Excited States of *N*-Salicylidenealkylamines Chelating to Zinc(II)

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For several different forms of *N*-salicylidenealkylamines (Schiff bases), the absorption and emission spectra, and the yields, lifetimes, and polarizations of the emissions were measured. The neutral Schiff bases exist in two forms, the enolimine and the ketoamine, in an alcoholic solution. All anions of the Schiff bases emit a moderate fluorescence at room temperature and a strong fluorescence and a very weak phosphorescence at 77K. Chelating to Zn^{2+} and Be^{2+}, they strongly emit a fluorescence and phosphorescence similar to those of the free anions. In the bis-bidentate complexes, the phosphorescence increases and the fluorescence decreases compared to those of the mono-bidentate complexes—this change in the emission yields may be due to the increase in the intersystem crossing rate, enhanced by an interaction between the ligands perpendicular to each other.

It is well known that many aromatic chelating reagents, such as 8-quinolinol,[1] *N*-salicylideneanilines,[2] β-diketones,[3] and azo dyes with a hydroxyl group at their ortho position,[4] fluoresce strongly on coordinating to a light metal ion and that the first three of the above compounds phosphorescence at a lower temperature on coordinating to a heavy metal ion. We (Ohno and Kato) recently proved that the excited states of the bidentate ligands (β-diketones, 1,10-phenanthroline, and 2,2′-bipyridine) were influenced by the following coordination effects; (1) the metal-ligand bond(s) prevent(s) the excited state from undergoing internal conversion,[5] (2) the metal-ligand bond(s) using a nonbonding orbital raise(s) the levels of $^1(n\text{-}\pi^*)$ and $^3(n\text{-}\pi^*)$, followed by a change in the rates of the radiative and nonradiative processes,[6] and (3) a weak ligand-ligand interaction produces a larger spin-orbit interaction[5] and a delocalization of the excited state through the ligands, resulting in a decrease in the nonradiative transition rate.[5,6] However, no strong molecular exciton interaction in the bis- and tris-bidentate complexes was observed in the absorption spectra, even at 4.2 K,[7] contrary to the expectations based on the circular dichroic spectra.[8]

In order to confirm such coordination effects, the emissions of several *N*-salicylidenealkylamine complexes were examined.

Experimental

Material. Bis(*N*-salicylideneisopropylaminato)zinc(II)[9] ($Zn(Sal\text{-}propyl)_2$), bis(*N*-salicylidenemethylaminato)zinc(II) ($Zn(Sal\text{-}methyl)_2$), bis(*N*-salicylidenecyclohexylaminato)zinc(II) ($Zn(Sal\text{-}ch)_2$), and (*N,N′*-disalicylidene-1,2-propanediaminato)zinc(II)[10] (Zn(Sal-pn)) were prepared from $Zn(CH_3COO)_2\cdot 2H_2O$ and salicylaldehyde and the appropriate amines.

Free Ligands. *N*-salicylidenecyclohexylamine (H-sal-ch), *N,N′*-disalicylideneethylenediamine (H_2-sal-en), and *N*-(3-methoxysalicyliden)methylamine (H-methoxy-sal-methyl) were prepared from the appropriate amines and salicylaldehyde or 3-methoxysalicylaldehyde, and were purified by means of recrystallization or distillation. $Zn(CH_3COO)_2\cdot 2H_2O$ was recrystallized from acetic acid, and $Be_4O(CH_3COO)_6$, from ethanol and then from chloroform.

Measurements. The absorption and emission spectra, the quantum yields, the lifetimes, and the polarizations of the emissions were measured in the ways described in the preceding papers.[5,6]

Procedures. The free ligands were dissolved in a mixture of methanol and ethanol (1:4 by volume) or methylcyclohexane, while the neutral complexes were dissolved (10^{-5}—10^{-4} M) in the mixed solvent in which the complexes did not practically dissociate. The solutions of the mono-bidentate complexes were prepared by dissolving the bis-bidentate complexes and an excess of $Zn(CH_3COO)_2\cdot 2H_2O$ or $Be_4O(CH_3COO)_6$. The $Zn(Sal\text{-}ch)^+$ solution was prepared from H-sal-ch and an excess of $Zn(CH_3COO)_2\cdot 2H_2O$.

