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Mixed Ligand Complexes Derived from the Reactions of Diaquabis(3-hydroxy-2-methyl-4-pyronato)-cobalt(II), -nickel(II), and -zinc(II) with Pyridine and 4-Substituted Pyridines

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The pyridine(py), 4-methylpyridine(4-Me-py) and 4-cyanopyridine(4-CN-py) adducts of bis(3-hydroxy-2-methyl-4-pyronato) complexes (ML_2) of cobalt(II), nickel(II), and zinc(II) have been synthesized: $CoL_2(py)_n$ (where $n=2$ or 3), $NiL_2(py)_3$, $ZnL_2(py)$, $ML_2(4\text{-Me-py})_2$ (where M=Co(II), Ni(II), and Zn(II)), $ML_2(4\text{-CN-py})$ (where M=Co(II) and Zn(II)), and $NiL_2(4\text{-CN-py})_2$. Based on the magnetic, spectral, and thermogravimetric data, three of these complexes, $ZnL_2(py)$ and $ML_2(4\text{-CN-py})$ (where M=Co(II) and Zn(II)), are presumed to have a five-coordinate structure, while the other complexes are presumed to be octahedral. In the case of the 4-cyanopyridine complexes, the infrared spectra show that the pyridine-ring nitrogen is linked to the metal ion and that the nitrogen atom of the nitrile group is not coordinated.

In previous papers it was reported that, when treated with 2,2′-bipyridine(bpy) or 1,10-phenanthroline (phen), the aqua ligands of the diaquabis(3-hydroxy-2-methyl-4-pyronato) complexes of Co(II), Ni(II), and Zn(II) were replaced by the base,1) whereas bis(3-hydroxy-2-methyl-4-pyronato)palladium(II) gave mixed ligand complexes, $[PdL(bpy)]ClO_4$ and $[PdL(phen)]ClO_4$.2) On the other hand, an aliphatic amine, such as ethylenediamine(en), propylamine(pa), and benzylamine(ba), replaced both of the ligands in $[PdL_2]$ to afford a complex containing 3-hydroxy-2-methyl-4-pyronate (Fig. 1) as counter ions, $[Pd(en)_2]L_2 \cdot 2H_2O$,2) $[Pd(pa)_4]L_2$, or $[Pd(ba)_4]L_2$.3) In the course of our studies it was noticed that pyridine and 4-substituted pyridines react with diaquabis(3-hydroxy-2-methyl-4-pyronato) complexes of Co(II), Ni(II), and Zn(II) to produce five- or six coordinate mixed-ligand complexes containing the pyronate anion and the base.

This paper will report on the syntheses and structural studies of the pyridine, 4-methylpyridine, and 4-cyanopyridine adducts of bis(3-hydroxy-2-methyl-4-pyronato) complexes of Co(II), Ni(II), and Zn(II).

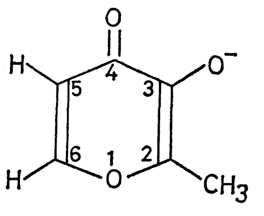

Fig. 1. 3-Hydroxy-2-methyl-4-pyronate anion.

Experimental

Materials. The preparation of three diaquabis(3-hydroxy-2-methyl-4-pyronato) complexes of Co(II), Ni(II), and Zn(II), ($CoL_2(OH_2)_2$, $NiL_2(OH_2)_2$, and $[ZnL_2(OH_2)_2] \cdot 1/2H_2O$) has previously been reported.1) Reagent-grade pyridine, 4-methylpyridine, and 4-cyanopyridine were used without further purification. The ethanol was purified by the fractional distillation of the ternary azeotrope, benzene–ethanol–water. The mercury(II) tetrakis(isothiocyanato)-cobalt(II) was prepared according to the literature4) and was used as a referecne substance for the magnetic measurements.

