study of the corresponding isotope-labeled complexes as reported by Musso and

Table IV. The M—O stretching bands (cm^{-1}) for the metal complexes of 3-substituted 2,4-pentanediones

Ligand	Be ^{II}	Cu ^{II}	Pd ^{II}	Al ^{III}	Cr ^{III}	Fe ^{III}	Co ^{III}
PAA	1042	470	474	508	466	451	473
	856	313	305		350	315	385
	845						
	499						
BrPAA	1034	463	—	—	470	453	478
	844	298			355	312	386
	482						
CPAA	1037	467	—	—	—	452	—
	853	314				312	
	489						
NPAA	1031	468	—	—	—	453	474
	855	313				311	384
	505						
BAA	859	465	478	505	469	452	479
	508	292	297		372	318	391
NBAA	1015	465	—	—	467	456	—
	863	310			363	317	
	507						

Abbreviations for ligands are described in Table III.

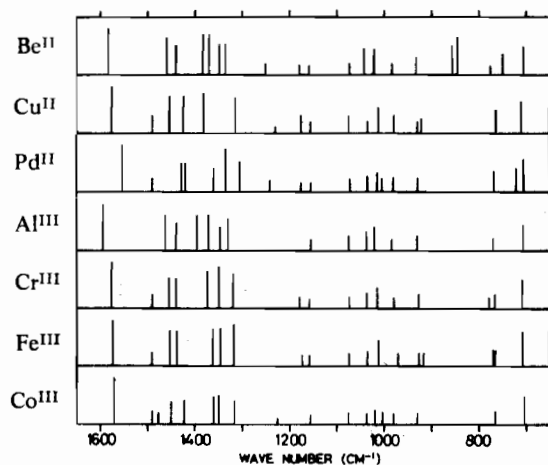


Figure 1. Observed vibrational frequencies of various metal complexes of 3-phenyl-2,4-pentanedione in the 1600-700 cm^{-1} region.

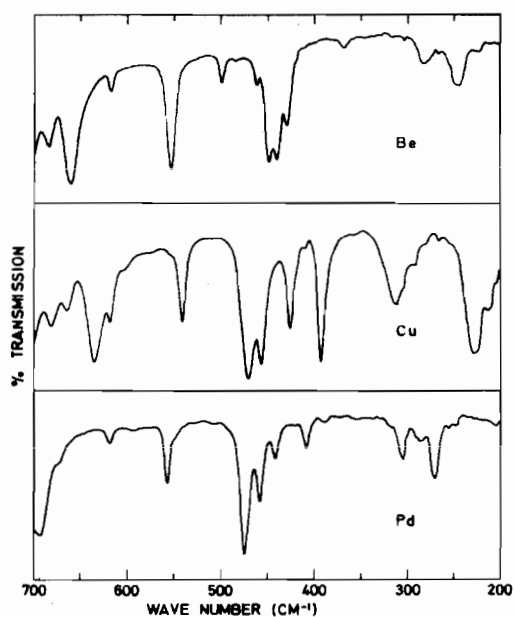


Figure 2. Far infrared spectra of divalent metal complexes of 3-phenyl-2,4-pentanedione (nujol mull method).

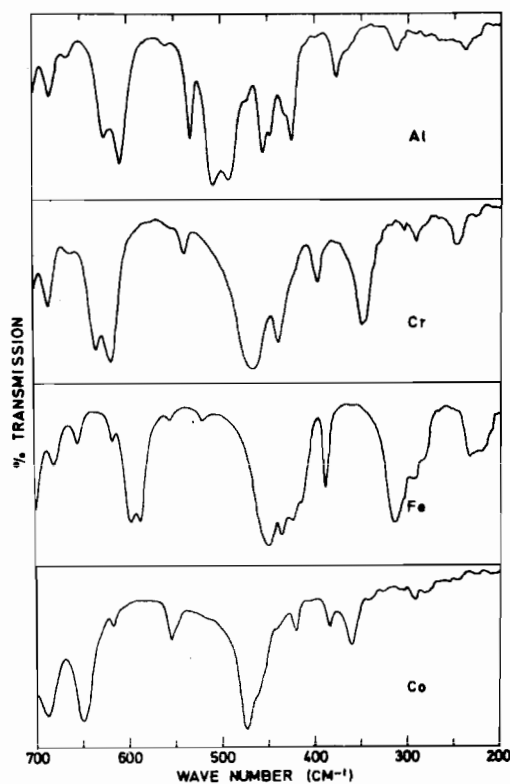


Figure 3. Far infrared spectra of trivalent metal complexes of 3-phenyl-2,4-pentanedione (nujol mull method).

