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The Effect of Steric Condition on the Structure of Cobalt(II), Nickel(II), and Copper(II) Complexes with Schiff Bases Obtained from Salicylaldehyde Derivatives and 9-Aminofluorene

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Cobalt(II), nickel(II), and copper(II) complexes with *N*-(9-fluorenyl)salicylideneaminates (abbreviated as X-sal-fl) have been examined in relation to the effect of steric condition on the structure of the metal complexes. Compounds of the type M(X-sal-fl)$_2$ and their pyridine adducts were isolated as crystals. Complexes of the type Cu(X-sal-fl)Cl were also obtained. Both in the solid state and in non-donor solvents, the complexes Co(X-sal-fl)$_2$ have a tetrahedral configuration, and Ni(X-sal-fl)$_2$ and Cu(X-sal-fl)$_2$ have a square-planar configuration. Possible structures of the pyridine adducts are discussed. The results indicate that the steric hindrance caused by fluorenyl is greater than that by diphenylmethyl.

Transition metal complexes with *N*-substituted salicylideneaminates (abbreviated as X-sal-R, a) vary widely in structure, depending upon the steric conditions arising from the substituent R.[1–3] Many 3d metal complexes with *N*-isopropyl- and *N*-diphenylmethylsalicylideneaminates (b, c)[4] were synthesized and the steric effect of the substituents on the structure of the metal complexes was discussed. The present work deals with cobalt(II), nickel(II), and copper(II) complexes with *N*-(9-fluorenyl)salicylideneaminates (d), whose steric condition is expected to differ slightly from that of the *N*-diphenylmethyl-derivatives.

Experimental

Materials. Analytical data of the new complexes are given in Tables 1 and 2.

Bis[N-*(9-fluorenyl)salicylideneaminato*]*metal(II) Complexes, M(X-sal-fl)$_2$ (M=Co, Ni, Cu).* These complexes were obtained as crystals by methods similar to those reported previously.[1,2,4] Two methods were used. (A) To a suspension of bis(salicylaldehydato)metal(II) (0.01 mol) in ethanol (20 ml) was added 9-aminofluorene (0.02 mol) at 60 °C under stirring. (B) To a solution of X-salicyldehyde (0.01 mol) in ethanol (25 ml) was added 9-aminofluorene (0.01 mol) at 60 °C and the mixture was stirred for 30 min. A solution of the appropriate metal(II) salt (0.005 mol) in ethanol (15 ml) was added to the resulting solution and stirred for 15 min, followed by addition of an aqueous solution of sodium carbonate (0.01 mol).

In both cases the reaction mixture was heated on a water-bath at 60 °C for about 2h. The resulting precipitate was recrystallized from chloroform.

The cobalt(II), nickel(II), and copper(II) complexes obtained are orange, olive-green and olive-green, respectively. They are moderately soluble in chloroform and benzene with the exception of bis[*N*-(9-fluorenyl)-2-hydroxy-1-naphthylmethyleneaminato]nickel(II), abbreviated as Ni(5,6-benzo-sal-fl)$_2$, which is less soluble than the others. They are almost insoluble in methanol, ethanol and acetone. The cobalt(II) and nickel(II) complexes are almost insoluble in cold pyridine but soluble in hot pyridine, accompanied by colour change. The copper(II) complexes are soluble in pyridine at room temperature, the colour of the solution changing gradually with time.

Bis[N-*(9-fluorenyl)salicylideneaminato*]*metal(II) Monopyridine Adducts, M(X-sal-fl)$_2$·py (M=Co, Ni, Cu).* These adducts were obtained as crystals when a hot saturated solution of the parent complex was allowed to stand overnight in a