Preparation of Complexes. *Bis(3-hydroxy-2-methyl-4-pyronato)bis(pyridine)cobalt(II) Pyridine,* $[CoL_2(py)_2](py)$ ***(1)***: In 10 ml of hot pyridine–ethanol (1 : 2 by volume) we dissolved 1.0 g of $CoL_2(OH_2)_2$, the solution was then heated on a hot-plate for 10 min with stirring and stored overnight in a refrigerator. The brown precipitate thus obtained was filtered and dried *in vacuo* at room temperature. The yield was 1.4 g (87%).

Bis(3-hydroxy-2-methyl-4-pyronato)bis(pyridine)cobalt(II), $[CoL_2(py)_2]$ ***(2)***: This compound was produced when Complex **1** was kept at *ca.* 95 °C for 2 h in an atmosphere of flowing nitrogen (50 ml/min).

The corresponding pyridine adducts of Ni(II) and Zn(II), $[NiL_2(py)_2](py)$ (**3**) and $[ZnL_2(py)]$ (**4**), were also prepared, by the method used for Complex **1** using $NiL_2(OH_2)$ and $[ZnL_2(OH_2)_2] \cdot 1/2H_2O$ instead of $CoL_2(OH_2)_2$, in 92 and 93% yields respectively.

Bis(3-hydroxy-2-methyl-4-pyronato)bis(4-methylpyridine)cobalt(II), $[CoL_2(4\text{-Me-py})_2]$ ***(5)***: One gram of $CoL_2(OH_2)_2$ was added little by little to 5 ml of 4-methylpyridine with stirring. The mixture was heated on a hot-plate with stirring for 15 min, and then cooled to room temperature. The brown precipitate thus obtained was filtered, washed with ethanol and petroleum ether, and dried *in vacuo* at room temperature. The yield was 1.3 g (91%).

In a similar fashion, $[NiL_2(4\text{-Me-py})_2]$ (**6**) and $[ZnL_2(4\text{-Me-py})_2]$ (**7**) were obtained in 98 and 86% yields respectively.

(4-Cyanopyridine)bis(3-hydroxy-2-methyl-4-pyroanato)cobalt(II), $[CoL_2(4\text{-CN-py})]$ ***(8)***: To an ethanol solution (120 ml) of 4-cyanopyridine (0.52 g, 0.005 mol) we added 1.72 g (0.005 mol) of $CoL_2(OH_2)_2$. The mixture was heated on a hot-plate with stirring. The solution was concentrated to begin the formation of a precipitate, and was then left standing overnight in a refrigerator. The brown precipitate thus obtained was filtered, washed with ethanol, and dried *in vacuo* at room temperature. The yield was 1.4 g (67%).

The corresponding 4-cyanopyridine adducts of Ni(II) and Zn(II), $[NiL_2(4\text{-CN-py})_2]$ (**9**) and $[ZnL_2(4\text{-CN-py})]$ (**10**), were also prepared by the reaction of $NiL_2(OH_2)_2$ or $[ZnL_2(OH_2)_2] \cdot 1/2H_2O$ respectively with two or three times as many moles of 4-cyanopyridine in a manner similar to that used for Complex **8**. The yields were 81% and 80 respectively.

Analyses and Measurements. The metal contents in these complexes were determined by atomic absorption spectroscopy. The visible and ultraviolet reflection spectra were

