January, 1989] *Bull. Chem. Soc. Jpn.*, **62**, 45—50 (1989)

Aggregation of Complexes Coordinated with *N,N'*-Bis(5-alkylsalicylidene)-ethylenediamine: ^{1}H NMR Peak Shifts and Paramagnetic Broadening Investigations

Kazuo Miyamura,* Keiki Satoh, and Yohichi Gohshi
Department of Industrial Chemistry, Faculty of Engineering, The University of Tokyo,
Hongo, Bunkyo-ku, Tokyo 113
(Received May 27, 1988)

Nickel(II) complexes coordinated with *N,N'*-disalicylideneethylenediamine (salen) substituted by a series of *n*-alkyl side chains have been synthesized. Drastic improvement in the solubility towards chloroform brought about by the increase in alkyl side chain lengths realised an extremely high concentration of 0.5 mol·dm^{-3}. Due to aggregation, their ^{1}H NMR spectra in $CDCl_3$ were strongly dependent on the concentration especially in the high concentration region. The alkyl chain length has very little influence on the dependency, indicating that the aggregation is caused by the complex–complex interaction rather than by the hydrophobic interaction between the alkyl side chains. Assuming a monomer–dimer equilibrium, the aggregation constant is determined from the concentration dependence. Further, the structure of the aggregate is estimated by combining the results of the concentration dependence, and the paramagnetic broadening caused by adding the corresponding copper(II) complex. The paramagnetic broadening investigation also indicated a close contact of copper(II) complex to nickel(II) complex.

The importance of aggregation in the field of coordination chemistry has been recognized recently from the studies on chlorophylls,[1—4] vesicles,[5,6] and others.[7—9] In particular, the intensive studies on the chlorophyll aggregate suggested it has different properties from the monomeric species. This is effectively used in photosynthesis.[2] It can be said that the aggregation of the chlorophyll molecules alters their photochemical properties. It is also well-known that some properties in highly dense solutions are not the mere extrapolation of those in thin solutions. It is the phenomenon of aggregation that is responsible for these changes. The changes accompanying the aggregation phenomenon, which in many cases have been treated as experimental errors, are now under investigation and have increasing importance.

Complexes of *N,N'*-disalicylideneethylenediamine, usually abbreviated as salen, are known to form dimers in the crystalline state.[10,11] They have been studied extensively because of some interesting properties which they exhibit. For example, cobalt(II) complex of salen coordinates a dioxygen molecule reversibly similar to that observed for hemoglobin.[12] The chemistry of salen is interesting not only because of its porphyrin-like nature, but also for the simplicity in its synthesis. Thus, it is relevant to examine the aggregating nature of salen complexes, and to investigate the property changes due to the aggregation.

However, a problem arises in studying the aggregation of salen complexes because of their low solubilities. Generally, the phenomenon of aggregation becomes conspicuous in the high concentration region, because high concentration creates extra occasions for solute molecules to meet and aggregate. However, at high concentrations, precipitation tends to occur as a result of molecular aggregation, and this interferes with the investigation of aggregation in solution. Thus it is important to increase the solubility of the solute to investigate the phenomenon of aggregation. The introduction of alkyl chains causes an increase in their solubility towards organic solvents, such as chloroform, consequently providing us an opportunity to investigate their behaviour in the high concentration region.[13]

In a previous letter,[14] we have reported briefly that the chloroform-*d* solution of salen type complexes, substituted by hexyl groups, exhibit concentration dependence in ^{1}H NMR due to aggregation. Such a phenomenon is not observed for the unsubstituted complex because of its low solubility. In this paper, the equilibrium of aggregation and the aggregating structure are discussed, together with the experimental procedures.