Results and Discussion

Free Ligands. The near UV absorption spectra of H-sal-ch, H_2-sal-en, and H-methoxy-sal-methyl in the mixed solvent of methanol and ethanol consist of two bands, as is shown in Fig. 1; one has the band peak at 25×10^3 cm^{-1} (K-band), and the other, at 31.5×10^3 cm^{-1} (E-band). At 77 K, the intensity of the K-band increases and that of the E-band decreases. In methylcyclohexane, the E-band is intensified at room temperature and the K-band is so weakened that it can barely be detected at 77 K (see Fig. 1). The observed changes in the band intensity with the solvents and the temperatures suggest the presence of an equilibrium between the ketoamine and the enolimine:

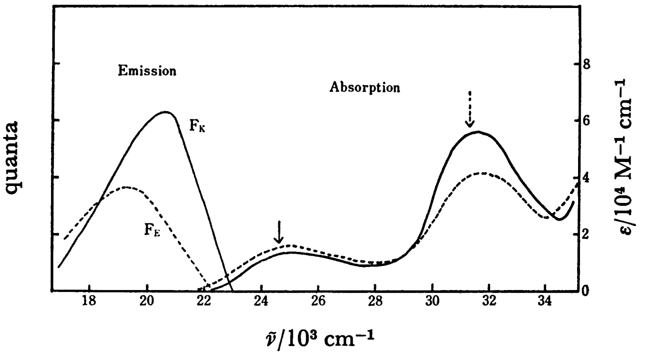
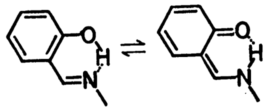


Fig. 1. Absorption and emission spectra of H-sal-ch in a mixture of methanol and ethanol (1:4 by volume). ——: The absorption spectrum at room temperature, -----: the absorption spectrum at 77 K, F_K: the fluorescence spectrum at 77 K on excitation with 24.5×10^3 cm^{-1} light (↓), and F_E: the fluorescence spectrum at 77 K on excitation with 31.5×10^3 cm^{-1} light (↓).



According to Hoffman *et al.*,[11] who have proposed a similar equilibrium for salicylideneisopropylamine in some solvents by measurements of IR and UV spectra, the K-band is attributable to the ketoamine, and the E-band, to the enolimine.

A weak and structureless fluorescence is observed when the ketoamine of H-sal-ch is excited at 77 K in both alcohol and methylcyclohexane. As the temperature is raised, the fluorescence fades and escapes from detection at room temperature ($\Phi_F < 10^{-4}$). The enolimine at 77 K emits much weaker fluorescence (F_E) with a very large Stokes shift (12000 cm^{-1}), which has a spectrum a little different from the fluorescence (F_K) of the ketoamine, as Fig. 1 shows. A similar situation may be seen in H_2-sal-en and H-methoxy-sal-methyl (see Table 1). It is probable that the fluorescence on the excitation of the enolimine may come from the kind of ketoamine, with some difference in the rotation of the C–N bond and/or the solvation from the directly excited ketoamine. In the cases of some (*N*-nitrosalicylidene)-anilines[12] and *N*-(2-hydroxynaphthylidene)aniline,[13] which exist in an equilibrium with their ketoamines in the ground state, Becker and Richey considered the weak fluorescences with maxima different from those of the ketoamines to come from the kind of ketoamine with the anilino group and the salicylidene or the naphthylidene group in different planes.

TABLE 1. THE SPECTRAL DATA

Compounds	$\tilde{\nu}_{max}$ of abs.	$\tilde{\nu}_{max}$ of fluo. R.T.[a]	$\tilde{\nu}_{max}$ of fluo. 77 K	$\tilde{\nu}_{max}$ of phospho.
H-sal-ch enolimine	31600	—	—	—
H-sal-ch ketoamine	25100	—	21100	—
Sal-ch	28400	22400	24700	21500
H_2-sal-en enolimine	31750	—	—	—
H_2-sal-en ketoamine	24700	—	21600	—
Sal-en	27900	21650	24200	20800
H-methoxy-sal-methyl enolimine	34000	—	—	—
H-methoxy-sal-methyl ketoamine	23900	—	20000	—
Zn(Sal-ch)$^+$	28200	22400	24600	21900
Zn(Sal-ch)$_2$	28300	22400	24600	21900
Zn(Sal-propyl)$^+$	28200	22700	24200	21800
Zn(Sal-propyl)$_2$	28200	22600	24400	21700
Zn(Sal-pn)	28000[b]	22200	24100	21400
Zn(Sal-methyl)$^+$	28500	22700	24700	21800
Be(Sal-methyl)$^+$	—	23400	24100	22300

a) Room temperature. b) Shoulder.