Table 1. Color and analytical data of the isolated complexes

Complex		Color	Found (Calcd), % C	H	N	M	Magnetic moment B. M. (K)
$[CoL_2(py)_2](py)$	**1**	brown	59.19 (59.35)	4.60 (4.61)	7.74 (7.69)	10.49 (10.78)	4.84 (289)
$[CoL_2(py)_2]$	**2**	yellow brown	56·38 (56.54)	4.46 (4.31)	6.14 (5.99)	12.86 (12.61)	5.02 (302)
$[CoL_2(4\text{-Me-py})_2]$	**5**	brown	57.86 (58.19)	4.80 (4.88)	5.55 (5.65)	11.76 (11.90)	4.87 (302)
$[CoL_2(4\text{-CN-py})]$	**8**	brown	52.15 (52.32)	3.53 (3.41)	6.63 (6.78)	13.97 (14.26)	4.66 (301)
$[NiL_2(py)_2](py)$	**3**	green	59.53 (59.37)	4.65 (4.61)	7.58 (7.72)	10.66 (10.75)	3.17 (303)
$[NiL_2(4\text{-Me-py})_2]$	**6**	green	57.90 (58.22)	4.70 (4.89)	5.64 (5.66)	11.57 (11.86)	3.23 (303)
$[NiL_2(4\text{-CN-py})_2]$	**9**	green	55.69 (55.75)	3.53 (3.51)	10.72 (10.83)	11.26 (11.35)	3.16 (303)
$[ZnL_2(py)]$	**4**	white	51.64 (51.74)	3.86 (3.83)	3.48 (3.55)	16.59 (16.57)	
$[ZnL_2(4\text{-Me-py})_2]$	**7**	pale yellow	57.48 (57.44)	4.81 (4.82)	5.56 (5.58)	12.71 (13.03)	
$[ZnL_2(4\text{-CN-py})]$	**10**	yellow	51.45 (51.51)	3.24 (3.36)	6.36 (6.67)	15.17 (15.58)	

obtained with a Shimadzu MPS-5000 recording sepctrophotometer. The infrared spectra (4000—200 cm^{-1}) were obtained with a Jasco DS-701G infrared spectrophotometer in Nujol mull between CsI plates. The magnetic susceptibility was determined at room temperature by the Faraday method with an automatically recording magnetic balance (Shimadzu Seisakusho Co., Ltd.). Mercury(II) tetakis(isothiocyanato)cobaltate(II) was used as a reference substance. The diamagnetic corrections were calculated from Pascal's constants. The thermogravimetric curves were obtained with a Shimadzu TGA-20B thermobalance at a heating rate of 5 °C/min in an atmosphere of nitrogen flowing at 50 ml/min. The PMR spectra were measured in $CDCl_3$ at 100 MHz with a JNM-PS-100 spectrometer (Japan Electron Optics Lab. Co., Ltd.) using tetramethylsilane as the internal reference. The molecular weight was determined in chloroform at 35 °C with a vapor-pressure osmometer of the Hitachi Perkin-Elmer 115 type, employing benzil as a reference substance.

Results and Discussion

Ten mixed-ligand complexes isolated are listed in Table 1, together with their colors and analytical and magnetic data. As may be seen in Table 2, the observed molecular weights of Complexes **5**—**10** are remarkably smaller than the calculated values, indicating that these complexes dissociate extensively in solution. Furthermore, the electronic spectra of the nickel(II) and cobalt(II) complexes in ethanol (**1**, **2**, **3**, **5**, and **6**) or chloroform (**8** and **9**) changed on the addition of the corresponding base to the solution, suggesting again the dissociation of these complexes in solution. Therefore, the structural study of the complexes was done mainly on the basis of thermogravimetic, IR, reflection-spectral, and magnetic data in the solid state.

Thermogravimetric Data. The thermogravimetric (TG) curves for the pyridine, 4-methylpyridine, and 4-cyanopyridine complexes are given in Figs. 2 and 3.

Table 2. Molecular weight data in chloroform

Compound		Calcd	Found
$[ZnL_2(py)]$	**4**	394.7	390,[a] 410[b]
$[CoL_2(4\text{-Me-py})_2]$	**5**	495.4	283[a]
$[NiL_2(4\text{-Me-py})_2]$	**6**	495.2	342[a]
$[ZnL_2(4\text{-Me-py})_2]$	**7**	501.8	337[b]
$[CoL_2(4\text{-CN-py})_2]$	**8**	413.3	335,[a] 339[c]
$[NiL_2(4\text{-CN-py})_2]$	**9**	517.1	248,[a] 295[c]
$[ZnL_2(4\text{-CN-py})_2]$	**10**	419.7	299,[b] 300[c]

a) At 1.0×10^{-3} M. b) At 1.5×10^{-3} M. c) At 2.0×10^{-3} M.