TABLE 1. ANALYTICAL DATA OF NICKEL(II) AND COBALT(II) COMPLEXES

Compound	Calcd, %			Found, %			μ	Mp °C
	C	H	N	C	H	N		
Ni(H-sal-fl)$_2$	76.58	4.50	4.47	76.45	4.51	4.36	dia	263
Ni(5-Br-sal-fl)$_2$[a]	58.70	3.22	3.40	58.41	3.37	3.55	dia	269
Ni(5-Cl-sal-fl)$_2$	69.00	3.77	4.02	68.89	3.84	4.01	dia	288
Ni(3-CH$_3$O-sal-fl)$_2$[b]	72.44	4.78	4.02	72.64	4.92	4.43	dia	206
Ni(5,6-benzo-sal-fl)$_2$	79.25	4.43	3.85	79.08	4.41	3.87	dia	195
Co(H-sal-fl)$_2$	76.55	4.50	4.46	76.51	4.48	4.38	4.06	185
Co(5-Br-sal-fl)$_2$	61.17	3.34	3.57	60.84	3.37	3.75	4.23	235
Co(5-Cl-sal-fl)$_2$	68.97	3.76	4.02	68.55	3.79	4.16	4.23	217
Co(5,6-benzo-sal-fl)$_2$	79.22	4.43	3.85	78.99	4.47	3.83	4.21	236
Ni(5-Br-sal-fl)$_2$·py[c]	62.53	3.62	4.86	62.11	3.82	4.89	dia	dec
Ni(5-Cl-sal-fl)$_2$·py	69.71	4.03	5.42	69.62	3.95	5.45	dia	dec
Ni(5,6-benzo-sal-fl)$_2$·py	79.32	4.64	5.23	78.91	4.58	5.15	dia	dec
Co(5-Cl-sal-fl)$_2$·py	70.27	4.03	5.42	69.99	4.03	5.89	4.25	dec
Co(5,6-benzo-sal-fl)$_2$·py	78.69	4.62	5.22	78.90	4.62	5.28	2.52	dec

μ: BM at room temperature. a) With 1/3 CHCl$_3$. b) With 1/2H$_2$O. c) Notation py denotes a pyridine molecule.

Table 2. Analytical data of copper(II) complexes

Compound	Calcd, %			Found, %			Mp °C
	C	H	N	C	H	N	
Cu(H-sal-fl)$_2$	75.99	4.46	4.43	75.91	4.45	4.46	205
Cu(5-Br-sal-fl)$_2$[a]	58.08	3.14	3.36	58.13	3.29	3.39	217
Cu(5-Cl-sal-fl)$_2$[a]	65.13	3.69	3.80	65.34	3.81	3.90	207
Cu(5-NO$_2$-sal-fl)$_2$[b]	64.90	3.81	7.56	64.42	3.84	7.55	239
Cu(5,6-benzo-sal-fl)$_2$	78.92	4.41	3.85	78.68	4.39	3.84	220
Cu(5,6-benzo-sal-fl)$_2$·py	78.45	4.60	5.18	78.91	4.50	5.17	dec
Cu(H-sal-fl)Cl	62.66	3.68	3.65	62.84	3.83	3.60	174
Cu(5-Br-sal-fl)Cl	51.97	2.84	3.03	52.26	2.95	3.12	177
Cu(5-Cl-sal-fl)Cl	57.68	3.14	3.35	57.68	3.23	3.54	179

a) 1/3 $CHCl_3$. b) 1/2H_2O.

refrigerator. The cobalt(II) and nickel (II) complexes are reddish brown, and the copper(II) complex is dark green. They are soluble in cold pyridine, chloroform and acetone and almost insoluble in methanol and ethanol. They do not lose a pyridine molecule in the atmosphere at room temperature.

Cu(X-sal-fl)Cl (X=H, 5-Br, 5-Cl). Salicylaldehyde (0.01 mol) was added to a solution of copper(II) chloride hydrate (0.01 mol) in ethanol (20 ml) under stirring at 70 °C. After 10 min a solution of sodium carbonate (0.005 mol) in water (5 ml) was added to the resulting solution; a yellowish green precipitate appeared in the solution. To this mixture was added 9-aminofluorene (0.01 mol), and stirred for 1 h at 70 °C. Brown microcrystals were filtered off and washed with ethanol. Recrystallization was unsuccessful.

They are insoluble in benzene, methanol, ethanol and water but are soluble in chloroform, undergoing decomposition.

Measurements. Electronic absorption spectra of the complexes were measured on a Shimadzu MPS 50L spectrophotometer. Solubility of some complexes in appropriate solvents was too low for spectral measurements. Infrared spectra of the complexes were recorded as Nujol mulls using a Hitachi EPI-S2 infrared spectrophotometer and a Hitachi 215 infrared spectrophotometer.