Experimental

5-Alkylsalicylaldehydes (alkyl=ethyl, butyl, hexyl, octyl) were synthesized by the Reimer-Tiemann reaction[15] from the corresponding commercially available (Kantoh Chemical Co.) *p*-alkylphenols. 5-Dodecyl-and 5-decylsalicyclaldehydes were synthesized by the same procedure from the corresponding *p*-alkylphenols obtained by ordinary Friedel-Crafts acylation and Clemmensen reduction from phenol and the corresponding alkanoyl chlorides, the procedure for which is given elsewhere.[16] All other reagents used were commercially available and were of reagent grade.

[*N,N'*-Bis(5-hexylsalicylidene)ethylenediaminato]nickel(II) [Ni(1-6)]. Nickel acetate tetrahydrate (0.50 g, 2 mmol) and ethylenediamine (0.12 g, 2 mmol) were added to 100 cm^3 of ethanol in a 200 cm^3 flask with stirring. After the mixture had become a clear blue solution, 5-hexylsalicylaldehyde (0.83 g, 4 mmol) was added drop by drop to the solution. The reaction mixture was then refluxed for 3 h. The precipitate formed was filtered and recrystallized from chloroform-ethanol mixed solvents. The yield was 0.7 g

(71%)

Found: C, 68.15; H, 7.75; N, 5.90%. Calcd for $C_{28}H_{38}N_2NiO_2$: C, 68.15; H, 7.75; N, 5.70%. ^{1}H NMR ($CDCl_3$) δ=0.87 (3H, t, J=6.9 Hz, CH_3CH_2-) 1.28 (10H, m), 1.52 (2H, t, J=6.9 Hz, benzyl-CH_2), 3.41 (2H, s, H_e), 6.74 (1H, d, J=2.1 Hz, H_c), 6.93 (1H, d, J=8.9 Hz, H_a), 7.02 (1H, dd, J=2.2 and 8.7 Hz, H_b), 7.33 (1H, s, H_d).

Other [*N,N'*-Bis(5-alkylsalicyclidene)ethylenediaminato]nickel(II) [Ni(1-*n*)](*n*=2,4,8,10,12). A series of [*N,N'*-bis(5-alkylsalicylidene)ethylenediaminato]nickel(II) (alkyl=ethyl, butyl, octyl, decyl, dodecyl) were obtained from the corresponding 5-alkylsalicylaldehydes by a similar procedure to [*N,N'*-bis-(5-hexylsalicylidene)ethylenediaminato]nickel(II) as described above. The yields of the complexes tend to decrease with the complexes of longer alkyl chains, but they were never under 40%.

Found for [Ni(**1-2**)]: C, 63.15; H, 5.90; N, 7.35%. Calcd for $C_{20}H_{22}N_2NiO_2$: C, 63.05; H, 5.80; N, 7.35%. Found for [Ni(**1-4**)]: C, 65.20; H, 6.85; N, 6.25%. Calcd for $C_{24}H_{30}N_2NiO_2$: C, 65.20; H, 6.85; N, 6.35%. Found for [Ni(**1-8**)]: C, 69.80; H, 8.30; N, 4.95%. Calcd for $C_{32}H_{46}N_2NiO_2$: C, 69.95; H, 8.45; N, 5.10%. Found for [Ni(**1-10**)]: C, 71.55; H, 9.05; N, 4.60%. Calcd for $C_{36}H_{54}N_2NiO_2$: C, 71.40; H, 9.00; N, 4.65%. Found for [Ni(**1-12**)]: C, 72.55; H, 9.60; N, 4.10%. Calcd for $C_{40}H_{62}N_2NiO_2$: C, 72.60; H, 9.45; N, 4.25%.

[*N,N'*-Bis(5-hexylsalicylidene)ethylenediaminato]copper(II) [Cu(1-6)]. Copper(II) acetate monohydrate (0.48 g, 2.4 mmol) and 5-hexylsalicylaldehyde (1.1 g, 5.3 mmol) were added to 100 cm^3 of ethanol in a 200 cm^3 flask with stirring. The mixture was then refluxed for 2 h. The green precipitate of bis(5-hexylsalicylaldehydato)copper(II) formed (0.8 g, 1.6 mmol) was filtered and dispersed again in ethanol. To this dispersion, ethylenediamine (0.11 g, 1.6 mmol) was added drop by drop. The reaction mixture was then refluxed for 3 h. The precipitate formed was filtered and recrystallized from hot ethanol. The yield was 0.4 g. (15%).

