The Coordinative Behavior of the Ethereal Oxygen Atom in Cobalt, Nickel and Copper Complexes with Schiff Bases Obtained from Salicylaldehyde Derivatives and 2-(Aminomethyl)furan

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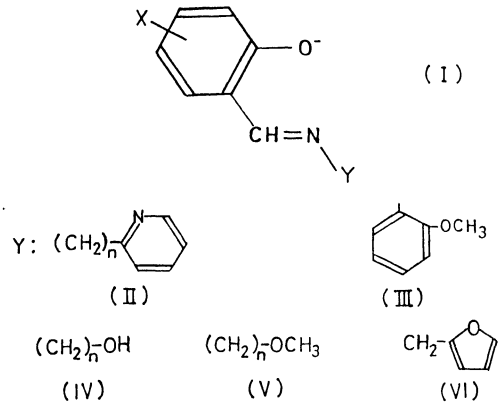
Cobalt(II), cobalt(III), nickel(II), and copper(II) complexes with *N*-(2-furylmethyl)salicylideneaminates (abbreviated as X-sal-fum) were synthesized. In addition to the M (X-sal-fum)$_2$ type complexes, those of the formula Cu(X-sal-fum)Cl were obtained in crystals. The complexes Co(X-sal-fum)$_3$ are six-coordinate, octahedral. The cobalt(II) complex is four-coordinate, tetrahedral and the nickel(II) complexes are four-coordinate, planar. In these complexes, the ligands X-sal-fum function as bidentates, the furan oxygen atom not being bound to the metal ions. The results are compared with those reported previously for related ligands. It is most likely that the complexes Cu(X-sal-fum)Cl consist of binuclear complexes with spin-spin interaction between copper(II) ions.

Ligands of the type (I), which bear a donor atom in Y, form various complexes with transition metal ions. The structure of these metal compleses is expected to vary in a delicate and complicated way. In previous papers, the present authors studied the synthesis and structure of transition metal complexes with ligands (II),[1] (III), (IV),[2] and (V).[3,4] As extension of these studies, various metal complexes with *N*-(2-furylmethyl)-salicylideneiminates (VI, abbreviated as X-sal-fum) have been synthesized and their structure has been examined in the present work. The results are compared with those of the corresponding complexes with related ligands.



Experimental

Materials. Analytical data of new complexes obtained in the present work are shown in Table 1.

Bis[N-*(2-furylmethyl)salicylideneaminato)copper(II), Cu(X-sal-fum)*$_2$. To a suspension of bis(salicylaldehydato)copper(II) (0.01 mol) in 90% ethanol (50 ml) was added 2-aminomethylfuran (0.02 mol) drop by drop at about 60 °C. The resulting suspension was heated at the same temperature with stirring for about 30 min. An olive green precipitate was recrystallized from acetone to yield olive green (X=H, 5-Cl and 5-Br) or yellow brown (X=3-CH$_3$O) crystals. They are soluble in chloroform, benzene and acetone and moderately soluble in ethanol. The solubility of the complexes with X=5-Br and 3-CH$_3$O is lower than that of the others with X=H and 5-Cl.

Cu(X-sal-fum)Cl (X=H, 5-Cl). A solution of the Schiff base (0.01 mol) in ethanol (50 ml) was added at about 60 °C to a solution of copper(II) chloride dihydrate (0.01 mol) in a small amount of water. The mixture was stirred at

TABLE 1. ANALYTICAL DATA OF METAL COMPLEXES WITH X-sal-fum

Compound	Calcd, %			Found, %			μ[a]
	C	H	N	C	H	N	
Cu(H-sal-fum)$_2$	62.13	4.35	6.04	62.10	4.42	6.16	1.89
Cu(5-Cl-sal-fum)$_2$	54.09	3.40	5.26	53.16	3.46	5.15	1.83
Cu(5-Br-sal-fum)$_2$	46.72	2.94	4.54	45.91	2.93	4.61	1.83
Cu(3-CH$_3$O-sal-fum)$_2$	59.59	4.62	5.35	59.11	4.56	5.32	1.95
Cu(H-sal-fum)Cl	48.17	3.37	4.68	47.59	3.42	4.60	1.31
Cu(5-Cl-sal-fum)Cl	43.19	2.72	4.20	42.99	2.90	4.34	0.92
Ni(H-sal-fum)$_2$	62.78	4.39	6.10	62.16	4.44	5.97	dia
Ni(5-Br-sal-fum)$_2$	46.72	2.94	5.54	46.13	3.03	4.74	dia
Ni(3-CH$_3$O-sal-fum)$_2$	60.15	4.66	5.40	59.42	4.66	5.35	dia
Co(5-Br-sal-fum)$_2$	46.70	2.94	4.54	46.42	3.00	4.57	4.35
Co(H-sal-fum)$_3$	65.55	4.58	6.37	65.46	4.59	6.43	dia
Co(5-Cl-sal-fum)$_3$	56.67	3.57	5.51	55.64	3.57	5.46	dia
Co(5-Br-sal-fum)$_3$	48.24	3.04	4.69	47.31	3.04	4.68	dia
Co(3-CH$_3$O-sal-fum)$_3$	62.48	4.84	5.61	62.29	4.83	5.59	dia

a) μ: BM at room temperature.

