Properties and Configuration of Manganese(II), Cobalt(II), Nickel(II), Copper(II) and Zinc(II) Chelates of Acetoacetylferrocene

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(Received April 2, 1974)

Physical and chemical properties of manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II) chelates of acetoacetylferrocene were investigated. The solubility decreased in the order $CHCl_3 > CH_2Cl_2 > C_6H_5Cl > C_6H_4(CH_3)_2 > C_6H_6$, the chelates being more soluble in pyridine. It was found from magnetic data that the configuration is octahedral for the aquo or pyridine adduct of manganese(II), cobalt(II) and nickel(II) chelates, square planar for anhydride of copper(II) chelate, distorted octahedral for its pyridine adduct, and quasi-tetrahedral for the anhydride of manganese(II) chelate. The d-d transition of electronic spectra was analysed by O_h symmetry for cobalt(II) and nickel(II) chelates, and by C_{2h} symmetry for copper(II) chelate. Assignment of the d-d transition for manganese(II) chelate was difficult.

It is of interest to investigate the behavior and properties of the chelates of acetoacetylferrocene ($C_5H_5FeC_5H_4COCH_2COCH_3$) in which the terminal methyl group in pentane-2,4-dione is replaced by a bulky ferrocenyl group. The bidentate ligand has been reported by several workers,[1-4] some of the first transition metal chelates being synthesized.[1-3] However, the properties and configuration of the chelates do not seem to have been reported. We wish to report on the solubility of the manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II) chelates, and the configuration and assignment of the ligand field band of each chelate in the organic solvent and in the solid state.

Experimental

Synthesis of Ligand. The ligand was synthesized by the procedure described previously.[1]

Preparation of Chelates. Each chelate of manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II) was prepared by the procedure reported previously.[1] The chelate obtained was dissolved in chloroform, and the filtrate was evaporated to a small volume under reduced pressure at room temperature. The chelate precipitated immediately on addition of four-fold petroleum ether to the concentrated solution. After being cooled overnight at about 0 °C, the precipitate was filtered, and washed thoroughly with petroleum ether.

Preparation of Pyridine Adduct. A solution obtained by dissolving 0.5 g of the chelate in 50 ml of pyridine was evaporated to about 10 ml under reduced pressure at room temperature. The pyridine adduct precipitated on addition of 40 ml of petroleum ether was filtered after being cooled overnight at about 0 °C, and washed thoroughly with petroleum ether.

Solubility Measurements. Excess chelate was added to 50 ml of various organic solvents which was warmed to 50 °C, and dissolved thoroughly. The resulting solution was allowed to stand at 25±0.1 °C for 3 hr, and then filtered. A 25 ml portion pipetted from this solution was evaporated completely under reduced pressure at room temperature. The solubility was measured by weighing the precipitated chelate.

Spectral Measurements. Solid reflectance spectra were measured with a Shimadzu QR-50 spectrophotometer with a diffuse reflectance attachment. Absorption spectra in ultraviolet and visible regions were measured with the same instrument. Infrared absorption spectra were measured with a Shimadzu IR-27G spectrophotometer on KBr pellets.

Molecular Weight Measurements. Molecular weights of the chelates were determined with a Shibayama recording cryoscope in bromoform, nitrobenzene, dioxane and dimethyl sulfoxide.

Magnetic Moment Measurements. The magnetic moment of the chelates in the solid state or in the organic solvent was measured by the Gouý method at room tempreature.

Results and Discussion

Solubility. The solubility of chelates reported[1] was determined in various organic solvents of different polarity. The results are given in Table 1.

Solubility decreases in the order $CHCl_3 > CH_2Cl_2 > C_6H_5Cl > C_6H_4(CH_3)_2 > C_6H_6$, which is in line with the decrease of polarity of solvent. All chelates, besides those given in Table 1, are soluble in pyridine, slightly soluble in methanol, ethanol and acetone, and almost insoluble in petroleum ether.

Composition of Chelates. It has been reported that the composition of the chelates (Table 1) is 2 : 1, other chelates except copper chelate being the bisaquo adduct.[1] When such chelates were recrystallized with a mixture of chloroform–petroleum ether, a change in color was recognized in manganese and zinc chelates. The results of elemental analysis and molecular weight determination are given in Table 2.