When sodium ethoxide is added as a base to an H-sal-ch ethanol solution, a new absorption band ($\tilde{\nu}_{max}$: 28400 cm^{-1}) appears and both the K-band and the E-band disappear, as Fig. 2 shows. In the case of H_2-sal-en, the band peak is at 27900 cm^{-1}. This new band is undoubtedly attributable to the anion. As is shown in Fig. 2, the anion emits a new fluorescence with $\tilde{\nu}_{max}$: 24700 cm^{-1} at 77 K and 22400 cm^{-1} at room temperature. The large red shift (2300 cm^{-1}) with a rise in the temperature is probably due to the reorientation of the solvent molecules around the excited molecule with a larger dipole moment. The absence of the intramolecular H-bonding allows large yields of the fluorescence: $\approx 10^{-1}$ at 77 K and $\approx 10^{-2}$ at room temperature. Moreover, a weak phosphorescence with $\tilde{\nu}_{0-0}$ at 21500 cm^{-1} was observed by using the sector method (see Fig. 2). A similar situation is seen in the basic nonaqueous solution of H_2-sal-en.

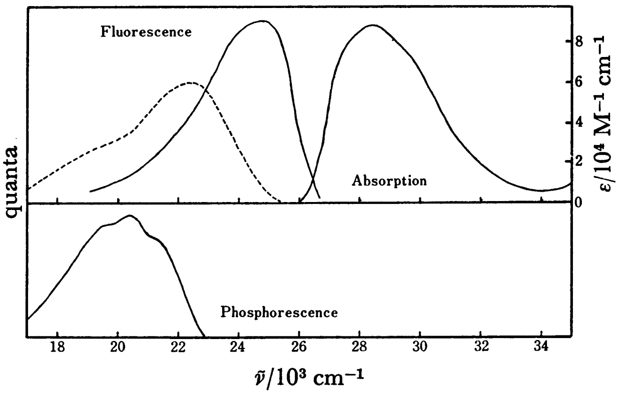


Fig. 2. Absorption and emission spectra of Sal-ch in ethanol containing sodium ethoxide at 77 K and room temperature.
——: The absorption, fluorescence, and phosphorescence (the lower section) spectra of 77 K, and ----: the fluorescence spectrum at room temperature.

In a 0.01 N NaOH methanol solution containing 20% water, both the absorption and fluorescence spectra of H-sal-ch and H_2-sal-en are different from those of the corresponding anions in the ethanol including sodiumc ethoxide; the $\tilde{\nu}_{max}$ of the absorption band is 26000 cm^{-1}, and that of the fluorescence is 19200 cm^{-1} at room temperature and 22500 cm^{-1} at 77 K for both H-sal-ch and H_2-sal-en. This behavior is the same as that of salicylaldehyde in the same solvent; therefore, it can be concluded that the species exhibiting these absorption and emission spectra is the salicylaldehyde anion. It is thus probable that the spectra of H_2-sal-en and H-sal-methyl in the methanolic KOH which were reported by Water *et al.*[14] are the absorption spectra of the salicylaldehyde anion.

Coordinating Forms of Sal-ch, Sal-propyl, and Sal-pn. When $Zn(CH_3COO)_2 \cdot 2H_2O$ is added to an alcoholic solution of H-sal-ch, both the absorption and fluorescence spectra are changed into forms very similar to those of the anion (see Figs. 2 and 3). Moreover, the same spectrum is obtained for a Zn(Sal-ch)$_2$ (3×10^{-5} M) solution with an excess (10^{-3} M) of $Zn(CH_3COO)_2 \cdot 2H_2O$. It may easily be concluded that the new band is due to the formation of Zn(Sal-ch)$^+$. It is noticeable that the coordinating Sal-ch has a broad asymmetric absorption band with a long tail on the higher-frequency side; this band may be supposed to consist of two different transitions.

On the excitation of Zn(Sal-ch),$^+$ a strong fluorescence is observed at room temperature and at 77 K. As Fig. 3 shows, the band peak of the fluorescence is red-