this temperature for about 30 min. A brown crystalline precipitate was filtered off and washed with ethyl ether. Any attempt to recrystallize was unsuccessful. The compounds are dark brown (X=H) and yellowish brown (X=5-Cl), respectively. They are insoluble in water, but are soluble in chloroform, benzene, acetone, diethyl ether and ethanol to undergo decomposition.

The corresponding 5-bromo-complex (X=5-Br) was obtained as dark brown microcrystals. Although the elemental analysis for carbon, hydrogen and nitrogen slightly deviates from the formula Cu(5-Br-sal-fum)Cl, its properties agree with those expected for this compound. For example, the electronic spectrum and temperature dependence of magnetic susceptibilities are remarkably similar to those of Cu(H-sal-fum)Cl. The ν(C-O) band appears at about 1558 cm^{-1}, a value which lies in the same region as those of Cu(H-sal-fum)Cl and Cu(5-Cl-sal-fum)Cl.

Bis[N-*(2-furylmethyl)salicylideneaminato]nickel(II)*, *Ni(X-sal-fum)$_2$*. The complexes were prepared by a method similar to that for the corresponding copper(II) complexes. They are olive-green. Their solubility is similar to that of the copper(II) complexes.

Bis[N-*(2-furylmethyl)-5-bromo-salicylideneaminato]cobalt(II)*, *Co-(5-Br-sal-fum)$_2$*. The complex was prepared as red crystals by a method similar to that for the corresponding copper(II) complexes. Its solubility is similar to that of the copper(II) complexes.

Tris[N-*(2-furylmethyl)-salicylideneaminato]cobalt(III)*, *Co(X-sal-fum)$_3$*. The complexes were prepared as dark green crystals by a method similar to that for the copper(II) complexes, except that the ligand to metal ratio was 3 : 1 and that the reaction was conducted for about two to three hours. Addition of such an oxidizing agent as hydrogen peroxide accelerates the oxidation of cobalt(II) to cobalt(III). Their solubility is similar to that of the copper(II) and nickel(II) complexes.

Measurements. Electronic absorption spectra of the complexes were measured on a Shimadzu MPS-50L spectrophotometer. Infrared spectra were obtained from Nujol mulls using a Hitachi EPI-S2 infrared spectrophotometer.

Magnetic measurements at room temperature were carried out by the Gouy method using $CoHg(SCN)_4$ as a calibrant. Magnetic susceptibilities over a temperature range (76—320 K) were measured by the Faraday method. The temperature was controlled with an electric regulating system. For the complexes Cu(X-sal-fum)Cl, the Bleaney-Bowers Eq. 1 was found to hold,

$$\chi_A = g^2N\beta^2/3kT(1+1/3\exp(-2J/kT))^{-1} + N\alpha \quad (1)$$

where the symbols have their usual meanings.

Results and Discussion

Cobalt(II), Cobalt(III), and Nickel(II) Complexes. Both the bis(Schiff base)cobalt(II) and tris(Schiff base)cobalt(III) have been isolated. The cobalt(II) complex Co(5-Br-sal-fum)$_2$ is paramagnetic with a moment of 4.35 BM and shows an electronic absorption spectrum typical of the tetrahedral cobalt(II) complex, as shown in Table 2. The d-d band at about 8.2 kK may be assigned to a transition $^4T_1(F) \leftarrow {}^4A_2$. The cobalt(III) complexes Co(X-sal-fum)$_3$ are diamagnetic, and their electronic spectra are typical of the six-coordinate cobalt(III) complexes. The band at about 16.4—16.6 kK may be assigned to a transition $^1T_{1g} \leftarrow {}^1A_{1g}$, in the scheme of O_h field symmetry. Their d-d band maxima lie at almost the same frequencies as those of the corresponding *N*-alkylsalicylideneaminato-complexes.[5] In any of these complexes, the furan oxygen atom is not bound with the cobalt ion.