It was found that the water molecules coordinated to manganese and zinc chelates are dehydrated more easily than the bisaquo adduct of cobalt and nickel chelates.

The molecular weight agreed with the calculated one of the monomeric structure for other chelates except nickel. The molecular weight of the nickel chelate varies with the polarity of solvent, and has been found to be a monomer in bromoform (0.99D) or nitrobenzene (3.99D), and a dimer in dioxane (0.45D).

It is well known that bis(pentane-2,4-dionato)nickel(II) anhydride in the solid state has a trimeric structure, in which nickel(II) ion is octahedrally coordinated.[5] However, when a terminal methyl group in pentane-2,4-dione is replaced by a bulky ferrocenyl group, the steric hindrance among the substituents seems to prevent trimerization. Thus, the bisaquo adduct of the nickel chelate in a solvent such as dioxane

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Table 1. Solubility of chelates
L : $FcCOCHCOCH_3$, Temp. : 25±0.1 °C

Complexes	Solubility (g/100 ml)				
	$CHCl_3$	CH_2Cl_2	C_6H_5Cl	$C_6H_4(CH_3)_2$	C_6H_6
$MnL_2 \cdot 2H_2O$	4.48	3.64	1.14	0.77	0.40
$CoL_2 \cdot 2H_2O$	4.53	2.22	1.85	0.77	0.54
$NiL_2 \cdot 2H_2O$	3.37	2.22	0.76	0.88	0.68
CuL_2	1.62	1.23	0.53	0.09	0.27
$ZnL_2 \cdot 2H_2O$	3.11	1.21	1.20	0.48	0.56

Table 2. Elemental analysis and molecular weight
L : $FcCOCHCOCH_3$

Complexes	Mp (°C)	Elemental analysis C (%) Found	Calcd	H (%) Found	Calcd	Molecular weight Found (1)	Calcd (2)	(1)/(2)	Appearance
MnL_2	271—273	57.04	56.70	4.53	4.42	613[a]	593.2	1.03	Black-brown
						646[b]		1.09	
$CoL_2 \cdot 2H_2O$		Previously reported.[1]				634[a]	633.2	1.00	
						628[a]		0.99	
						654[c]		1.03	
$NiL_2 \cdot 2H_2O$		ditto				723[a]	633.0	1.14	Red-orange
						605[b]		0.96	
						1140[c]		1.80	
CuL_2		ditto				621[a]	601.8	1.03	Golden brown
						644[b]		1.07	
						609[c]		1.01	
ZnL_2	234—236	55.94	55.72	4.44	4.34	657[a]	603.6	1.08	Red-orange
						627[b]		1.04	
						630[d]		1.04	

The molecular weight was measured in the following solvents; a) bromoform, b) nitrobenzene, c) dioxane, d) dimethyl sulfoxide.

Table 3. Elemental analysis and molecular weight of pyridine adducts
L : $FcCOCHCOCH_3$, py : pyridine

Complexes	Mp (°C)	Elemental analysis C (%) Found	Calcd	H (%) Found	Calcd	N (%) Found	Calcd	Molecular weight Found (1)	Calcd (2)	(1)/(2)	Appearance
$MnL_2 \cdot 2py$	267—270	61.06	60.74	4.85	4.84	4.11	3.73	726[a]	751.2	0.97	Brown
$CoL_2 \cdot 2py$	186—187	60.21	60.42	4.56	4.81	3.61	3.71	729[a]	755.2	0.97	Yellow-orange
$NiL_2 \cdot py \cdot H_2O$	190—192	56.90	57.11	4.71	4.79	1.83	2.02	694[b]	694.0	1.00	Orange
$CuL_2 \cdot 2py$	197—199	60.31	60.05	4.55	4.78	3.39	3.69	708[c]	759.8	0.93	Brown
$ZnL_2 \cdot 2py$	159—161	60.18	59.91	4.96	4.76	3.40	3.68	758[a]	761.6	1.00	Red-brown

The molecular weight was measured in the following solvents: a) dimethyl sulfoxide, b) nitrobenzene, c) dioxane.

with a low polarity is suggested to be similar in structure to the dimeric octahedral structure of bis(1,5-dialkyl-2,4-pentanediono)nickel(II) monohydrate.[6]

The results of elemental analysis and molecular weight measurement of the pyridine adducts are given in Table 3.