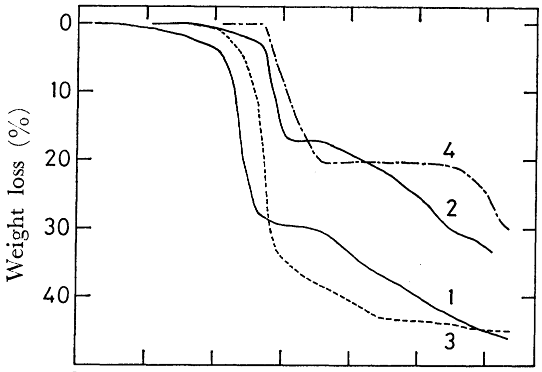

Fig. 2. The TG curves for complexes **1**(1), **2**(2), **3**(3), and **4**(4).

Complex **1** begins to liberate pyridine at around 30 °C and loses two molecules up to *ca.* 160 °C to give $CoL_2(py)$ (weight loss at 160 °C; found: 29.54%, calcd for 2 py: 28.95%.). The TG curve does not show distinctly whether or not the two pyridine molecules are liberated in two steps, but Complex **2** was

Table 3. Characteristic IR bands (cm^{-1}) of the isolated complexes

Complex		ν(C=O)	ν(C=C)		ν(M–O)	Base					
[CoL$_2$(py)$_2$](py)	**1**	1600 vs	1572 vs	1512 s	443m	624m	603w	430w	421m	413 vw	
[CoL$_2$(py)$_2$]	**2**	1595 vs	1571 vs	1518 s	451m	619m	421m				
[NiL$_2$(py)$_2$](py)	**3**	1598 vs	1570 vs	1510 s	450m	628m	604m	438m	427w	413 vw	
[ZnL$_2$(py)]	**4**	1601 vs	1568 vs	1510 vs	470m	640m	420m				
[CoL$_2$(4-Me-py)$_2$]	**5**	1602 vs	1577 vs	1514 s	443m	1017m	723m	526m	493m	488m	
[NiL$_2$(4-Me-py)$_2$]	**6**	1601 vs	1572 vs	1510 s	448m	1019m	723m	529m	496m	489m	
[ZnL$_2$(4-Me-py)$_2$]	**7**	1603 vs	1569 vs	1518 s	447m	1017m	724m	527m	494m	488m	
[CoL$_2$(4-CN-py)]	**8**	1604 vs	1579 vs	1511 s	458m	2230m	1613 sh[a)]	1095 sh	1061 vw	1016w	
[NiL$_2$(4-CN-py)$_2$]	**9**	1595 vs	1575 vs	1516 s	460w	2238m	1608 sh[a)]	1092w	1060w	1018w	
[ZnL$_2$(4-CN-py)]	**10**	1600 vs	1582 vs	1515 s	463m	2241m	1615 sh[a)]	1605 sh[a)]	1094 sh	1063w	1017m

a) The band overlaps with the ν(C=O) band of the pyronate ligand.

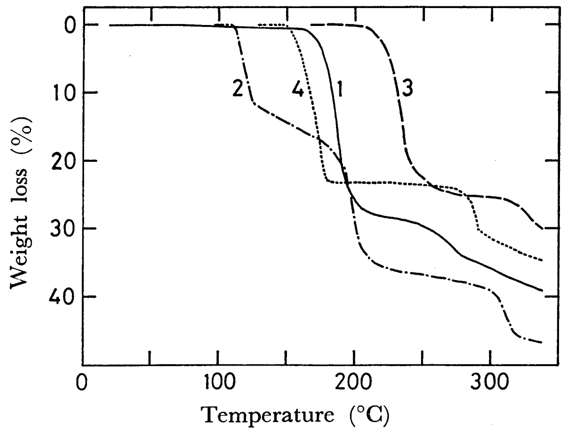

Fig. 3. The TG curves for complexes **5**(1), **7**(2), **8**(3), and **10**(4).

obtained by keeping Complex **1** at *ca.* 95 °C for 2 h in an atmosphere of flowing nitrogen. Complex **2** loses a further pyridine molecule in the same temperature range in which Complex **1** loses two pyridine molecules (weight loss at 160 °C; found: 17.14%, calcd for py: 16.93%.). Based on these results and on the IR spectral data, which indicate that an uncoordinated pyridine molecule is contained in Complex **1**, but not in Complex **2**, it may be concluded that the former complex loses an uncoordinated pyridine molecule most easily. The pyridine in the residual compound, CoL$_2$(py), seems to be held much more tightly. Complex **3** begins to decompose at *ca.* 80 °C, and no stable intermediate is detected. Complex **4**, on the other hand, begins to liberate pyridine at 120 °C to give ZnL$_2$ in the temperature range of 160—250 °C to give ZnL$_2$ (weight loss at 200 °C; found: 20.31%, calcd for py: 20.04%.).