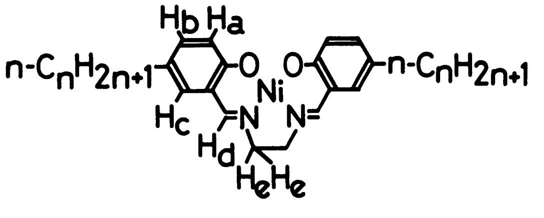
Found: C, 67.85; H, 7.20; N, 5.75%. Calcd for $C_{28}H_{38}CuN_2O_2$: C, 67.50; H, 7.70; N, 5.60%. Magnetic susceptibility μ_{eff}=1.89 B.M. (22 °C).

^{1}H NMR Measurements. The concentration dependence of ^{1}H NMR spectra was measured at 35 °C using a Hitachi R-40 90 MHz spectrometer. 400 MHz Superconducting ^{1}H NMR spectra were obtained with a JEOL spectrometer. The chloroform-d containing 1% of TMS supplied from Merck Japan Co., was used as solvent. A 5 cm^3 measuring flask was used to prepare the sample solution. The solutions of different concentration were prepared stepwise, adding the complex in small portions each time after the measurement had been completed.

Other Measurements. Visible absorption spectra were recorded with a Hitachi 340 spectrophotometer. Infrared spectra were obtained with a Jasoc IRA-2 spectrophotometer. Magnetic susceptibility measurements were performed with a Shimadzu torsion magnetometer MB-100 at Ochanomizu University.

Results and Discussion

The salen type ligands used in this paper have two alkyl (C_nH_{2n+1}) side chains of the same length, and are abbreviated as (**1-*n***). The results of elemental analyses accord well with the assumed structures. The IR spectra of nickel(II) and copper(II) complexes of (**1-*n***) exhibit a peak assignable to ν(C=N) at 1620 cm^{-1}, corresponding to the formation of a Schiff base in the complex.



(1-n)

The nickel(II) and copper(II) complexes of (**1-*n***) in chloroform (2×10^{-4} mol·dm^{-3}) exhibit almost an identical electronic spectra regardless of their alkyl chain length, and also, they do not show notable change either in peak positions or in absorption coefficients in the concentration region of 2×10^{-5} to 4×10^{-4} mol·dm^{-3}. Thus, the spectra of the (**1-6**) complexes are given in Fig. 1 as the representatives of the series, together with those of the unsubstituted complexes. The spectral profiles of alkyl-substituted complexes are similar to that of the unsubstituted complexes, which adopt the square-planar 4 coordination geometry. Thus it can be concluded that the complexes of (**1-*n***) also adopt the square-planar geometry. This is confirmed by the magnetic susceptibility measurements of the crystal of [Ni(**1-12**)]. It shows that the [Ni(**1-12**)] is diamagnetic as are most of the square-planar nickel(II) complexes. The μ_{eff} values for [Cu(**1-*n***)] (*n*=6, 12) are 1.89 and 1.91