From the composition of the pyridine adducts, they were recognized to be monomeric in the solvents used. Thus, when the chelates (Table 2) were isolated from pyridine solution, the hexa-coordinate chelates of $ML_2 \cdot 2py$ type were obtained from the bisaquo adduct of the cobalt chelate by ligand exchange reaction, and from the anhydride of the manganese, copper and zinc chelates by coordination of pyridine molecules. It is of interest that $NiL_2 \cdot py \cdot H_2O$ chelate, in which one water molecule was replaced by a pyridine molecule, is obtained from the bisaquo adduct of the nickel chelate.

A black-brown bispyridine adduct of CuL_2 turned gradually golden brown on exposure to the air, while

Table 4. Magnetic moments
L : $FcCOCHCOCH_3$

Complexes	Magnetic moment BM (K)		Complexes	Magnetic moment in solid state BM (K)
	in solid state	in py		
$MnL_2 \cdot 2H_2O$	5.94 (301)	5.52 (304)	$MnL_2 \cdot 2py$	5.64 (296)
MnL_2	4.32 (295)	5.79 (304)		
$CoL_2 \cdot 2H_2O$	4.89 (304)	4.77 (303)	$CoL_2 \cdot 2py$	4.75 (296)
$NiL_2 \cdot 2H_2O$	3.49 (302)	3.50 (302)	$NiL_2 \cdot py \cdot H_2O$	3.64 (296)
CuL_2	1.91 (296)	2.14 (306)	$CuL_2 \cdot 2py$	2.10 (293)

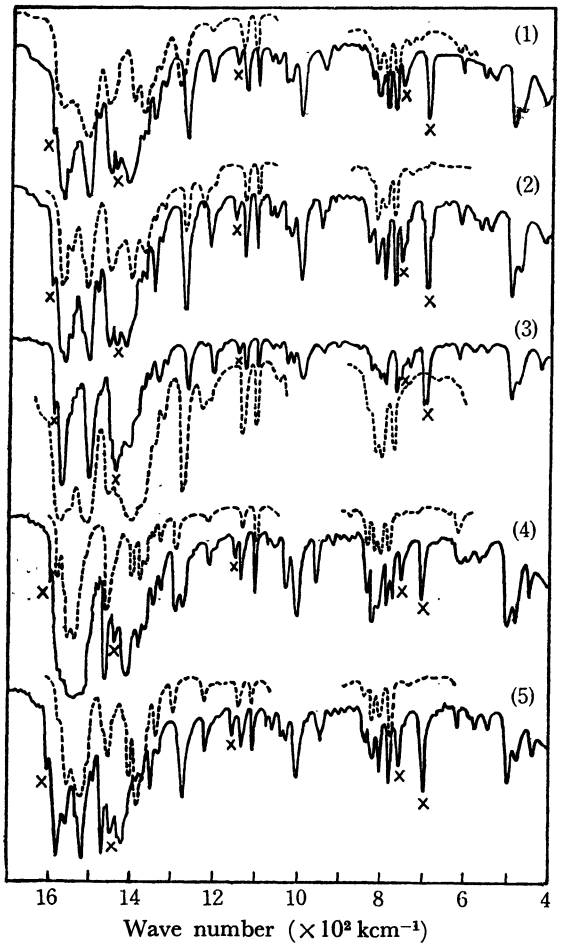

Fig. 1. IR Spectra.
——: (1) $MnL_2 \cdot 2py$, (2) $CoL_2 \cdot 2py$, (3) $NiL_2 \cdot py \cdot H_2O$, (4) $CuL_2 \cdot 2py$, (5) $ZnL_2 \cdot 2py$, ----: (1) MnL_2, (2) $CoL_2 \cdot 2H_2O$, (3) $NiL_2 \cdot 2H_2O$, (4) CuL_2, (5) ZnL_2, L: $FcCOCHCOCH_3$

other pyridine adducts were stable under the same conditions.

The presence of pyridine molecules in such chelates is also confirmed by IR spectra (Fig. 1).

