Unusually Strong Interactions Mediated by Both $\pi-\pi$ Stacking and CH−π Interactions Present in the Dimer of Nickel(II) Complex Coordinated with *n*-Butyl-Substituted Salen[1]

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It is becoming one of the major concerns of chemists to explore the applications of metal complexes as molecular devices. Among the materials under investigation, liquid crystalline complexes are one of the major targets. We reported that the crystalline nickel(II) salen[1] complexes with long alkyl side chains (dodecyl and hexyl) exhibit peculiar double-melting behavior.[2] Upon heating, the crystal (K) changes first into the smectic E (S_E) liquid crystalline phase, then to the smectic A (S_A) phase, and finally to the isotropic liquid (IL) phase.[3] Another striking feature of this double melting is that the second phase transition is accompanied by a shrinkage of layers by 5 Å.

We recently succeeded in solving the crystal structure of the dibutyl-substituted [Ni(salen)] complex {abbreviated [Ni(C4-salen)]} and found that, in the crystal, the complex molecules stack in the form of dimers with both $\pi-\pi$ stacking and CH−π interactions. Such a structure is totally different from other dimer structures reported for the complexes of salen derivatives[4−8] or analogous ligands. This is probably the first example of dimer formation mediated by both $\pi-\pi$ stacking and CH−π interactions for such complexes. Further, this structural feature clarifies the mechanism of the "double-melting" phenomenon observed for the dodecyl- and hexyl-substituted analogues.

A series of [Ni(salen)] complexes substituted with various chain length alkyl groups was synthesized so as to examine their aggregation behavior in solution.[9] Crystallization of the dibutyl-substituted complex from chloroform−ethanol solution gave single crystals suitable for X-ray crystallographic analysis, containing one molecule of chloroform per complex molecule. X-ray crystallographic analysis was performed with a Rigaku AFC7R diffractometer using the Patterson method.[10]

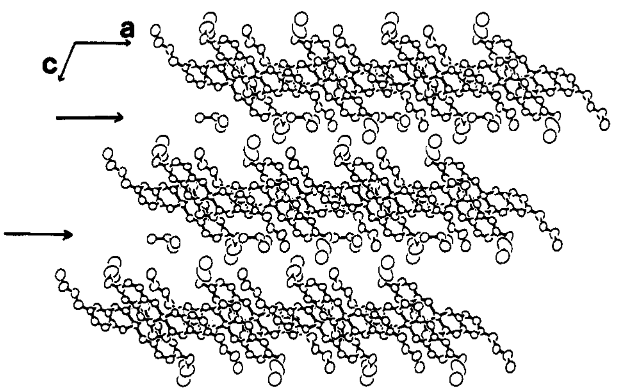

Figure 1. Crystal packing of [Ni(C4-salen)]•$CHCl_3$ viewed from the *b* axis. Alternate packing of layers of complexes and those of chloroform with butyl groups of the complexes (indicated by the arrows) can be seen.

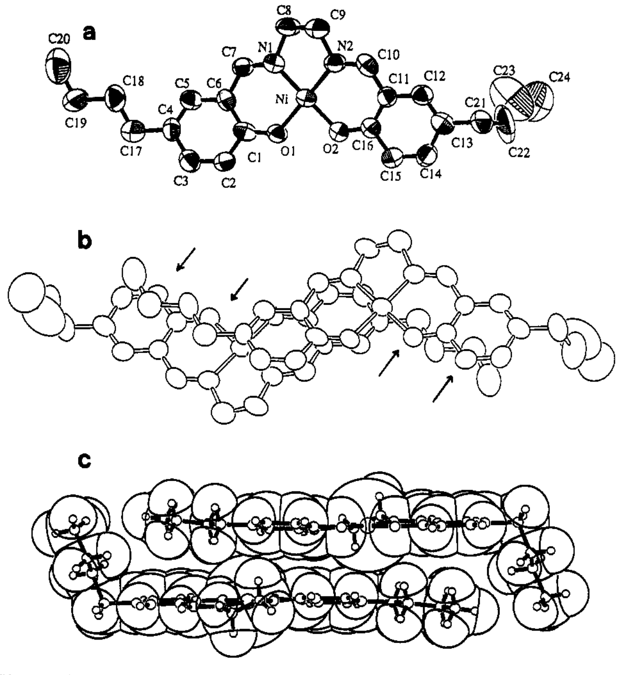

Figure 2. (a) ORTEP drawing of [Ni(C4-salen)]. (b) Top view of [Ni(C4-salen)] dimer. (c) Side view of the dimer with van der Waals radii. $\pi-\pi$ stacking and CH−π interactions (indicated by the arrows) can be seen.