As shown in Table 1, complexes of the type Ni(X-sal-fum)$_2$ 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) complex in non-donor solvents as well as in the solid state. The band at about 16 kK may be assigned to a $d_{x^2-y^2} \leftarrow d_{xy}$ transition. No absorption is observed at about 10—11 kK or lower frequencies, where the octahedral or tetrahedral nickel(II) complex is expected to absorb. Accordingly, it may be concluded that no association of the planar complexes occurs in solution at room temperature. In these nickel(II) complexes, the ligands X-sal-fum are found to function as bidentates, the furan oxygen atom not being bound to the nickel(II) ion.

It may be interesting to compare the results in the present work with those for related ligands as regards the coordination of the oxygen atom in the side chain Y. Of the ligands (III)—(VI), *n* being 2, (IV) has the highest ability to function as a terdentate ligand; the alcoholic oxygen atom is bound to the nickel(II) ion. Previous studies have shown that the nickel(II) complexes Ni(X-sal-Y)$_2$, Y being CH(R)CH(R)OH, have an octahedral configuration, in which the OH-group is bound to the nickel(II) ion.[6]

The oxygen atom in CH_3O has slightly lower capacity

TABLE 2. MAIN ABSORPTION MAXIMA OF M(X-sal-fum)$_2$ AND M(X-sal-fum)$_3$

Compound	Solvent	ν (log ε)
Ni(H-sal-fum)$_2$	$CHCl_3$	16.2(1.84), 23.7(3.66)
Ni(3-CH_3O-sal-fum)$_2$	$CHCl_3$	16.1(1.91), 23.6(3.62)
	Nujol	16.0
Ni(5-Br-sal-fum)$_2$	Nujol	16.0
Co(5-Br-sal-fum)$_2$	$CHCl_3$	8.2(1.67), 11.4(1.49), 26.4(3.93)
Co(H-sal-fum)$_3$	$CHCl_3$	16.6(2.48), 25.7(3.95)
Co(5-Cl-sal-fum)$_3$	$CHCl_3$	16.6(2.58), 25.2(3.95)
Co(5-Br-sal-fum)$_3$	$CHCl_3$	16.6(2.57), 25.2(3.92)
Co(3-CH_3O-sal-fum)$_3$	$CHCl_3$	16.4(2.62), 25.1(3.92)

ν: 10^3 cm^{-1}, sh: shoulder.

to be coordinated with the nickel(II) ion. It was revealed previously that $Ni(H\text{-}sal\text{-}CH_2CH_2OCH_3)_2$ is square-planar in the solid state, the OCH_3-group not being bound to the nickel(II) ion, although complexes of the type $Ni(H\text{-}sal\text{-}CH(R)CH_2OCH_3)_2$ have a six-coordinate, octahedral configuration with the CH_3O-group bound to the nickel(II) ion.

The present study shows that of the ligands (III)—(VI), n being 2, the furan oxygen atom in (VI) has the lowest tendency to be bound to the nickel(II) ion. In this respect, the ligand (III) seems to lie between (IV) and (VI). Previous studies have revealed that the CH_3O-group is bound to the metal ion in many of the $Ni(X\text{-}sal\text{-}o\text{-}CH_3O\text{-}C_6H_4)_2$ and $Co(X\text{-}sal\text{-}o\text{-}CH_3O\text{-}C_6H_4)_2$ type complexes.[3,7]

Summarizing the discussion given above, the following order may be derived as to the donor strength of the oxygen atom in Y of the ligands (I): $CH_2CH_2OH > C_6H_4OCH_3(o\text{-}) > CH_2CH_2OCH_3 > CH_2$-furyl.

Copper(II) Complexes. Two types of copper(II) complexes have been isolated. The complexes $Cu(X\text{-}sal\text{-}fum)_2$ (X=H, 5-Cl, 5-Br, 3-CH_3O) in non-donor solvents show electronic absorption spectra with the first d-d band at about 17 kK, typical spectra being shown in Fig. 1. The absorption curves are similar to those of the complexes $Cu(X\text{-}sal\text{-}n\text{-}alkyl)_2$, the d-d band maxima being at nearly the same frequencies, a fact which implies that the complexes $Cu(X\text{-}sal\text{-}fum)_2$ may have an essentially planar, four-coordinate configuration.[8-10] Their magnetic moments also lie in the range from 1.83 to 1.95 BM, in agreement with the square-planar configuration. The spectra also show that the complexes in pyridine form pyridine adducts, in which the copper(II) ion assumes a coordination number exceeding four.