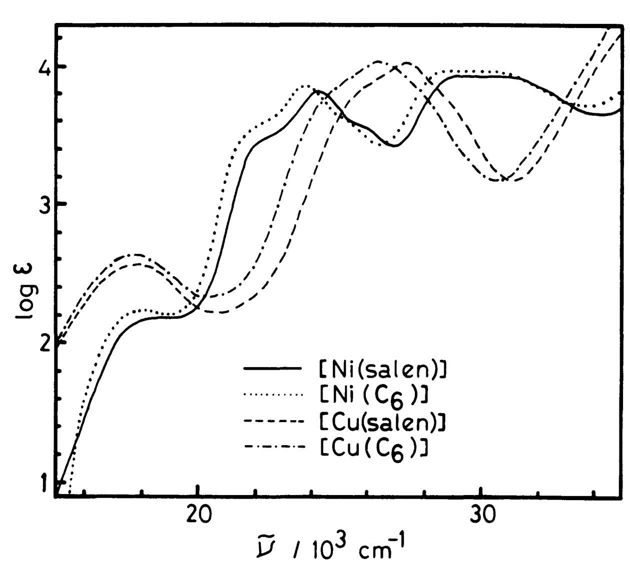


Fig. 1. Electronic spectra of [M(**1-6**)] and [M(salen)] (M=Ni, Cu).

B.M., which are in the range of normal monomeric copper(II) complexes.

However, a slight red shift on alkyl substitution can be noticed in the UV-region of the electronic spectra (Fig. 1). These red shifts are 500 and 1000 cm^{-1} for nickel(II) and copper(II) complexes, respectively. Similar red shifts are reported for the binuclear salen type complexes of (**2**).17),18) The shifts for nickel(II) and copper(II) complexes of (**2**) are 600 and 1200 cm^{-1} respectively. ESR study on the copper(II) complex of (**2**) revealed that the red shift is due to the interaction of two salen complex moieties in the complex. However, the concentration, at which the electronic spectra of (**1**-*n*) complexes are measured (2×10^{-4} $mol\cdot dm^{-3}$), is far below the region of aggregation, as is shown later in this text. This means that the shift in electronic spectra of the (**1**-*n*) complexes cannot be attributed to the aggregation phenomenon dealt with in this paper. It can be considered that in (**1**-*n*), alkyl groups are directly attached to the benzene rings, possibly affecting the electronic state of salen moiety, while that is not the case in (**2**). It is, therefore, probable that the red shifts observed for the (**1**-*n*) complexes are due to the electronic effect of the substituted alkyl groups.

The Concentration Dependence in ^{1}H NMR. The ^{1}H NMR spectra of [Ni(**1**-*n*)] in chloroform-*d* are measured on a 400 MHz spectrometer, and almost all the peaks have been assigned. The assignment of the aromatic protons (H_a, H_b, and H_c) can be made by spin decoupling investigations. Geminal protons H_a and H_b split into doublets by the coupling, and a long-range coupling between H_b and H_c is also observed. Some other protons are also identified, on the basis of the assumed structure. ^{1}H NMR spectra of other nickel(II) complexes exhibit similar spectra and are assigned according to the same procedures. However, it is found that the positions of the peaks assigned to H_c and H_d differed slightly, each time one measures the ^{1}H NMR, although there are no differences in the sample solution except for their concentration.

On increasing the concentration, the signals assigned to the protons H_c and H_d, clearly showed up-field shifts. In Fig. 2 are given the concentration dependences of H_d for the nickel(II) complexes of (**1**-*n*). The shifts were observed only for H_c and H_d, and neither aliphatic protons nor the H_a and H_b protons of the benzene rings showed observable shifts. These up-field shifts become conspicuous above a concentration of ca. 10^{-3} $mol\cdot dm^{-3}$, and, in the case of [Ni(**1**-**8**)], they move ca. 0.5 and 0.8 ppm upwards for H_c and H_d respectively, until the solution saturates at 0.51 $mol\cdot dm^{-3}$.

The up-field shifts can be attributed to the aggregation of the complex, because there are no other interactions that are affected by the change in the concentration. It is well-known that the protons located above an aromatic ring exhibit a peak shift in ^{1}H NMR to an upper field due to the strong diamagnetic effect of the ring current formed in the aromatic ring.19) Thus, in the aggregate of [Ni(**1**-*n*)], the benzene ring of (**1**-*n*) is assumed to be placed above the protons H_c and H_d of another molecule of [Ni(**1**-*n*)], and vice versa. As the ^{1}H NMR spectrum of [Ni(**1**-*n*)] exhibits the shifts and not the splittings, a rapid equilibrium between the aggregate and the monomeric species is indicated.