The absorption bands assignable to pyridine are observed in the spectra of the adducts. Thus, the absorption of $\nu_{C=C}$ on the pyridine ring is observed at about 1595 cm^{-1}, but that of $\nu_{C=N}$ could not be confirmed because of the overlapping with the strong absorption band of the chelates $\nu_{C=O}$ appearing at about 1570 cm^{-1}. There is a tendency that the absorption of $\nu_{C=O}$ shifts slightly towards the low wave number side by the coordination of pyridine. The absorption of ring vibration and δ_{CH} of adjacent hydrogen on pyridine were recognized at about 1135, 750 and 695 cm^{-1}. The absorption of ν_{M-O} of the pyridine adduct shifted to the low wave number side in comparison with that of the anhydrous or hydrous chelates as follow; from 426 cm^{-1} to 418 cm^{-1} for $MnL_2 \cdot 2py$, from 419 cm^{-1} to 415 cm^{-1} for $CoL_2 \cdot 2py$, from 422 cm^{-1} to 418 cm^{-1} for $NiL_2 \cdot py \cdot H_2O$, from 450 cm^{-1} to 445 cm^{-1} for $CuL_2 \cdot 2py$ and from 438 cm^{-1} to 422 cm^{-1} for $ZnL_2 \cdot 2py$.

Magnetic Moments. The magnetic moments of each chelate measured in the solid state or in pyridine are given in Table 4.

a) Manganese Chelate: The magnetic moment of 5.94 BM in the solid state of $MnL_2 \cdot 2H_2O$ agreed with 6.02 BM of bis(pentane-2,4-dionato)manganese(II) dihydrate,[7] and also with 5.92 BM of the theoretical spin-only moment which indicates the octahedral structure of a high-spin type. As the moment of 5.52 BM in pyridine is close to 5.64 BM in the solid state of $MnL_2 \cdot 2py$, the bisaquo adduct is thought to change into the pyridine adduct in pyridine solution. The moment of 4.32 BM in the solid state of MnL_2 anhydride showed a slightly higher value than the theoretical value of n=3, being close to 4.55 BM of phthalocyanine manganese(II) chelate which is considered to have a quasi-tetrahedral structure rather than a square planar one.[8] In contrast, the anhydride in pyridine showed a moment of 5.79 BM which corresponds to that of $MnL_2 \cdot 2py$. From the above results, MnL_2 anhydride, which is considered to have a quasi-tetrahedral structure, has been found to change into an octahedral structure by the coordination of two pyridine molecules in pyridine.

b) Cobalt and Nickel Chelates: The magnetic moment of 4.75—4.89 BM in the solid state or in pyridine of $CoL_2 \cdot 2H_2O$, and in the solid state of $CoL_2 \cdot 2py$ is in the range 4.4—5.6 BM of all cobalt(II) complexes which indicates the octahedral structure. $NiL_2 \cdot 2H_2O$ in the solid state or in pyridine, and $NiL_2 \cdot py \cdot H_2O$ in the solid state showed a moment of 3.50 and 3.64 BM, respectively. The bisaquo adduct of the nickel chelate in chloroform also showed a moment of 3.50 BM. The values were slightly higher than 3.2 BM of bis(pentane-2,4-dionato)nickel(II) dihydrate[9] and 3.32 BM of hexaamminenickel(II) chloride[10] which have octahedral structures. Thus, the aquo or pyridine adduct of the cobalt and nickel chelates were found to have the octahedral structure.

c) Copper Chelate: The magnetic moment in the solid state of CuL_2 showed a higher value than the

Table 5. Absorption band and extinction coefficient
L : $FcCOCHCOCH_3$

Complexes	C_6H_6				$CHCl_3$			
	kcm^{-1}	log ε	kcm^{-1}	log ε	kcm^{-1}	log ε	kcm^{-1}	log ε
MnL_2	32.7	4.32	21.4	3.43	32.7	4.27	21.3	3.42
$CoL_2 \cdot 2H_2O$	31.4	4.36	21.6	3.42	32.7	4.14	21.4	3.30
$NiL_2 \cdot 2H_2O$	31.2	4.24	21.8	3.29	32.4	4.14	21.4	3.31
CuL_2	31.0	4.42	21.8	3.40	31.2	4.36	21.4	3.39
ZnL_2	32.8	4.33	21.6	3.34	32.5	4.26	21.3	3.32
$MnL_2 \cdot 2py$	32.6	4.31	21.7	3.48	32.7	4.30	21.6	3.42
$CoL_2 \cdot 2py$	31.5	4.34	21.7	3.34	33.3	4.30	21.8	3.52
$NiL_2 \cdot py \cdot H_2O$	30.2	4.08	22.0	3.13	32.4	4.20	21.8	3.39
$CuL_2 \cdot 2py$	30.9	4.52	21.7	3.42	31.0	4.53	21.4	3.50
$ZnL_2 \cdot 2py$	32.2	4.29	21.5	3.35	32.0	4.18	21.6	3.24