The TG curve for Complex **7** shows that the liberation of 4-methylpyridine takes place in three steps: *i.e.*, $ZnL_2\cdot 2B \xrightarrow[110\text{—}125\,°C]{-0.6B} ZnL_2\cdot 1.4B \xrightarrow[125\text{—}190\,°C]{-0.4B} ZnL_2\cdot B \xrightarrow[190\text{—}250\,°C]{-1B} ZnL_2$ (where B is 4-methylpyridine), although the metastable intermediate compounds have not been isolated. The TG curves for Complexes **8** and **10** indicate that these complexes lose 4-cyanopyridine in a single step (weight loss of **8** at 290 °C; found: 25.28%, calcd for 4-CN-py: 25.19%, and weight loss of **10** at 270 °C; found: 24.12%, calcd for 4-CN-py: 24.81%.).

For the five-coordinate complexes, a rough order of thermal stability, is estimated from the temperature at which the complexes begin to lose weight, is: ZnL$_2$(py)≤ZnL$_2$(4-CN-py)<CoL$_2$(4-CN-py).

Infrared Spectral Data. The infrared spectral data for the isolated complexes are shown in Table 3. In all of these complexes, the 3-hydroxy-2-methyl-4-pyronate ligand is coordinated to the metal ion through the two oxygen atoms of the carbonyl and hydroxyl groups, since the frequencies of the C=O and C=C stretching vibrations are smaller by *ca.* 50 cm^{-1} than those in the free ligand.[1)] The coordination of pyridine can be readily inferred from the shift of the 604 (an inplane ring deformation) and 405 cm^{-1} (an out-of-plane ring deformation) bands for uncoordinated pyridine to about 625 and 420 cm^{-1} respectively.[5—7)] The magnitude of the frequency shift depends on the stereochemistry of the complex and on the radii of the metal ions.[6)] For Complexes **1** and **3**, the bands due to both the coordinated and uncoordinated pyridines are observed. However, Complex **2** shows bands due to coordinated pyridine only. From these results, which are consistent with those of the thermogravimetric analysis, it may be concluded that two of the pyridine molecules in Complexes **1** and **3** are coordinated, while one is uncoordinated. Clark and Williams indicated that the 604 cm^{-1} band is more sensitive to the stereochemistry of the complex, but the frequencies of both the 604 and 405 cm^{-1} bands increase with a decrease in the ionic radius of the metal for the series of polymeric octahedral chloro compounds, M(py)$_2$Cl$_2$, where M=Mn(II), Fe(II), Co(II), Ni(II), and Cu(II).[7)] Complex **4** shows absorption at 640 and 420 cm^{-1}; the position of the former band is apparently higher than those of the other pyridine complexes. This difference may stem from the difference in stereochemistry, since the zinc complex has a five-coordinate structure, while the others are octahedral.

For the 4-methylpyridine complexes of metal halides, Gill and Kingdon previously noted that the bands due to 4-methylpyridine move to higher frequencies except for the band at 728 cm^{-1}, which moves to

TABLE 4. PMR SPECTRA OF THE ZINC(II) COMPLEXES IN CHLOROFORM SOLUTION (δ, ppm)

Compound	L⁻				py or 4-Me-py		
	CH_3	H^5	H^6	$J_{5,6}$	H^2, H^6	H^3, H^5	H^4 or CH_3
py					8.54	7.19	7.57
4	2.42	6.49	7.68	5.2 Hz	8.59	7.34	7.78
4-Me-py					8.41	7.06	2.31
7	2.47	6.53	7.69	5.2 Hz	8.42	7.12	2.34

a lower frequency.[8] They further pointed out that the magnitude of the shift of the bands in the monomeric octahedral complexes increases with the series from the manganese to the nickel complexes, particularly for the 996, 515, and 484 cm^{-1} bands of the free ligand. Table 3 shows that these tendencies are also observed in Complexes **5**, **6**, and **7** obtained in the present study, revealing that both of the 4-methylpyridine molecules are coordinated to the metal ion in these complexes.