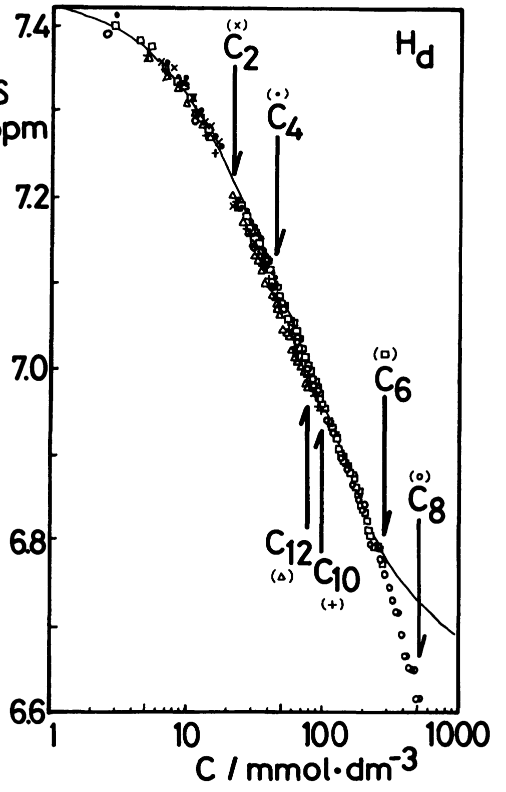


Fig. 2. Concentration dependence of ^{1}H NMR of [Ni(**1**–*n*)] in $CDCl_3$. Arrows indicate the concentration of saturation.

The length of the alkyl chains have little effect on the concentration dependence. The major effect of the alkyl side chains is the modification of the solubility of the complex. The saturation concentration, which is indicated by arrows in Fig. 2, increases as the alkyl chain length increases, until it reaches its maxima for the (**1**-**8**) complex, and then decreases. The shift, on the other hand, has a slight tendency to increase with the alkyl length, but the amount is not large enough to be positively affirmed. However, it can be concluded that the complex-complex interaction rather than the hydrophobic interaction of the side chains is responsible for the aggregation.

Theoretical Treatment of the Concentration Dependences. The concentration dependence observed contains information on the distribution of the complex molecules present in the solution to the monomeric species and the aggregates. If the aggregation occurs at low concentration, the shift of ^{1}H NMR should begin to appear at a low concentration. Therefore, the equilibrium constant of aggregate formation can be determined from the concentration dependence of the shift. At the primary stage of aggregation, i.e. in a relatively low concentration region, an equilibrium between the monomeric and dimeric species ought to be dominant in the solution. Assuming, therefore, an equilibrium between monomer and dimer for the first order approximation, the chemical shifts for a given proton (δ) at any concentration (C) are given as

$$\delta = \delta_d + (\delta_m - \delta_d)(\sqrt{1+8CK} - 1)/4CK$$

where K, δ_m, and δ_d stand for the equilibrium constant (=[dimer]/[monomer]^2), chemical shifts of monomer and dimer, respectively.[20] The shape of the curve for this equation is a sigmoidal curve, in which the δ value changes from δ_m (C=0) to δ_d (C=infinity).

Calculations to fit the theoretical curves to the observed data of H_c and H_d were performed, and the results are summarised in Table 1. The data for [Ni(**1-2**)] is insufficient to derive K and δ values, and the values calculated for [Ni(**1-4**)] are not accurate enough for the same reason. The curves given in Fig. 2 are those calculated for [Ni(**1-6**)]. The result shows that K, δ_m, and δ_d are almost identical regardless of the difference in the alkyl chain length. A slight increase of K in proportion to the chain length can be observed, but is not large enough to be confirmed. The calculated curves fit well to the data up to ca. 0.2 mol·dm^{-3}, but begin to drift apart from the data thereafter. In the case of [Ni(**1-8**)], the drift becomes extremely large because of the high concentration it reaches, and it shows completely different dependence from the theoretical curve. This is probably due to the formation of highly associated aggregates, such as trimers, etc.