Junge.⁷ The two strong bands in the 1600-1500 cm^{-1} region observed for 2,4-pentanedione complexes seem to be merged into one strong band in the present chelate systems, and this band is assumed to be primarily due to the $\text{C}=\text{O}$ stretching vibration. When 3-(*p*-nitrophenyl)-2,4-pentanedione and 3-(*p*-nitrobenzyl)-2,4-pentanedione are used as ligands, the asymmetric and the symmetric NO_2 vibrational mode appear evidently at around 1515 cm^{-1} and 1350 cm^{-1} , respectively. On the other hand, in the case that 3-(*p*-cyanophenyl)-2,4-pentanedione is a ligand molecule, the band near 2220 cm^{-1} is due to the CN stretching mode.

In the regions $1300-1050\text{ cm}^{-1}$ and $900-700\text{ cm}^{-1}$, there are observed several absorption bands which are characteristic of benzene C—H in-plane bending and out-of-plane wagging vibrations, respectively. In addition to these vibrational modes, the aromatic C—Br stretching mode in the 3-(*p*-bromophenyl)-2,4-pentanedione complexes is expected to appear in the former region although the definite position is not certain in the present work. On the other hand, the latter region involves the C—N stretching mode for the nitro-compounds; *i.e.*, in the $854-860\text{ cm}^{-1}$ range.

The CH_3 rocking mode in the $1050-1000\text{ cm}^{-1}$ region resulted in a larger number of bands in most cases by introducing a substituent at the 3-position of 2,4-pentanedione.

In the lowest frequency region in this work, $700-200\text{ cm}^{-1}$, the vibrational spectra of all the metal complexes became much more complicated than the corresponding 2,4-pentanedione complexes, due to the presence of an extra substituent. However, a strong band in the $450-500\text{ cm}^{-1}$ range and another band of various intensity in the $300-400\text{ cm}^{-1}$ range are assigned to the metal-oxygen stretching coupled with other vibrational modes for the copper, palladium, chromium, iron and cobalt complexes. Behnke and Nakamoto⁹ has assigned the lower frequency band near 300 cm^{-1} to the C— CH_3 bending mode in their study of the 2,4-pentanedione-platinum(II) complexes. On the other hand, Mikami, Nakagawa and Shimanouchi¹⁰ have observed that the lower frequency band is most metal-sensitive. The latter assignment is preferred in the present work as described above.

The spectra of all the beryllium complexes are markedly different from those of the corresponding complexes of other metals in three regions; $1050-1000\text{ cm}^{-1}$, $900-700\text{ cm}^{-1}$ and $700-200\text{ cm}^{-1}$. In conformity with the previous assignments made by Nakamoto *et al.*³ for the 2,4-pentanedione complex, the strong bands appearing near 1030 cm^{-1} and in $860-830\text{ cm}^{-1}$, and the medium band near 500 cm^{-1} are assigned to the Be—O stretching mode coupled slightly with other vibrational components. It is reasonable to expect that the beryllium complexes demonstrate their metal-sensitive bands in relatively higher frequency region than other metal complexes, due to the light mass of beryllium atom and the very short Be—O distance.

Judging from the relative positions of the C=O bands in the $1600-1500\text{ cm}^{-1}$ range among the metal complexes of each 3-substituted 2,4-pentanedione, delocalization of ligand π -electrons in a chelate ring tends to increase in the following sequence:

for divalent metals, $\text{Be} < \text{Cu} < \text{Pd}$

for trivalent metals, $\text{Al} < \text{Cr} \leq \text{Fe} \leq \text{Co}$.