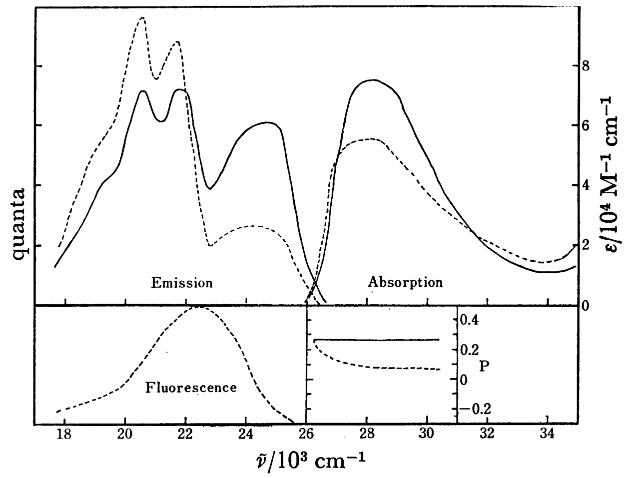
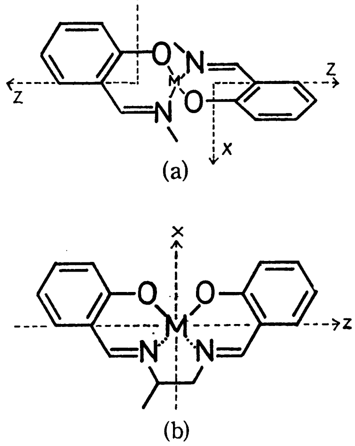


Fig. 3. Excitation polarization spectra of fluorescence, absorption and emission spectra of Zn(Sal-ch)$^+$ and Zn(Sal-ch)$_2$.
The upper section consists of the absorption and emission spectra at 77 K. ----: Zn(Sal-ch)$_2$, ——: Zn(Sal-ch)$^+$ ([Zn(Sal-ch)$_2$]: 3×10^{-5} M and Zn(CH$_3$COO)$_2$: 10^{-3} M).
The lower section consists of the fluorescence of Zn(Sal-ch)$^+$ at room temperature and the excitation polarization spectra of the fluorescence at 77 K.

shifted from 24400 to 22400 cm^{-1} by a rise in the temperature, as in the case of the anion. In addition to the fluorescence, there is observed a strong phosphorescence with a $\tilde{\nu}_{0-0}$ value of 21800 cm^{-1}, which is near to the weak phosphorescence of the anion. In the case of Sal-pn, the absorption, fluorescence, and phosphorescence spectra of the coordinating Sal-pn are similar to those of Sal-en, as Table 1 shows. Further, all coordinating Schiff bases, even at room temperature, retain the high fluorescence yields obtained at 77 K.

The high fluorescence yields of the coordinating Schiff bases may have two causes. One is that the electronic state of the ligand is not similar to those of the ketoamine and the enolimine, but to that of the anion. The other is the rigid chelation to the zinc ion, suppressing the internal conversion, which usually depresses the fluorescence yields of the anions at room temperature. The high phosphorescence yields may thus be caused not by a spin-orbit interaction due to the zinc ion, but by the formation of the rigid chelation, because the complex of the lighter metal ion—Be^{2+} has a yield similar to those of the Zn-complexes.



(a)

(b)

Fig. 4. Intramolecular axes of the complexes of salicylidenealkylamine (a) and Sal-pn (b).

Ligand-Ligand Interaction. In the cases of Be(Sal-methyl)$_2$, Zn(Sal-ch)$_2$, and Zn(Sal-propyl)$_2$, the interligand interaction is considered not to be large because they have four coordinating atoms (2 N and 2 O) at the appexes of the tetrahedron, as has been shown by means of X-ray analysis in the case of Zn(Sal-propyl)$_2$[15] (see Fig. 4-a). They have an asymmetric absorption band similar to those of the monobidentate complexes, as Fig. 3 shows. The asymmetric band is resolved into two bands by measuring the excitation polarization spectrum of the fluorescence of Zn(Sal-ch)$_2$.*

TABLE 2. THE QUANTUM YIELDS AND THE RATE CONSTANTS FROM THE TRIPLET STATES AT 77 K

Compounds	Φ_F	Φ_P	Φ_P/Φ_F	Φ_T	k_r+k_{nr}	k_r	k_{nr}
Zn(Sal-ch)$^+$	0.41	0.38	0.93	0.59	1.45	0.93	0.52
Zn(Sal-ch)$_2$	0.19	0.52	2.7	0.81	4.19	2.69	1.50
Zn-(Sal-propyl)$^+$	0.27	0.35	1.3	0.73	2.53	1.21	1.32
Zn-(Sal-propyl)$_2$	0.12	0.41	3.3	0.88	3.91	1.82	2.09
Zn(Sal-pn)	0.23	0.40	1.7	0.77	2.00	1.03	0.97
Zn-(Sal-methyl)$^+$	0.35	0.31	0.88	0.65	—	—	—
Zn-(Sal-methyl)$_2$	0.19	0.40	2.2	0.81	—	—	—
Be(Sal-methyl)$^+$	—	—	2.0	—	—	—	—
Be(Sal-methyl)$_2$	—	—	3.8	—	—	—	—