Porphyrin complexes, including chlorophylls, also show this kind of up-field shifts.[20,21] The equilibrium constants for them are in the same order as the K values obtained here, indicating that the nickel complexes of (**1-*n***) are expected to have a similar aggregating ability to that of the porphyrin complexes. The differences between δ_m and δ_d for porphyrin complexes proved to be slightly larger than those observed for the (**1-*n***) complexes.

However, the ^{1}H NMR of the unsubstituted salen complex exhibited no observable shift. This is because the solubility of [Ni(salen)] (ca. 2×10^{-4} mol· dm^{-3}) is far lower than the concentration at which the salen type complex starts to aggregate. In other words, the crystallization takes place prior to the aggregation in [Ni(salen)]. It is apparent, therefore, that the effect of the aliphatic side chains is to increase the solubility of the complex, and to reveal the ability to aggregate in the solution, which is hidden in the complex of low solubility.

Paramagnetic Broadening Caused by Copper(II) Complex. Other information on aggregation phenomenon is obtained from the investigation of the paramagnetic broadening of ^{1}H NMR spectra caused by adding the corresponding copper(II) complex [Cu(**1-*n***)] to a $CDCl_3$ solution of [Ni(**1-*n***)]. In Fig. 3 is shown the spectral change of [Ni(**1-6**)] on adding [Cu(**1-6**)]. The change in the spectral profile becomes apparent on adding only 1% of the corresponding copper(II) complex. In Fig. 3, it is found that the peak at δ=3.4 (H_e) loses height drastically on the addition of the copper(II) complex. A similar phenomenon is also observed for the peaks at δ=6.6 (H_d) and 7.1 (H_c). Here again, the peaks of the protons H_c and H_d are broadened extensively, and in addition, the methylene protons of ethylenediamine moiety (H_e) are strongly affected. The intensity of the broadening observed is in the order of $H_e \approx H_d > H_c >$ other protons. It is found also that the peak width at half maxima and the amount of copper(II) complex added have a linear relation up to ca. 7%, although no special treatment such as deoxygenation was applied.

The paramagnetic broadening of ^{1}H NMR peaks is caused by the acceleration of the relaxation speed of activated protons placed near the unpaired electron of copper(II) complex (spin–spin relaxation).[22] Since the acceleration is due to the energy exchange between the spins of unpaired electrons of Cu^{2+} and ^{1}H nucleus, the observed paramagnetic broadening corresponds to the formation of [Ni(**1-6**)]–[Cu(**1-6**)] (abbr. Ni–Cu) aggregate. Protons subject to the intense

Table 1. Calculated Equilibrium Constants and δ Values for Monomer and Dimer of [Ni(**1-*n***)]

Complex	K/mol^{-1}·dm^3	H_c		H_d	
		δ_m	δ_d	δ_m	δ_d
[Ni(**1-2**)]	Not converged				
[Ni(**1-4**)]	9	6.81	6.07	7.44	6.40
[Ni(**1-6**)]	7.5	6.81	6.06	7.44	6.37
[Ni(**1-8**)]	8	6.81	6.00	7.47	6.25
[Ni(**1-10**)]	10	6.81	6.12	7.46	6.43
[Ni(**1-12**)]	9.5	6.80	6.09	7.45	6.40

In $CDCl_3$ at 35 °C.