Magnetic measurements were carried out at room temperature by the Gouy method. Powder diffraction patterns were obtained with a Rigakudenki 4001-A2 diffractometer using Co*Kα* radiation and an iron filter.

Results and Discussion

Nickel(II) and Cobalt(II) Complexes. Complexes of the type Ni(X-sal-fl)$_2$ are diamagnetic in the solid state, indicating that they have a four-coordinate, square-planar structure. They show electronic absorption spectra typical of the square-planar nickel(II) complexes in non-donor solvents or in the solid state (Table 3). A d-d band with a maximum at about 16000 cm^{-1}, which may be ascribed to a $d_{x^2-y^2}\leftarrow d_{xy}$ transition, is slightly lower than that of the *N*-diphenylmethyl analogue,[4] implying that the ligand field produced by X-sal-fl is weaker than that by X-sal-dpm (dpm, diphenylmethyl).

In spite of the steric hindrance, the tetrahedral species has neither been isolated as crystals nor detected in solution at room temperature for the nickel(II) complexes of the type Ni(X-sal-fl)$_2$. This finding is similar to that for Ni(X-sal-dpm)$_2$ but contrary to that for Ni(X-sal-*i*-C_3H_7)$_2$.[4]

Table 3. Main d-d absorption maxima of nickel(II) and cobalt(II) complexes of the type M(X-sal-fl)$_2$

Compound	Solvent	ν (log ε)
Ni(H-sal-fl)$_2$	$CHCl_3$	15.9(1.95)
	Nujol	16.0
	pyridine[a]	17.5(2.45)
Ni(5-Br-sal-fl)$_2$	$CHCl_3$	16.0(1.90)
	pyridine[a]	17.5(2.38)
Ni(5-Cl-sal-fl)$_2$	$CHCl_3$	15.9(1.90)
Ni(3-CH_3O-sal-fl)$_2$	$CHCl_3$	15.7(1.91)
Ni(5,6-benzo-sal-fl)$_2$	Nujol	16.0
Co(H-sal-fl)$_2$	$CHCl_3$	7.5(1.78),10.6(1.56)sh, 17.5(1.88)
	pyridine[a]	6.4(1.30), 10.5(0.81)
Co(5-Br-sal-fl)$_2$	$CHCl_3$	7.5(1.81),10.3(1.63)sh, 17.5(1.82)
Co(5,6-benzo-sal-fl)$_2$	$CHCl_3$	7.8(1.90),10.4(1.50)sh

ν: 10^3 cm^{-1}. a) With the solution obtained by heating at 70 °C for a few hours.

It has not been possible to isolate tris(Schiff base)-cobalt(III) complexes so far, probably owing to the steric condition. The cobalt(II) complexes Co(X-sal-fl)$_2$ are paramagnetic with magnetic moments of 4.0—4.3 BM, which lie in the range expected for the tetrahedral cobalt(II) complex. They also show electronic absorption spectra typical of the tetrahedral cobalt(II) complex (Table 3). The d-d band at 7500—8000 cm^{-1} with a shoulder at 10300—10600 cm^{-1} may be assigned to a transition $^4T_1(F)\leftarrow{}^4A_2$.

Monopyridine adducts of the type M(X-sal-fl)$_2$·py were isolated as crystals. Six-coordinate bis(pyridine)-adducts have neither been isolated in crystals nor detected in solution, in contrast to the *N*-diphenylmethyl analogues.[4] The steric hindrance due to the ligands X-sal-fl is thus greater than that due to X-sal-dmp.

The pyridine molecule in M(X-sal-fl)$_2$·py is not readily lost. No weight loss was observed when the adducts were heated at 100 °C for several hours. It is likely that the pyridine molecule is bound with the metal(II) ion in the adducts. This presumption seems to be borne out by the observation that the parent complexes are not soluble in pyridine at room temperature, and that the adducts M(X-sal-fl)$_2$·py isolated from hot pyridine are readily soluble in cold pyridine. Since the pyridine adducts show infrared ν(C–O)

(1520—1530 cm^{-1}) and ν(C=N) bands (1600—1610 cm^{-1}) at almost the same frequencies as those of the parent complexes, it is presumed that the ligands X-sal-fl in the pyridine adducts function as bidentates, as in the parent complexes. All these findings indicate that the pyridine adducts with cobalt(II) and nickel(II) complexes have a five-coordinate structure.