Ligand-ligand interaction in the bis-bidentate complexes is reflected in the yields and lifetimes of the emissions. Their phosphorescence yields with shorter lifetimes become larger by 0.06—0.14, as is shown in Table 2, compared with the yields of the corresponding monobidentate complexes. Assuming that the rate of internal conversion from the excited singlet state is much smaller than those of the fluorescence and the intersystem crossing processes, the sum of the triplet yield (Φ_T) and the fluorescence yield (Φ_F) becomes unity and the phosphorescence yield (Φ_P) is expressed as $\Phi_P = \Phi_T \cdot k_r/(k_r+k_{nr}) = (1-\Phi_F)\, k_r/(k_r+k_{nr})$, where k_r is the rate

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* The constant fluorescence polarization of the monobidentate complex suggests that the emitting dipole lies between the two absorption dipoles. This idea is partly supported by the large separation between the maxima of the absorption and the fluorescence spectra, in addition to the structureless band shapes. While the intensity of the transition along the z-axis is multiplied by a factor of 2 on biscoordination, the intensity of the transition along the x-axis is multiplied by a factor of $\sqrt{2}$. Therefore, the transition without the z-component has a larger angle against the transition with x- and z-components in the bis-bidentate complex than in the mono-bidentate complex. If the higher absorption transition has no z-component and if the emitting has both components, x and z, the value of the fluorescence polarization is smaller on excitation to the higher excited state.

constant of the radiative process and where k_{nr} is the rate constant of the nonradiative process from the triplet state. Then, the values of k_r and k_{nr} are calculated using the phosphorescence lifetime, $(k_r+k_{nr})^{-1}$. These values and Φ_T are shown in Table 2.

The increases in Φ_T and k_r are mainly caused by the increment in the spin-orbit coupling. Such an increase in the intersystem crossing rate ($k_{S\to T}$) due to intramolecular interaction has also been observed for some β-diketonato complexes,[5] diphenylmethane, and triphenylmethane.[16] The values of k_r and k_{nr} of Zn(Sal-ch)$_2$ and Zn(Sal-propyl)$_2$ are three times as large as those of Zn(Sal-ch)$^+$ and Zn(Sal-propyl)$^+$ respectively, as Table 2 shows; therefore, the increase in the k_{nr} may come from the larger spin-orbit coupling. This is in contrast with the cases of the tris-β-diketonato complexes and triphenylmethane, where the $k_{S\to T}$ values are larger and the k_{nr} values are smaller than those of the mono-β-diketonato complexes and toluene respectively. Even if the triplet delocalization through the two ligands of a Schiff base affects the k_{nr}, the effect will be canceled out by the chelation being less rigid than that in the mono-bidentate complex, which emits phosphorescence several hundreds times as strongly as does the free anion.

As for planar Zn(Sal-pn)[17] (see Fig. 4-b), the absorption band in the near UV region has a shoulder on the lower-frequency side, as Fig. 5 shows. The shoulder indicates the existence of another transition, which was suggested by Bosnich[10] on the basis of a Gaussian analysis of the asymmetric absorption band observed at room temperature. Since the fluorescence polarization is constant from $26\times10^3\,\text{cm}^{-1}$ to $31\times10^3\,\text{cm}^{-1}$ and is similar to that of Zn(Sal-ch)$^+$, the existance of two transitions does not indicate a large exciton splitting. Probably, a weak interaction between the salicylideneamine groups makes observable a second band which is hidden in the mono-bidentate complex.

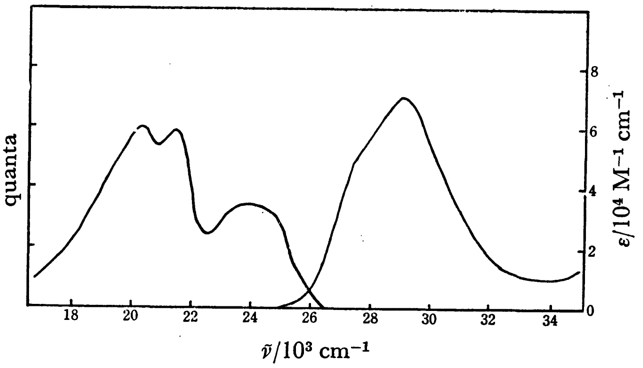

Fig. 5. Absorption and emission spectra of Zn(Sal-pn) in a mixture of methanol and ethanol at 77 K.

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