The crystal packing viewed from the *b* axis in Figure 1 shows that there are layers of [Ni(C4-salen)] and chloroform molecules stacked alternately. The structure, however, observed from the *ac* plane shows that the complexes stack in the form of dimers. Parts a and b of Figures 2 show the ORTEP drawing of [Ni(C4-salen)] and the dimer structure, respectively. The π conjugated systems of two salen moieties form a $\pi-\pi$ stacking structure with all the intermolecular distances between them being smaller than 4 Å.[11] This contrasts with the structure of the [Cu(salen)] dimer and its derivatives,[6,7] where there are interactions between copper and oxygen atoms, but there is no observed $\pi-\pi$ stacking. However, taking into account that the atoms in the conjugated system are polarized alternatively, the carbon atoms (C4) facing the nickel atoms in the dimer should be negatively polarized. In fact, all the pairs of atoms facing each other in the two conjugated systems are oppositely polarized and hence should attract each other strongly. This effect brings the atoms of one molecule, illustrated by van der Waals radii in Figure 2c, into close contact with those of another molecule.

Further, one of the two butyl groups in each molecule is found to form CH−π interactions with the conjugated system of another molecule. This is supported by the fact that the

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(1) Salen is an abbreviation of salicylideneethylenediamine. The nomenclature for [Ni(C4-salen)] is [*N,N'*-bis(5-butylsalicylidene)ethylenediaminato]nickel(II).

(2) Ohta, K.; Morizumi, Y.; Fujimoto, T.; Yamamoto, I.; Miyamura, K.; Gohshi, Y. *Mol. Cryst. Liq. Cryst.* **1992**, *214*, 161.

(3) Phase transition temperatures of the dodecyl-substituted analogue (°C): K to S_E, 116; S_E to S_A, 185; S_A to I.L., 253. Those of the hexyl-substituted analogue (°C): K to S_E, 126; S_E to S_A, 226; S_A to IL, 258.

(4) Gerloch, M. M.; Mabbs, F. E. *J. Chem. Soc. A* **1967**, 1900.

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

(6) Baker, E. N.; Hall, D.; Waters, T. N. *J. Chem. Soc. A* **1970**, 406.

(7) Bhadhade, M. M.; Srinivas, D. *Inorg. Chem.* **1993**, *32*, 6122.

(8) Gamovskii, A. D.; Nivorozhkin, A. L.; Minkin, V. I. *Coord. Chem. Rev.* **1993**, *126*, 1.

(9) The method of synthesis and the analytical data of the complex are given in the following article: Miyamura, K.; Satoh, K.; Gohshi, Y. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 45.

(10) Crystal data: $C_{25}H_{31}N_2O_2Cl_3Ni$, $M = 556.59$; monoclinic, space group $P2_1/a$; $a = 19.337(3)$ Å, $b = 10.587(2)$ Å, $c = 13.980(2)$ Å, $\beta = 111.02(1)°$; $v = 2671.5(7)$ Å^3; $Z = 4$; λ(Mo Kα) = 10.50 cm^{-1}, $R = 0.053$, $R_w = 0.038$ for 1926 reflections with $I > 3\sigma(I)$.

(11) Intermolecular distances (Å): Ni−C4', 3.916(9); O1−C5', 3.79(1); C1−C6' and C6−C1', 3.77(1); C7−C2', 3.83(1); N2−C3', 3.91(1).

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temperature factors of the butyl groups lying over the conjugated system are much smaller than those of the other butyl group.[12] In fact, the C−H bonds of C17 and C19 in Figure 2b point toward the middle of the six-membered chelate ring and the benzene ring, respectively.

In the dimer, the two stacked molecules are displaced by 5 Å in the direction of the molecular axes, which accords with the shrinkage of the layers during the smectic E to smectic A phase transition.[2] This fact clearly suggests that the smectic E phase is constituted of dimers and that, upon heating, the dimeric structure is disrupted to form a smectic A phase of monomers. The stabilization of the dimeric structure by the strong $\pi-\pi$ stacking and CH−π interactions may be the origin of the unusually wide temperature range of the smectic E phase.[3] This enables the phase transition to the liquid crystalline state to occur before the destruction of the dimeric structure, and thus double melting occurs. The alkyl groups protruding from the dimers, on the other hand, should take part in the formation of the liquid crystalline phases. This can be confirmed from the crystal structure in Figure 1, where these butyl groups occupy the space between the layers of the complexes. Such a structure is characteristic of a smectic phase. Finally, we point out that the presence of $\pi-\pi$ stacking, although not present between the dimers, is important for the application of these complexes as molecular devices, and that the formation of the liquid crystalline phase is also important for that purpose.

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Supplementary Material Available: Tables of atomic coordinates, anisotropic displacement parameters, and bond lengths and angles (14 pages); tables of observed and calculated structure factors (14 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(12) B_{eq} for butyl group with CH−π interaction: C17, 7.8(3); C18, 7.7(3); C19, 9.6(4); C20, 12.0(5). B_{eq} for another butyl group: C21, 8.5(3); C22, 17.0(7); C23, 19.4(9); C24, 17.2(7).