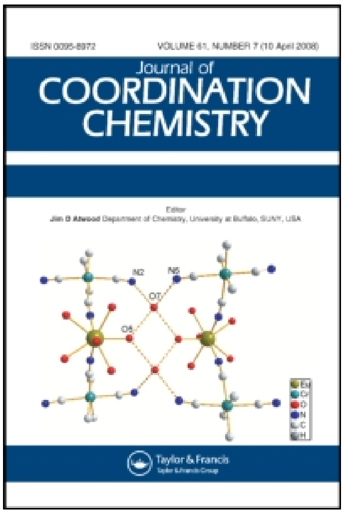

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AGGREGATION OF ALKYL SUBSTITUTED SALCHXN COMPLEXES STUDIED BY ^{1}H-N.M.R.

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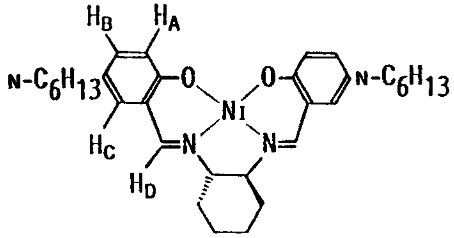
Abstract A difference in the ^{1}H-n.m.r. peak shift due to aggregation was observed between chloroform-d_1 solutions of optically active and racemic forms of chiral (4',4''-dihexyl-N,N'-disalicylidene)-1,2-diaminocyclohexanenickel(II) (**1**). The difference is caused by the formation of racemic dimer in the racemic form of **1**, which is not formed in the optically active form. The equilibrium constants of dimer formations and the aggregation structures were estimated from the concentration dependence of ^{1}H-n.m.r.

Keywords: Aggregation, salchxn complexes, dimer formations

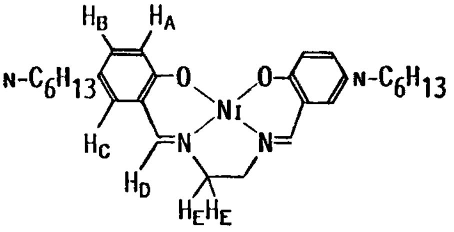
INTRODUCTION

Intermolecular bindings, such as aggregation, have been found to play important roles in organising molecules and giving them additional properties which they otherwise are not endowed with. In the field of co-ordination chemistry, studies of multi-nuclear complexes, including cluster molecules, are attracting the interest of many researchers. The phenomenon of aggregation can be regarded as a simple, though temporary, method of obtaining some multi-nuclear complexes. Thus, studies of the phenomenon of aggregation in the field of co-ordination chemistry are rapidly increasing in number.[1-3]

In a previous paper,[4] we reported that salen type complex, 4,4'-dihexyl-N,N'-disalicylidene-ethylenediaminenickel(II) (**2**) exhibited concentration dependence in ^{1}H-n.m.r. spectra. This observation was made possible by the introduction of long alkyl side chains which increased the solubility of the metal complexes in organic solvents such as chloroform, and thus enabled the investigation of the behaviour of the metal complexes in the extremely high concentration region. Similar phenomena in chloroform are observed with several porphyrin complexes,[5] including chlorophylls,[6] and are considered to be due to aggregation. To confirm that the concentration dependence observed in the salen type complex is also caused by aggregation and not by solvent effect, a novel stereochemical investigation was performed. Here, we wish to propose a stereochemical method of investigating the phenomenon of aggregation, and to report other important results obtained with chiral complex **1**, which proved that concentration dependence is indeed caused by aggregation.



1 (SS-isomer)



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EXPERIMENTAL

(1S,2S)- and (1RS,2RS)-(4',4''-dihexyl-N,N'-disalicylidene)-1,2-diaminocyclohexanenickel(II) (1)

Complex **1** is obtained readily by refluxing an ethanolic solution of nickel(II) acetate, hexyl substituted salicyl aldehyde and chiral diamine ((1S,2S)- or (1RS,2RS)-1,2-diaminocyclohexane), in a molar ratio of 1:2:1 for 4 h. Complex **1** precipitated upon cooling and was recrystallised from ethanol-chloroform mixture. Anal. [Found C,70.03; H,8.12; N,5.20%. Calc. for $C_{32}H_{44}N_2NiO_2$: C,70.21; H,8.10; N,5.12%].

Measurements

Visible absorption spectra were recorded with a Hitachi 340 spectrophotometer. The concentration dependence of ^{1}H-n.m.r. spectra was measured at 35°C using a Hitachi R-40 spectrometer.

RESULTS AND DISCUSSION

The complexes investigated are racemic (mixture of RR and SS) and optically active (SS) forms of **1**. The electronic spectrum of **1** in chloroform (concentration 2×10^{-4} mol•dm^{-3} $\varepsilon_{max}(\lambda_{max})$= 167 dm^{3}mol^{-1}cm^{-1} (550 nm), 7072 dm^{3}mol^{-1}cm^{-1} (420 nm), 8690 dm^{3}mol^{-1}cm^{-1} (350 nm), 8532 dm^{3}mol^{-1}cm^{-1} (325 nm)) resembles that of [Ni(salen)] with a slight red shift in the UV region. Red shift was also observed[4] in the case of **2**. Thus, it is assumed that **1** adopts the square-planar geometry in chloroform.