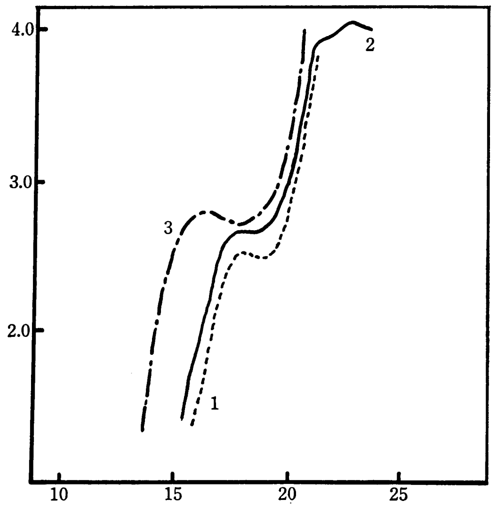


Fig. 1. Electronic absorption spectra of nickel(II) complexes: 1. Ni(5,6-benzo-sal-fl)$_2$·py, in Nujol, scale arbitrary; 2. Ni(5,6-benzo-sal-fl)$_2$·py, in pyridine; 3. Ni(5,6-benzo-sal-fl)$_2$, in Nujol, scale arbitrary.

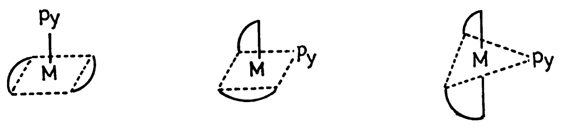
Since the nickel(II) complexes Ni(X-sal-fl)$_2$·py are diamagnetic, they are considered to be spin-paired, five-coordinate complexes. As shown in Fig. 1, the solid state spectra of Ni(X-sal-fl)$_2$·py, which are essentially similar to the spectra of their pyridine solutions, have a main d-d band at 17400—17800 cm^{-1}. The band maxima are much higher than those (15700—16000 cm^{-1}) of the parent complexes, which have a diamagnetic square-planar structure, and the intensity of the d-d bands for the pyridine adducts is significantly higher than of the parent complexes. These findings are also in agreement with the five-coordinate structure for the pyridine adducts. The principal spectral data are summarized in Table 4.

TABLE 4. MAIN d-d ABSORPTION MAXIMA OF M(X-sal-fl)$_2$·py, M^{II} BEING Co AND Ni

Compound	Solvent	ν (log ε)
Ni(5-Br-sal-fl)$_2$·py	Nujol	17.6
	pyridine	17.5(2.38)
Ni(5-Cl-sal-fl)$_2$·py	Nujol	17.6
	pyridine	17.4(2.37)
	$CHCl_3$	17.5(2.32)
Ni(5,6-benzo-sal-fl)$_2$·py	Nujol	17.8
	pyridine	18.0(2.62)
	$CHCl_3$	18.0(2.62)
Co(5-Cl-sal-fl)$_2$·py	Nujol	6.6, 11.7
	pyridine	6.7(1.38), 11.5(1.14)
	$CHCl_3$	5.3(1.20), 8.1(1.33)
Co(5,6-benzo-sal-fl)$_2$·py	Nujol	5.3, 8.3
	pyridine	5.5(1.42), 8.1(1.28)
	$CHCl_3$	5.5(1.50), 8.2(1.47)

ν: 10^3 cm^{-1}.

Two types of structure may be considered for the five-coordinate complexes, trigonal-bipyramidal and square-pyramidal. Spin-paired, five-coordinate, trigonal-bipyramidal nickel(II) complexes having NP_3Cl, NP_3Br, and NAs_3Br donors sets[6] were reported to show a d-d band at a much lower frequency than the pyridine adducts (N_3O_2 set) obtained in the present work (about 18000 cm^{-1}). Even the trigonal bipyramidal complex with the P_4Cl donor set shows the band at 17500 cm^{-1}, although the P_4Cl donor set is expected to produce considerably stronger ligand field than the N_3O_2 set. The trigonal-bipyramidal structure, therefore, seems to be unlikely. On the contrary, the spectra of Ni(X-sal-fl)$_2$·py may reasonably be interpreted on the basis of the model of spin-paired, five-coordinate, square-pyramidal stereochemistry.[5] For the square-pyramidal structure II rather than structure I (Fig. 2) is considered to be more likely, judging from their formation reaction; the pyridine adducts are obtained only on heating the parent complexes in pyridine. Simple axial addition of a pyridine molecule to the square-planar complex would readily produce structure I, for instance, without heating, if this species were stable enough at all. This, however, is not the case. The very high frequencies of the d-d band maxima for Ni(X-sal-fl)$_2$·py also favor structure II, suggesting that the bond between the nickel(II) ion and the axial fifth donor atom is weak.