The palladium complex demonstrates the C=O vibrational mode at the lowest frequency in the above range among the metal complexes of each corresponding ligand. The band-shift of this mode is seen to be minor among other transition metal complexes. The C=O bands in the beryllium and aluminum complexes are observed at relatively higher frequency than the other metal complexes as shown in Table III and the delocalization of π -electrons in a chelate ring of the

beryllium co-nplexes seems in general to be slightly greater than the corresponding aluminum complexes. Another C=O stretching mode appearing in the $1400-1360\text{ cm}^{-1}$ range varies in a manner parallel to the higher frequency mode among the metal complexes of each 3-substituted 2,4-pentanedione.

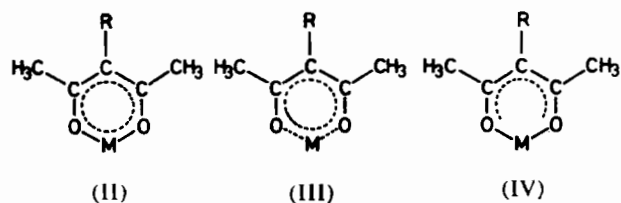
The metal-oxygen stretching modes appearing in the $700-200\text{ cm}^{-1}$ region may directly provide the information on the relative strength of coordinate bonds, and the force constant of the oxygen-metal bonds in the transition metal complexes of each ligand species follows the sequence:

for divalent metals, $\text{Cu} < \text{Pd}$

for trivalent metals, $\text{Fe} < \text{Cr} < \text{Co}$.

This is in agreement with the results obtained by the two research groups on the 2,4-pentanedione complexes.^{2,3,10} The coordinate bond of a palladium complex seems to be strongest among those of the transition metal complexes treated in this work.

In order to elucidate the electronic structure of various metal complexes investigated in this work in conformity with the electronic spectral data¹² as well as the present results, three structural forms are put forward below: *i.e.*, strong (II), weakly σ -bonded (III) and strongly σ -bonded (IV) chelate rings. In strong



chelates, ligand π -electrons as well as d-electrons of the metal tend to be well delocalized in a whole chelate ring. The palladium chelates are typical of this structure. In weakly σ -bonded chelates, ligand π -electrons are well extended to the coordinate bonds and tend to be delocalized in a whole chelate ring. Nevertheless, weak σ -bonding provides relatively weaker coordinate bonds as a whole. This seems to be the case for the iron complexes. As understood by investigating the $\pi \rightarrow \pi^*$ transition¹² and the carbonyl stretching mode for the first transition metal complexes of 3-substituted 2,4-pentanediones, π -electrons are well delocalized in a chelate ring and d-orbitals of a trivalent metal atom are involved in such a π -system. This π -electronic interaction in the iron complexes is relatively large among the trivalent metal complexes of present concern and greater than that in the corresponding chromium complexes. Nevertheless, the coordinate bonds involved in these iron complexes are weaker than those in the corresponding chromium complexes as the M—O stretching vibrations appearing in the far infrared region indicate. The above inconsistency can be ascribed to the weaker σ -bond character of the coordinate bonds in the iron complexes. Meanwhile, ligand π -electrons in the beryllium and aluminum complexes most likely tend to be delocalized only in a ligand part as judged from the C=O vibrational modes

and the electronic $\pi \rightarrow \pi^*$ transitions¹² of these metal complexes. The third structural form (IV) may be assigned to these non-transition metal complexes.