Concentration Dependence of ^{1}H-n.m.r.

To compare the aggregation behaviour of both racemic and optically active forms of **1**, the concentration dependence of ^{1}H-n.m.r. spectra was examined for both. The ^{1}H-n.m.r. spectra of **1** in chloroform-d_1 were assigned by their coupling patterns and by comparing the spectrum of **1** with that of **2**. On increasing the concentration, the signals assigned to the protons at 3-positions of benzene rings (H_c) and those of azomethine groups (H_d), clearly showed up-field shifts (Figure 1). The up-field shifts of **1** are smaller than those of **2**, also given in Figure 1.[4]

It is interesting to note that the concentration dependence of racemic **1** is clearly different from that of the optically active **1**. This is curious, because each molecule in both racemic and optically active **1** should exhibit, in their ordinary state, exactly the same ^{1}H-n.m.r. spectrum. The difference between the two becomes apparent only when they are placed in a chiral environment. Therefore, the fact that optically active and racemic **1** exhibit different concentration dependence in ^{1}H-n.m.r., strongly suggests that there exists an intermolecular interaction or, in other word, aggregation, since there are no other chiral species which make the

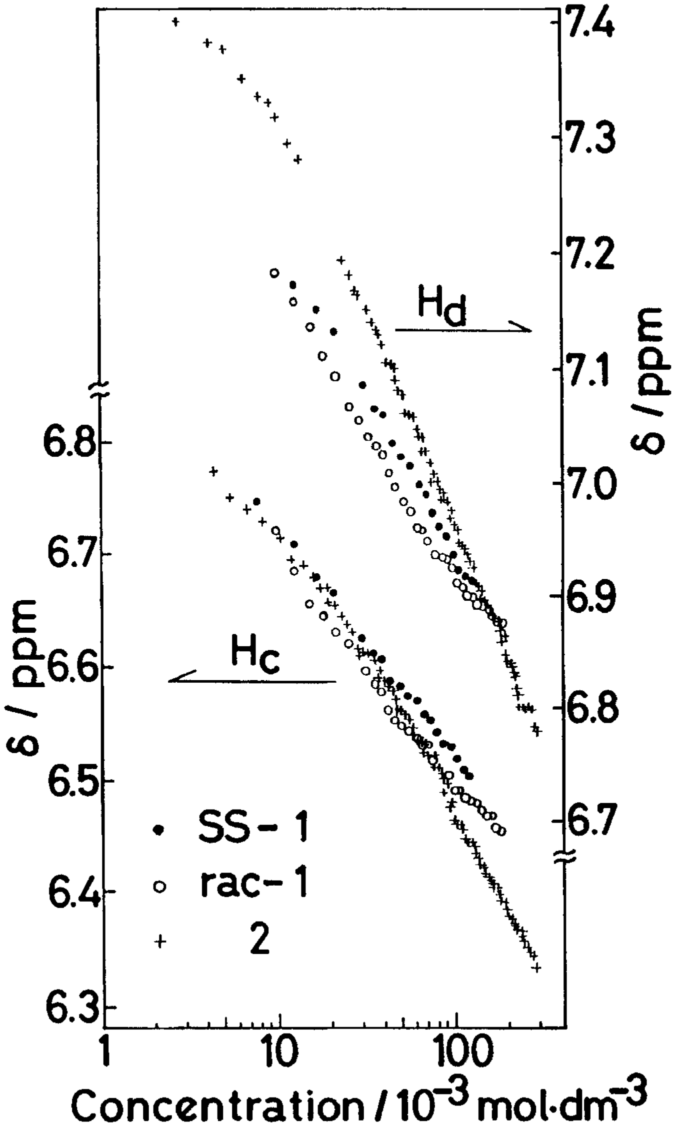

Figure 1. Concentration vs. ^{1}H-n.m.r. chemical shift of H_c and H_d of 1 and 2 in chloroform-d_1 at 35°C.

chiral environment around **1**, other than **1** itself in the solution. This also agrees with the fact that the up-field shift in ^{1}H-n.m.r. spectra is observed when a proton is placed over an aromatic ring. Thus, the approach of the aromatic ring to protons H_c and H_d caused by the aggregation seems to be the reason for the up-field shift.

$$\begin{array}{llll} & \text{monomeric RR + monomeric RR} \rightleftharpoons \text{(RR-RR) dimer} & K_1 & \\ (& \text{monomeric SS + monomeric SS} \rightleftharpoons \text{(SS-SS) dimer} & K_1 &) \\ & \text{monomeric RR + monomeric SS} \rightleftharpoons \text{(RR-SS) dimer} & K_2 & \end{array}$$