Table 6. Assignment of ligand field bands
L : $FcCOCHCOCH_3$

Complexes	Assignment	Absorption bands and extinction coefficient in $CHCl_3$		Absorption bands and extinction coefficient in py		Reflectance bands		The value obtained from Tanabe-Sugano diagram	
		kcm^{-1}	ε	kcm^{-1}	ε	Hydrate or anhydride kcm^{-1}	py adduct kcm^{-1}	aquo adduct kcm^{-1}	py adduct kcm^{-1}
$MnL_2 \cdot 2H_2O$		(13.0)	400	(15.5)	300	(15.0)	(15.0)		
MnL_2		9.1	45	(15.0)	250	8.8			
$CoL_2 \cdot 2H_2O$[a]	$^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$					(19.4)		19.4	
	$^4A_{2g}(F) \leftarrow$	(14.5)	23	(18.2)	36	(14.5)	(18.0)	15.5	18.1
	$^4T_{2g}(F) \leftarrow$	8.7	11	9.8	10	8.8	9.5	8.7(10*Dq*)	9.8(10*Dq*)
$NiL_2 \cdot 2H_2O$[a]	$^1E_g(D) \leftarrow {}^3A_{2g}(F)$	(15.5)	29	(13.2)	6	(15.4)	(13.0)	15.1	13.1
	$^3T_{1g}(F) \leftarrow$	(14.2)	14	(15.5)	9	(14.2)	(15.3)	14.8	15.6
	$^3T_{2g}(F) \leftarrow$	8.9	9	10.0	9	8.9	10.0	8.9(10*Dq*)	10.0(10*Dq*)
CuL_2	A_g or $B_{2g}(D) \leftarrow B_{3g}(D)$			15.0	93		15.2		
	B_{2g} or $A_g(D) \leftarrow$	(16.0)	74			(16.3)			
	$A_g(D) \leftarrow$			(10.5)	25	(14.5)	(10.3)		

Values in parentheses are the wave numbers of shoulder absorptions. a) The following values were the most suitable for electron repulsion parameter *B*: 860 cm^{-1} for aquo adduct and 840 cm^{-1} for pyridine adduct of cobalt chelate; 850 cm^{-1} for aquo adduct and 730 cm^{-1} for pyridine adduct of nickel chelate.

theoretical spin-only moment of 1.73 BM, being in the range 1.9—2.0 BM of all copper(II) complexes which indicates the tetra-coordinate square planar structure. As the value of CuL_2 in pyridine agrees with 2.10 BM in the solid state of $CuL_2 \cdot 2py$, it is suggested that CuL_2 in pyridine changes into the distorted octahedral structure by the coordination of two pyridine molecules to the central copper(II) ion in planar on both side along z axis.

Electronic Spectra. The absorption bands of each chelate in 20—40 kcm^{-1} region are given in Table 5.

Two bands of 31—33 kcm^{-1} and 21—22 kcm^{-1} are due to the chelated carbonyl group and the charge transfer between cyclopentadienyl-iron atom, respectively. The former in benzene shifted slightly to the low wave number side than that in chloroform, and the latter, to the high wave number side. The wave numbers of both bands for the pyridine adduct were practically unchanged as compared with those of the corresponding anhydrous or hydrous chelate.

The absorption spectra in chloroform or pyridine, and the diffuse reflectance spectra of solid state in 8—20 kcm^{-1} region are shown in Fig. 2. Assignment of ligand field bands is given in Table 6.

a) Manganese Chelate: The very weak band at about 9 kcm^{-1} was observed in the spectra of MnL_2 in chloroform and in the solid state. The spectral pattern of the anhydride chelate in pyridine is close to that of bisaquo adduct measured in chloroform or pyridine (not given in Fig. 2(1)). Such spectral change is due to the formation of $MnL_2 \cdot 2py$. Although the structure of the anhydride and bisaquo or bispyridine adduct of this chelate was presumed from the magnetic data, the assignment of ligand field band was difficult.