The complexes of the formula Cu(X-sal-fum)Cl (X=H, 5-Cl) at room temperature have subnormal magnetic moments of 1.31 and 0.92 BM, respectively,

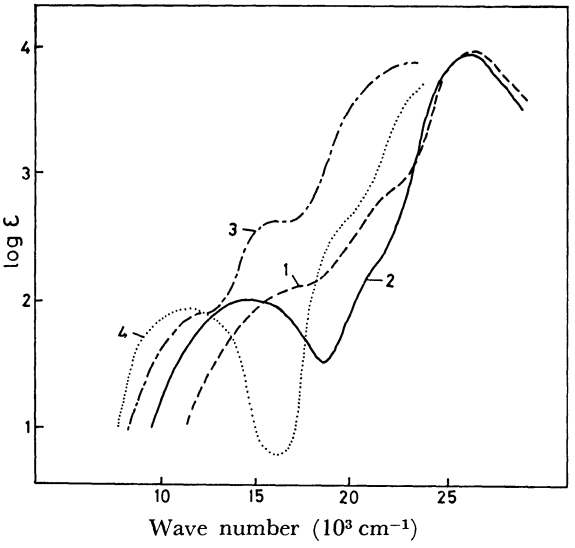


Fig. 1. Electronic absorption spectra of copper(II) complexes: 1, $Cu(5\text{-}Br\text{-}sal\text{-}fum)_2$, in $CHCl_3$; 2, $Cu(5\text{-}Br\text{-}sal\text{-}fum)_2$, in pyridine; 3, Cu(H-sal-fum)Cl, in Nujol; 4, Cu(5-Cl-sal-fum)Cl, in Nujol.

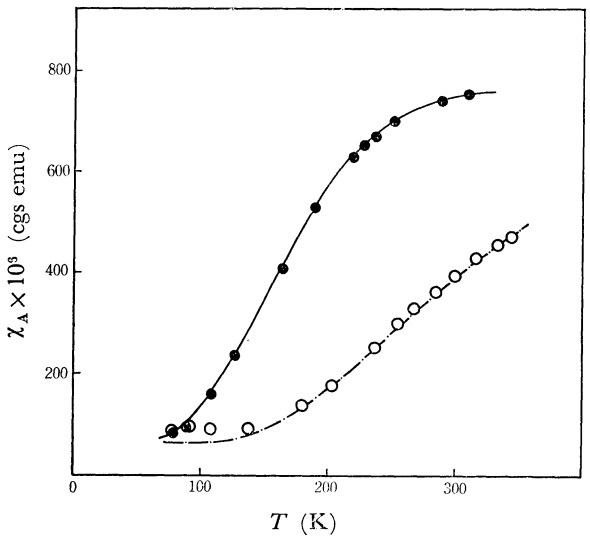


Fig. 2. Variation of magnetic susceptibilities, χ_A, with temperature: ●, Cu(H-sal-fum)Cl ($-2J=550$ cm^{-1}, $g=2.26$, $N\alpha=60\times10^{-6}$ emu); ○, Cu(5-Cl-sal-fum)Cl ($-2J=1000$ cm^{-1}, $g=2.05$, $N\alpha=60\times10^{-6}$ emu). The curves represent theoretical curves, which are calculated from Eq. 1, using values of J, g and $N\alpha$ given in parentheses.

which are much lower than the normal magnetic moments anticipated for the copper(II) complexes. A sort of interaction, therefore, may be expected to exist between two copper(II) ions. The magnetic susceptibility data over a temperature range 76—300 K, which are shown in Fig. 2, fit the Bleaney-Bowers Eq. 1, probably implying that these copper(II) complexes have a binuclear structure.

Their infrared ν(C–O) bands appear at 1555 (X=H) and 1550 cm^{-1} (X=5-Cl), respectively, which are found to be shifted toward higher frequencies than the typical bis(Schiff base)metal(II) complexes (1520—1530 cm^{-1}). Based on the criteria proposed previously,[11,12] the present finding seems to indicate that these complexes may have a structure with the phenolic oxygen atom bridging two cpoper(II) ions. The J value of Cu(Cl-sal-fum)Cl is significantly larger than that of Cu(H-sal-fum)Cl, a fact which suggests that the spin-spin interaction in the former is stronger than that in the latter.

As may be seen in Fig. 1, the spectrum of Cu(H-sal-fum)Cl widely differs from that of Cu(5-Cl-sal-fum)-Cl. Kato *et al.*[12] reported previously that the spectra of the Cu(X-sal-alkyl)Cl type complexes were classified into two groups, which were designated as B- and Y-type. The present study shows that the spectrum of Cu(H-sal-fum)Cl is similar to that of the B-type and that the spectrum of Cu(5-Cl-sal-fum)Cl is similar to that of the Y-type.

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