(I) (II) (III)

Fig. 2. Some possible structures for M(5,6-benzo-sal-fl)$_2$·py (M=Co, Ni, and Cu).

The d-d band maxima in the spectra of the pyridine adducts in chloroform are almost the same as those of the pyridine adducts in pyridine or in the solid state, indicating that the structure of the adducts in the solid state is retained in the chloroform solution.

TABLE 5. X-RAY POWDER DIFFRACTION DATA OF M(5,6-benzo-sal-fl)$_2$·py, USING Co$K\alpha$ RADIATION WITH AN IRON FILTER

M=Co		M=Ni	
d, Å	I	d, Å	I
11.41	100	11.41	100
8.81	15	8.78	12
6.94	12	6.94	10
5.69	40	5.71	45
4.95	6	4.95	6
4.77	7	4.77	7
4.38	7	4.38	7
4.14	8	4.12	7
3.65	4	3.65	4

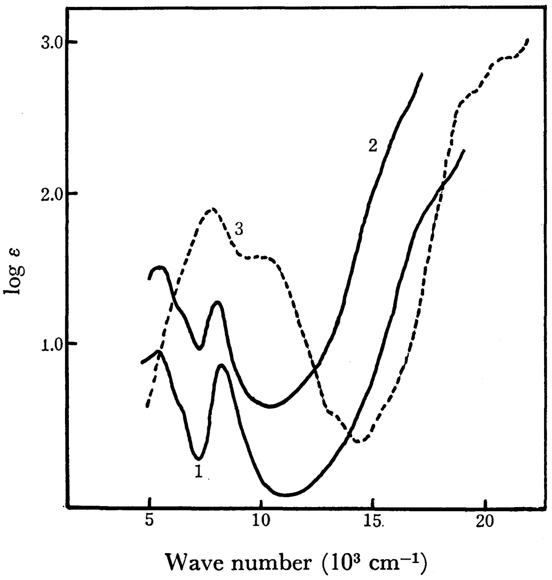


Fig. 3. Electronic absorption spectra of cobalt(II) complexes: 1. Co(5,6-benzo-sal-fl)$_2$·py, in Nujol, scale arbitrary; 2. Co(5,6-benzo-sal-fl)$_2$·py, in pyridine; 3. Co(5,6-benzo-sal-fl)$_2$, in chloroform.

Two types of cobalt(II) pyridine adducts were isolated as a solid, one being spin-paired and the other spin-free. One of them, Co(5,6-benzo-sal-fl)$_2$·py, is paramagnetic with a moment of 2.53 BM and is thus regarded to be a spin-paired, five-coordinate complex. Its X-ray powder diffraction pattern (Table 5) is almost the same as that of Ni(5,6-benzo-sal-fl)$_2$·py, which was presumed to consist of a spin-paired, five-coordinate complex. This is also borne out by the infrared spectrum in the whole 250—4000 cm^{-1} region of the cobalt(II) complex, which is slmost the same as that of the nickel(II) analogue. It is thus presumed that Co(5,6-benzo-sal-fl)$_2$·py has the same structure as that of Ni(5,6-benzo-sal-fl)$_2$·py, possibly a spin-paired, square-pyramidal structure. The solid state spectrum of this cobalt(II) compound is essentially similar to the spectrum of its pyridine solution having a rather narrow band at 8400 cm^{-1}, in addition to a band at about 5300 cm^{-1} (Fig. 3). The spectrum is found to be correlated with that of a spin-paired, five-coordinate, square-planar cobalt(II) complex.[7] A remarkable similarity of its solid spectrum to that of the spin-paired, square-planar cobalt(II) complex indicates that the bond between the cobalt(II) ion and the axial fifth donor atom is weak, as in the corresponding nickel(II) analogue.