The introduction of either phenyl or benzyl derivative at the 3-position of 2,4-pentanedione resulted in the lower frequency shift of C=O stretching vibration and the higher frequency shift of M-O stretching vibration. Thus, the substituents employed in this work are in favor of forming a stronger chelate ring. However, the characteristic bands cited here do not vary significantly among the various 3-substituted 2,4-pentanedione complexes of each metal species. The variation of far infrared spectra due to the change of ligand is shown in Figure 4 for the iron complexes. Thus, the effect of the substitution with a phenyl group on the electronic structure of a chelate ring is almost the same as that with a benzyl group; in addition, *p*-substituents of these groups do not cause much change on the nature of a chelate ring. The minor effect of a phenyl group is most likely due to the fact that the phenyl ring is twisted through a torsional angle of 70° from the mean plane of the metal-chelate ring as observed by X-ray crystallography of the copper chelate.¹⁸

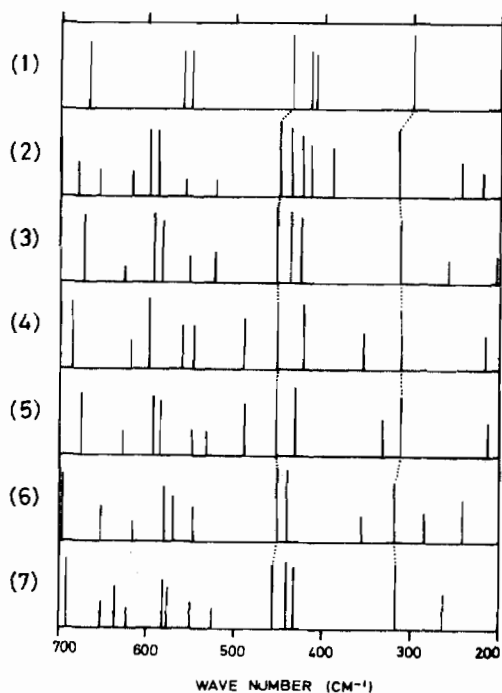


Figure 4. Observed vibrational frequencies of various iron complexes of 3-substituted 2,4-pentanediones in the 700-200 cm^{-1} region: 1, hydrogen; 2, phenyl; 3, *p*-bromophenyl; 4, *p*-cyanophenyl; 5, *p*-nitrophenyl; 6, benzyl; 7, *p*-nitrobenzyl.

Nmr Spectra. The nmr signal for the methyl protons in the metal complexes demonstrates downfield shift in general from the corresponding signal for the proton complex as shown in Table V. Similar nmr data for the 2,4-pentanedione complexes of beryllium, aluminum and palladium have been reported recently by Junge *et al.*¹⁹ Three effects seem to be responsible for this trend: reduction of electron density at the methyl groups, magnetic anisotropy caused by π -electron current in a chelate ring and an additional magnetic anisotropy due to a benzene ring as a result of metal-coordination. The third effect needs some explanation. The methyl groups of a metal complex may be exposed to a remote magnetic shielding effect caused by a benzene ring of another ligand in the same molecule.

Table V. Proton chemical shifts of the metal complexes of 2,4-pentanediones; CCl_4 solution, 40-41°C

Ligand	Metal	CH_3	δ , ppm $\text{C}_6\text{H}_5\text{CH}_2$	C_6H_5
2,4-Pentanedione	H	2.00	—	—
	Be ^{II}	2.04	—	—
	Pd ^{II}	2.02	—	—
	Al ^{III}	1.93	—	—
	Co ^{III}	2.12	—	—
3-Phenyl- 2,4-pentanedione	H	1.83	—	7.30
	Be ^{II}	1.87	—	7.31
	Pd ^{II}	1.77	—	7.29
	Al ^{III}	1.87	—	7.29
	Co ^{III}	2.00	—	7.29
3-Benzyl- 2,4-pentanedione	H	2.01	3.61	7.16
	Be ^{II}	2.06	3.72	7.22
	Pd ^{II}	2.04	3.72	7.25
	Al ^{III}	2.03	3.67	7.17
	Co ^{III}	2.20	3.78	7.16

However, the extent of this effect may vary as the steric configuration of a metal complex changes; almost negligible with square planar or tetrahedral coordination, but some influence with octahedral coordination.

In spite of the above presentation of various effects which may cause the shift of proton signals, it is rather difficult to estimate the contribution of each effect at the moment. The nmr signals for the benzene-protons in the 3-phenyl-2,4-pentanedione and the 3-benzyl-2,4-pentanedione complexes do not shift significantly from those in benzene (7.27 ppm) and in toluene (7.10 ppm), respectively.

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