Scheme. Dimer formation in tha case of racemic **1**

Theoretical Treatment

The aggregation equilibrium, at low concentration, exists between the monomeric species and its dimers. Thus, for the first order approximation, only the formation of dimeric species is assumed. In the case of the racemic mixture of **1**, formation of two types of dimers in the Scheme should be considered. (From now on, the abbreviations (RR) and (SS), which stand for (1R,2R)- and (1S,2S)-enantiomers of **1**, are used for simplicity.) First is the optically active dimer (RR-RR or SS-SS), in which the same enantiomers aggregate, and second is the racemic dimer (RR-SS), in which a pair of (RR) and (SS) enantiomers aggregate. Therefore, the observed chemical shift (δ_r) of racemic **1** is a weighted average of the chemical shifts of three species, monomer (RR and SS), optically active dimer (RR-RR and SS-SS), and racemic dimer (RR-SS). Using two equilibrium constants, K_1 and K_2, for optically active and racemic dimers respectively, and three chemical shifts, δ_m, δ_d(SS-SS), and δ_d(RR-SS) for monomer, optically active dimer, and racemic dimer, the observed chemical shift (δ_r) for a given proton of racemic **1** at any concentration (C) can be expressed as:

$$\delta_r = 2\delta_m[\text{monomeric SS}]/C + (4K_1\delta_d(\text{SS-SS}) + 2K_2\delta_d(\text{RR-SS}))[\text{monomeric SS}]^2/C \qquad \text{(Eq. 1)}$$

where [monomeric SS]$=(\sqrt{1+C(4K_1+2K_2)}-1)/(4K_1+2K_2)$.

On the other hand, only the formation of the SS-SS dimer (in parentheses in the Scheme) should be taken account of in the case of the optically active (SS) complex. Thus, assuming also an equilibrium between the monomeric complex and dimer for the first order approximation, the chemical shift (δ_o) for a given proton of optically active **1** at any concentration (C) can be given as:

$$\delta_o=\delta_d(\text{SS-SS})+(\delta_m+\delta_d(\text{SS-SS}))(\sqrt{1+8CK_1}-1)/4CK_1 \qquad \text{(Eq. 2)}$$

At first, calculations to fit the observed data of δ_o with Eq. 2 were performed, considering K_1, δ_m, and δ_d(SS-SS) as the variables. Then, calculations to fit the data of δ_r with Eq. 1 were performed, using the K_1, δ_m, and δ_d(SS-SS) values estimated from the calculations above as the constants, and considering K_2 and δ_d(RR-SS) as the variables. The estimated values for the equilibrium constants are K_1=20 and K_2=85 (mol^{-1}dm^3) obtained from the data of H_c, and K_1=25 and K_2=93 (mol^{-1}dm^3) from that of H_d. At the same time, the δ values are estimated as δ_m=6.88, δ_d(SS-SS)=6.33, and δ_d(RR-SS)=6.29 for H_c, and δ_m=7.43, δ_d(SS-SS)=6.84, and δ_d(RR-SS)=6.60 for H_d. Although the resulting equilibrium constants estimated from the data of the two protons H_c and H_d are a little different from each other, the values are of the same order and there is a rough relation of $4K_1 \approx K_2$ between them. This result indicates that the racemic dimer of **1** forms about 4 times more easily than the optically active dimer. Compared with **2**,[7] the K values obtained here, are 3 (K_1) to 12 (K_2) times as large. Therefore the introduction of cyclohexane ring to diamine moiety, the sole structural difference between **1** and **2**, seems to conduce aggregation. Although the exact reason for this effect is still uncertain, changes in the conformation of the five-membered chelate ring, in the aggregation structure, and in the solute-solvent interaction might be responsible.

The δ values estimated for monomeric **1** and **2**[7] are quite similar, while those for the dimers differ considerably. With regard to the structures of monomeric **1** and **2**, there are no prominent differences in the local environments around H_c and H_d, so the observation that monomers exhibit similar δ values is reasonable. On the other hand, the difference between the δ values of the dimer and the monomer for **1** is much smaller than that for **2**. The fact that the corresponding protons, H_c and H_d, exhibit upfield shift in **1** and **2**, though with a difference in the amount of shift, indicates that the dimers of **1** and **2** assume a piled structure similar to that discussed in the previous paper,[4] with different monomer-monomer distances in the dimer. The dimer of **1** may have a longer intermolecular distance than that of **2**, exhibiting only a small shift in ^{1}H-n.m.r. spectra.

The different concentration dependence of ^{1}H-n.m.r. for optically active and racemic forms of **1** strongly suggests that similar dependence observed for salen type complexes is also caused by aggregation.

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7) Aggregation of **2** could be treated just as in the case of optically active **1**. The K and δ values estimated for **2** in ref. 4) are as follows: K=7.5 $\mathrm{mol^{-1}dm^{3}}$, δ_m=6.81 and δ_d=6.06 for H_c, and δ_m=7.44 and δ_d=6.37 for H_d.