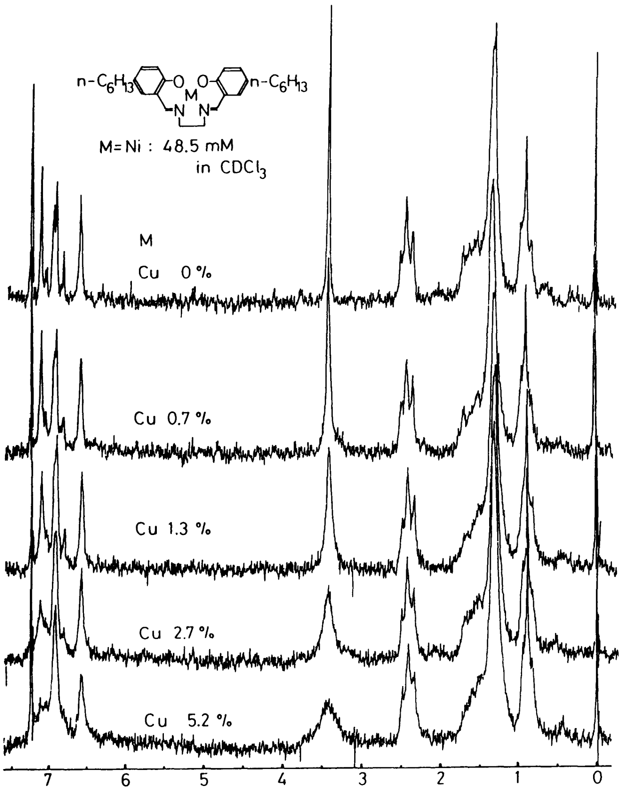


Fig. 3. Paramagnetic broadening of ^1H NMR spectra observed for [Ni(**1**-**6**)] by addition of [Cu(**1**-**6**)].

broadening, such as H_e and H_d, need to be placed near the Cu^{II} of [Cu(**1**-**6**)] in the Ni–Cu aggregate.

Paramagnetic broadening can also be caused by some other copper(II) complexes. Addition of bis(8-quinolinol)copper(II) or (*N,N'*-disalicylidene-1,3-propanediaminato)copper(II) also causes broadening in ^1H NMR spectrum of [Ni(**1**-**6**)]. This fact implies that [Ni(**1**-**6**)] aggregates with a variety of square-planar complexes. Thus, by observing the paramagnetic broadening, the structure of the heteronuclear aggregate of [Ni(**1**-*n*)] and copper(II) complex can be investigated.

Structure of the Aggregate. The protons that are affected strongly in the peak shift (H_c and H_d) and paramagnetic broadening (H_c, H_d, and H_e), seem to be in the same part of the complex. These protons are all located around the imino groups. In other words, the spectral changes observed for Ni–Ni (abbr. for dimer of [Ni(**1**-*n*)]) and Ni–Cu aggregates seem to be consistent with each other, implying similar structures for Ni–Ni and Ni–Cu aggregates. Assuming, therefore, that the structures of Ni–Ni and Ni–Cu aggregates are not very different, the structure of the aggregate in these systems can be evaluated from the amount and sign of the shift and broadening. The proposed structure for the aggregate in $CDCl_3$ solution is given in Fig. 4. In this aggregate, the protons H_c and H_d are placed above (and below) the aromatic rings, which lead to the shifts, and the protons H_c, H_d, and H_e are placed near to the Cu^{2+} of the neighbouring copper(II) complex, which cause broadening.

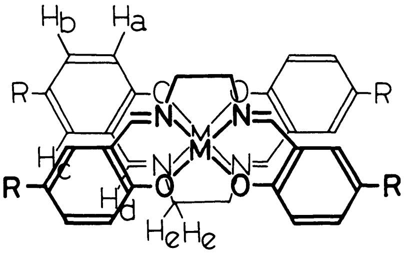


Fig. 4. Proposed aggregation structure (M=Ni, Cu).