With regard to the 4-cyanopyridine complexes, it is well known that, when the nitrile nitrogen is coordinated to a metal ion, the stretching frequency of the nitrile group moves to a higher value than that for the free ligand.[9-12] On the other hand, when the pyridine ring nitrogen is coordinated to the metal ion, the ν(CN) band at 2242 cm^{-1} suffers little influence, but the bands (1081, 1075sh, and 988 cm^{-1}) due to the ring-breathing mode suffer appreciable shifts.[9-12] In complexes **8**, **9**, and **10**, the nitrile stretching frequency is decreased a little and the ring-breathing frequencies are shifted (Table 3). These data suggest that 4-cyanopyridine in these complexes is coordinated to the metal ion *via* the ring nitrogen.

The metal-oxygen stretching bands are assigned tentatively by reference to the literature.[1,13]

PMR Spectra of Zn(II) Complexes. The PMR data for Complexes **4** and **7** in $CDCl_3$ solutions are shown in Table 4. The assignments are based on the relative peak areas and on a comparison with the spectra of $[ZnL_2(OH)_2]\cdot 1/2H_2O$,[1] pyridine, and 4-methylpyridine.[14] In the spectrum of Complex **4**, the resonance peaks due to pyridine are shifted downfield on ligation as compared to those of free pyridine. The shifts for the 2 and 6 protons are much smaller than those for the 3, 5, and 4 protons. The molecular weight of this complex was determined to be 400± 10 in chloroform, very close to the calculated value of 394.7, indicating that the compound is stable and retains the five-coordinate structure in chloroform. However, it is not certain whether the complex has a square pyramidal structure or a trigonal bipyramidal structure. In the case of Complex **7**, only one set of resonance peaks due to the pyrone and 4-methylpyridine was observed, although the data of the molecular weight of this complex indicated that the complex dissociates extensively in chloroform. This result suggests that the dissociation and addition reactions of 4-methylpyridine in **7** are so rapid as to average the magnetic environments. The magnitudes of the downfield shift of the 2 and 6 protons of pyridine and 4-methylpyridine are considerably small as compared with those of the 3 and 5 protons of the base. This might be attributable to the operation of the magnetic anisotropy effect of the carbonyl group of the pyronate ligand on the 2 and 6 protons. Unfortunately, Complex **10** is not soluble enough to give a PMR spectrum in nondonor common solvents.

The analogous pyridine or 4-methylpyridine adducts of bis(acetylacetonato)zinc(II) have been previously reported by Graddon and Weeden.[15] Their measurement of the molecular weight of the compounds showed that the mono-adducts, [Zn(acac)$_2$(py)] and [Zn(acac)$_2$(4-Me-py)], are monomeric in benzene and triphenylmethane, whereas [Zn(acac)$_2$(4-Me-py)$_2$] dissociates in these solutions to form a five-coordinate mono-adduct, while [Zn(acac)$_2$(py)$_2$] is extremely unstable, losing pyridine rapidly even in the solid state to give monopyridine compound. From these properties of the adducts and the absence of crystal-field stabilization in the octahedral zinc(II) complexes, they inferred that the five-coordinate adduct is more favorable for Zn(II) than the octahedral bis-adduct.[15] In the present pyridine, 4-methylpyridine, and 4-cyanopyridine adducts of bis(3-hydroxy-2-methyl-4-pyronato)zinc(II), the five-coordinate adducts seem also to be favorable, although we could not isolate $[ZnL_2(4\text{-Me-py})]$.