In contrast to Co(5,6-benzo-sal-fl)$_2$·py, Co(5-Cl-sal-fl)$_2$·py is paramagnetic with a moment of 4.25 BM, indicating that the latter is a spin-free, five-coordinate cobalt(II) complex. The solid state spectrum of Co(5-Cl-sal-fl)$_2$·py, which is very similar to the spectrum of its pyridine solution, differs a great deal from that of the tetrahedral cobalt(II) complex as well as from that of the six-coordinate, octahedral compex. lIn contrast, the solid spectrum is similar to the spectra of the spin-free, five-coordinate cobalt(II) complexes.[8]

The spectrum of Co(5-Cl-sal-fl)$_2$·py in chloroform differs considerably from its solid state spectrum, but is remarkably similar to the solid spectrum of Co(5,6-benzo-sal-fl)$_2$·py, which was presumed to have a spin-paired, five-coordinate structure (Fig. 4). It is interesting to note that the conversion of the spin state, probably accompanied by configurational change, occurs in this pyridine adduct on going from the solid state to the chloroform solution. If the pyridine molecule were lost from Co(5-Cl-sal-fl)$_2$·py on dissolution in chloroform, remaining complex Co(5-Cl-sal-fl)$_2$ would assume a tetrahedral configuration.

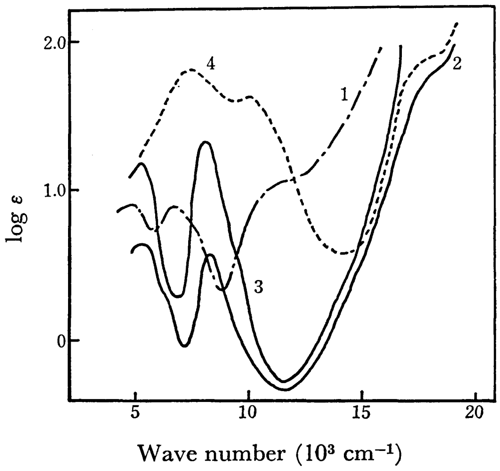


Fig. 4. Electronic absorption spectra of cobalt(II) complexes: 1. Co(5-Cl-sal-fl)$_2$·py, in Nujol, scale arbitrary; 2. Co(5-Cl-sal-fl)$_2$·py, in Nujol; 3. Co(5-Cl-sal-fl)$_2$·py, in chloroform; 4. Co(5-Cl-sal-fl)$_2$, in chloroform.

The pyridine solutions of Co(H-sal-fl)$_2$ and Co(5-Br-sal-fl)$_2$, obtained by heating the complexes in pyridine, show electronic absorption spectra similar to the solid spectrum of Co(5-Cl-sal-fl)$_2$·py, which was presumed to have a spin-free, five-coordinate complex.

Copper(II) Complexes. Electronic absorption spectra of copper(II) complexes of the type Cu(X-sal-fl)$_2$ in non-donor solvents have a d-d band at about 16000 cm^{-1}. From the frequency of the band, it may be reasonable to assume that these copper(II) complexes in non-donor solvents have an essentially square-planar configuration.

The complexes Cu(X-sal-fl)$_2$ are soluble in pyridine at room temperature, but the colour of the solution changes with time. The complexes, which are originally olive-green, turn bluish green immediately upon dissolution in pyridine, becoming greenish brown by reflected light (orangish brown by transmitted light) after more than 24 h. Absorption spectra of Cu(5-Cl-sal-fl)$_2$ in pyridine are shown as representative data in Fig. 5.