This structure of the dimer is different from that obtained for the crystal of [Cu(salen)]·$CHCl_3$ by the crystallographic study.[10)] The dimer in the crystal has weak apical bonds between copper(II) of a [Cu(salen)] molecule and the coordinating oxygen atoms of another molecule in the dimer. This structure in the crystal does not explain the observation that the protons around the imino groups are strongly affected by aggregation. On the other hand, the proposed structure agrees well with that observed in [Co(salen)]·$CHCl_3$,[11)] which is notable for its oxygen coordinating nature.[12)] The result obtained here suggests that [Co(salen)]·$CHCl_3$ probably crystallizes in a dimeric form in $CHCl_3$.

Although an assumption that the homonuclear (Ni–Ni) and heteronuclear (Ni–Cu) aggregates take similar aggregating structures must be made, the combination of peak shift and broadening investigations proved effective in estimating the aggregating structure of the salen type complexes.

The authors thank Dr. Yutaka Fukuda of Ochanomizu University for his help in obtaining magnetic susceptibility data. The present work was partly supported by a Grant-in-Aid for Scientific Research No. 5950614 from the Ministry of Education, Science and Culture.

References

1) "Porphyrins and Metalloporphyrins," ed by K. M. Smith, Elsevier, Amsterdam (1975).

2) T. M. Cotton, A. D. Trifunac, K. Ballschmiter, and J. J. Katz, *Biochim. Biophys. Acta*, **368**, 181 (1974).

3) R. J. Abraham and K. M. Smith, *J. Am. Chem. Soc.*, **105**, 5734 (1983).

4) R. P. H. Kooyman and T. J. Shaafsma, *J. Am. Chem. Soc.*, **106**, 551 (1984).

5) K. Monserrat, M. Graetzel, and P. Tundo, *J. Am. Chem. Soc.*, **102**, 5527 (1980).

6) W. E. Ford, J. W. Otvos, and M. Calvin, *Nature (London)*, **274**, 507 (1978).

7) K. Miyamura and S. Yoshikawa, *Kagaku*, **36**, 1020 (1981).

8) J. Le Moigne and J. Simon, *J. Phys. Chem.*, **84**, 170 (1980).

9) A. Takeuchi, S. Yamada, and H. Yokoi, *Bull. Chem. Soc. Jpn.*, **58**, 2987 (1985).

10) E. N. Baker, D. Hall, and T. N. Waters, *J. Chem. Soc. A*, **1970**, 406.

11) W. P. Schaefer and R. E. Marsh, *Acta Crystallogr., Sect. B*, **25**, 1675 (1969).

12) M. Calvin, R. H. Bailes, and W. K. Wilmarth, *J. Am. Chem. Soc.*, **68**, 2254 (1946).

13) T. Yamamura, *Chem. Lett.*, **1977**, 773.

14) K. Miyamura and Y. Gohshi, *Chem. Lett.*, **1986**, 1145.

15) I. Fells and E. A. Moelwyn-Hughes, *J. Chem. Soc.*, **1959**, 398.

16) S. R. Sandler and W. Karo, "Organic Functional Group Preparations I," 2nd ed., Academic Press, New York (1983), p. 11.

17) T. Izumitani, H. Okawa, and S. Kida, *Chem. Lett.*, **1981**, 483.

18) T. Izumitani, M. Nakamura, H. Okawa, and S. Kida, *Bull. Chem. Soc. Jpn.*, **52**, 2122 (1982).

19) B. I. Ionin and B. A. Ershov, "NMR Spectroscopy in Organic Chemistry," Plenum Press, New York (1970), p. 101.

20) R. J. Abraham, B. Evans, and K. M. Smith, *Tetrahedron*, **34**, 1213 (1978).

21) R. J. Abraham, G. H. Barnett, E. S. Bretschneider, and K. M. Smith, *Tetrahedron*, **29**, 553 (1973).

22) "NMR of Paramagnetic Molecules," ed by G. N. La Mar, W. D. Horrocks, Jr., and R. H. Holm, Academic Press, New York (1973).