Electronic Spectra and Magnetic Data. The reflection spectra of the cobalt(II) and nickel(II) complexes are shown in Figs. 4 and 5 respectively, their magnetic moments being listed in Table 1. Complexes **2**, **5**, and **8** show bands at 7.4(sh), 8.7, 17.8, and *ca.* 23.0 kK; 9.3, 16.8(sh), 17.8, and 21.7 kK; and 8.0, *ca.* 17.5, *ca.* 20.0, and 22.2 kK, respectively. From the spectra and the observed magnetic moments of **2**(5.02 B.M.), **5**(4.87 B.M.), and **8**(4.66 B.M.), it may be inferred that Complexes **2** and **5** are octahedral and Complex **8** is octahedral or five-coordinated, since the magnetic moments previously reported for the high-spin octahedral and five-coordinate cobalt(II) complexes lie in the ranges of 4.7—5.2 and 4.3—5.5 B.M. respectively.[16] However, taking account of the IR data for Complex **8**, which show that 4-cyanopyridine is coordinated to the cobalt ion solely with the ring nitrogen, the possibility of an octahedral structure for Complex **8** seems to be excluded. Furthermore, it has been reported that, for high-spin metal complexes, the five-coordination is favored in the order of: Co(II), Cu(II), Zn(II)>Fe(II), Ni(II)>Mn(II).[17] In the present work, the 4-CN-py adduct of cobalt(II) and Zn(II) complexes have one 4-CN-py moleucle, while the corresponding nickel(II) adducts has two 4-CN-py molecules, in conformity with the above series,

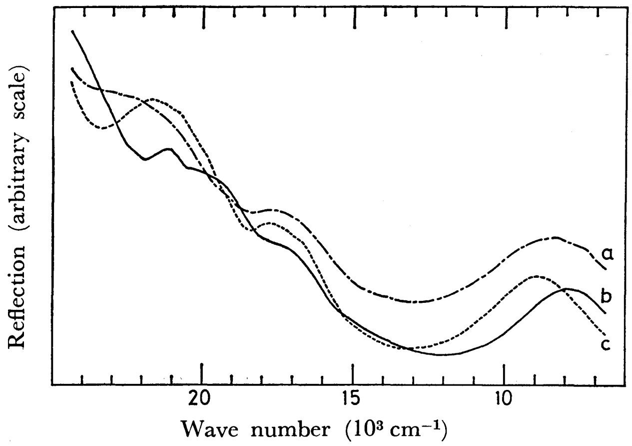

Fig. 4. The reflection spectra of complexes **2**(a), **8**(b), and **5**(c).

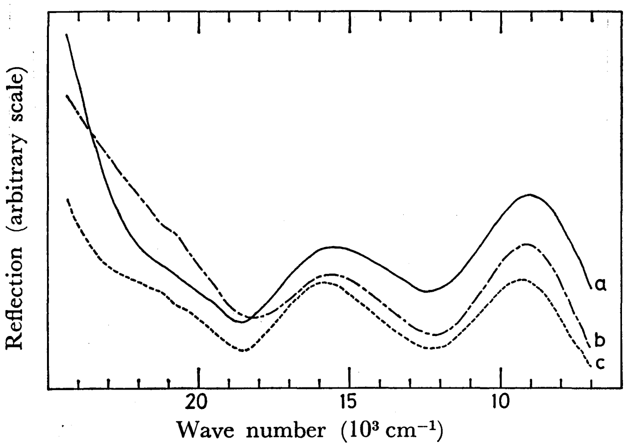

Fig. 5. The reflection spectra of complexes **9**(a), **3**(b), and **6**(c).

The reflection spectra of Complexes **9**, **3**, and **6** in the 20—7 kK region exhibit bands at 9.0 and 15.5 kK; 9.2 and 15.6 kK, and 9.3 and 15.8 kK respectively. The order of the increasing wave numbers of the bands is consistent with the order of the increasing ligand-field strength of the base, (4-CN-py<py<4-Me-py). The spectra and the observed magnetic moments of **3**(3.17 B.M.), **6**(3.23 B.M.), and **9**(3.16 B.M.) suggest that these complexes are octahedral.

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