The spectrum obtained within 8 min after dissolution in pyridine (curve 2) has a broad d-d band, which shifts toward significantly lower frequencies than the d-d band of the original complex. It is recognized that curve 2 is similar to the spectrum expected for the five-coordinate species formed by axial addition of a pyridine molecule to the square-planar copper(II) complexes.[9] When dissolved in pyridine the first d-d band of the copper(II) complex shifts toward considerably lower frequencies, becoming also much broader than that of the complexes in non-donor solvents. In fact, curve 2

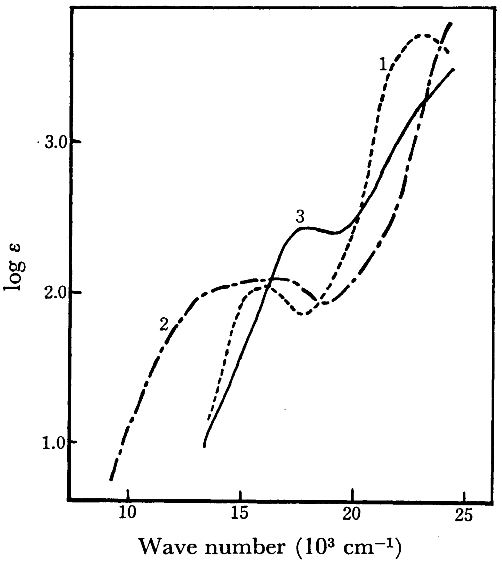
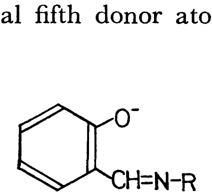


Fig. 5. Electronic absorption spectra of Cu(5-Cl-sal-fl)$_2$: 1. in chloroform; 2. in pyridine (measured within 8 min after dissolution); 3. in pyridine (measured after 24 h).

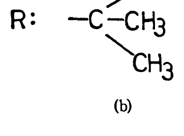
is very similar to the spectra of Cu(X-sal-dpm)$_2$ in pyridine.[4] The species corresponding to curve 2, therefore, may be assumed to have structure I in Fig. 2, or a structure slightly distorted from it.

The spectrum recorded after more than 24 h (curve 3), which differs entirely from curves 1 and 2, has a d-d band with a distinct maximum at about 18000 cm^{-1}. The pyridine adduct Cu(5,6-benzo-sal-fl)$_2$·py also shows a similar solid state spectrum having a d-d band at nearly the same frequency as that of curve 3. It is most likely that the main species existing after 24 h in pyridine may have the same structure as that of Cu(5,6-benzo-sal-fl)$_2$·py in the solid state. The pyridine adduct shows infrared ν(C–O) (1530 cm^{-1}) and ν(C=N) (1610 cm^{-1}), which are almost the same frequencies as those of the parent complexes. It is thus very likely that the ligand functions as a bidentate, as in the parent complexes.

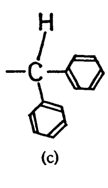
It seems that one of the most probable structures of the species corresponding to curve 3 is structure II in Fig. 2. The considerably high frequency of the d-d band maximum seems to exclude a trigonal-bipyramidal structure,[10] which would show the corresponding band at a much lower frequency. The bond between the copper(II) and the axial fifth donor atom would not be strong.



(a)



(b)



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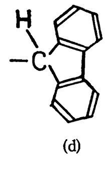

(d)

Complexes of the type Cu(X-sal-fl)Cl (X=H, 5-Br, 5-Cl) at room temperature have subnormal magnetic moments of 1.35, 1.34 and 1.39 BM, respectively, which are much lower than the normal magnetic moments expected for the d^9 system. A sort of interaction, therefore, may be expected to exist between two copper(II) ions, as in complexes of a similar type.[11–13] Their infrared ν(C–O) bands appear at 1550 (X=H), 1535 (X=5-Br) and 1540 cm^{-1} (X=5-Cl), respectively. They are significantly higher than those of Cu(X-sal-fl)$_2$, which appear at 1525 cm^{-1} for X=H, 5-Br and 5-Cl. Based upon the criteria proposed previously,[11–13] the present finding on the infrared spectra seems to indicate that these complexes have a binuclear structure with the phenolic oxygen atom bridging two copper(II) ions.

Their solid state electronic spectra, which are similar to each other, show the first d-d band as a shoulder at about 11500 cm^{-1} and the next shoulder at 15600 cm^{-1}, more intense absorption rising up in the higher frequency region. Kato *et al.*[12] classified the spectra of the Cu(X-sal-alkyl)Cl type complexes into two groups, designating them as B- and Y-type. The spectra of Cu(X-sal-fl)Cl are similar to those of B-type, their magnetic moments also being in the range expected for B-type complexes.

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