b) Cobalt and Nickel Chelates: The spectra of the bisaquo adduct of cobalt and nickel chelates are very much similar to each other, and show a shoulder at 13—16 kcm^{-1}. The absorption or reflectance band of about 9 kcm^{-1} observed on spectra of both chelates in chloroform or in the solid state shifts about 10 kcm^{-1} in pyridine. The electronic spectra of both chelates confirmed to have an O_h symmetry from the magnetic data were analysed from the Tanabe-Sugano diagram[11] for d^7 and d^8 configurations with the use of the measured

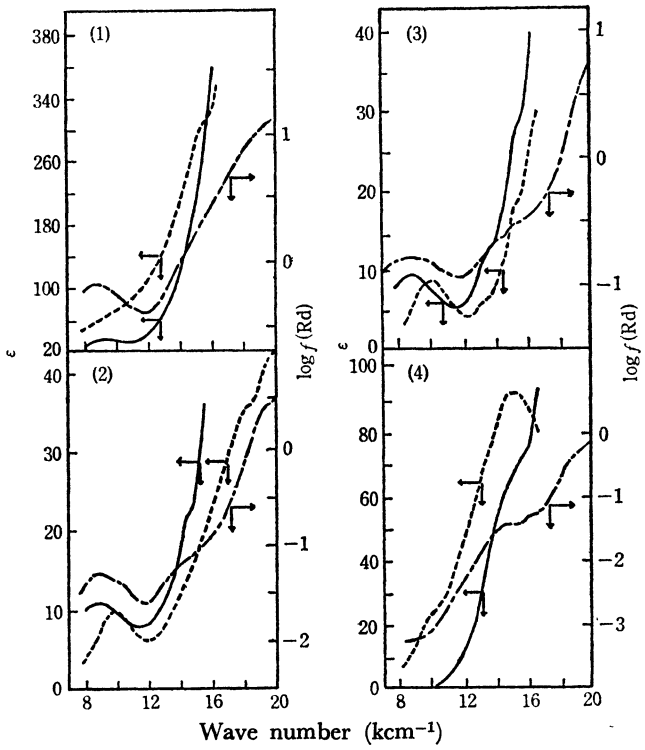

Fig. 2. Electronic spectra of each chelate.
Complexes: (1) MnL_2, (2) $CoL_2 \cdot 2H_2O$, (3) $NiL_2 \cdot 2H_2O$, (4) CuL_2, L: $FcCOCHCOCH_3$, ——: $CHCl_3$, ----: py, ——: Solid state

TABLE 7. β VALUES

Complexes	B_0[a] cm^{-1}	β $(B/B_0)\%$
$CoL_2 \cdot 2H_2O$	1120	77
$CoL_2 \cdot 2py$	1120	75
$NiL_2 \cdot 2H_2O$	1080	79
$NiL_2 \cdot py \cdot H_2O$	1080	68

a) B. N. Figgis, "Introduction to Ligand Field," Interscience Publishers, New York (1966), p. 52.

crystal field stabilization energy 10 *Dq* of both chelates and the electron repulsion parameter *B* (Table 6). The wave number of ligand field bands measured is very close to the values obtained from this diagram, each band can be assigned as shown in Table 6. In order to investigate the partial covalent bonding in the coordination bond of both chelates from the above results, the *B* parameters were compared with the B_0 parameter of free ion of cobalt(II) and nickel(II).

The degree of covalent bonding $(1-\beta)$ for both chelates is estimated to be 20—30% from the results given inTable 7.

c) Copper Chelate: The absorption bands of CuL_2 in pyridine appeared at 15.0 and 10.5 kcm^{-1}. The sharp band of the former corresponds to the shoulder observed at 13—16 kcm^{-1} in chloroform and in the solid state, and the shoulder of the latter suggests the formation of a pyridine adduct which has a distorted octahedral structure. Although the transition of absorption bands for bis(pentane-2,4-dioato)copper(II) was assigned to D_{4h}[12-14] or D_{2h}[15] symmetry, it is considered that the C_{2h} symmetry used by Allene[16] is better for the chelate with a ligand such as acetoacetylferrocene (Table 6).

d) Zinc Chelate: Since all zinc(II) complexes have a tetrahedral or octahedral structure, ZnL_2 or $ZnL_2 \cdot 2H_2O$ might also have such structures.

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