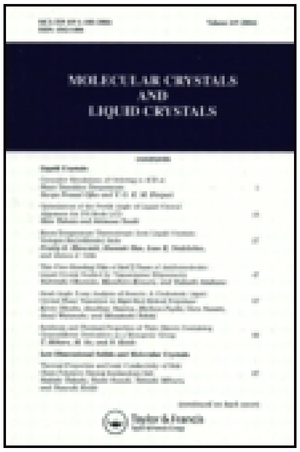

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New Tin-Schiff's Base Materials : Coordination Chemistry and Single Crystal Structure Determination

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New Tin-Schiff's Base Materials : Coordination Chemistry And Single Crystal Structure Determination

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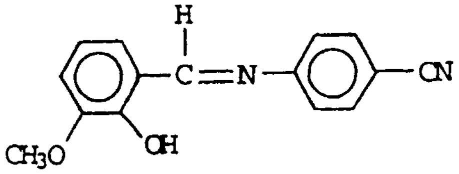
Some solid and crystalline materials derived from the reactions of diorganotin(IV) with salicylaldehyde- and 3-methoxysalicylaldehyde-substituted aliphatic and aromatic Schiff's bases have been synthesized at room temperature. The 1:1 and 1:2 molecular adducts thus obtained have been characterized by elemental analyses, differential scanning calorimetry and NMR spectroscopic techniques which indicated that the coordination to tin occurs through the hydroxyl oxygen. The single crystals of 1:1 and 1:2 (tin:Schiff's base) diphenyltin(IV) and dibutyltin(IV) adducts with 6-methoxy-1-[(4-cyanophenylimino)methyl]phenol and (2- (phenylethylimino) methyl) phenol have been carried out using the charged-coupled device (CCD) area detector and four-circle diffractometers, respectively. The geometries about the Sn atom in both 1:1 and 1:2 materials are trigonal bipyramidal and octahedral. The DSC spectra of the adducts possessing the long alkoxylated group at the lateral position appear to suggest the existence of liquid crystal/isotropic liquid biphasic region.

Keywords: Schiff's base; coordination chemistry; diphenyltin(IV) dichloride; single crystal structure; trigonal bipyramidal; biphasic region

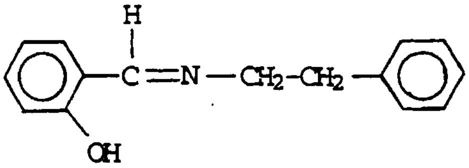
INTRODUCTION

As the coodination chemists, the hope to use the specific expertise to generalise and develop metallomesogenic systems based on functional ligands and other metals has served as an impetus to explore in the coordination chemistry of liquid crystals. In this respect, the initial move is to know some aspects that can be particularly interesting to get into, and to have a quick access to what is already known or has already been made in this field. Then, a systematic study should be adopted especially on the subject which involves in the generation of potential or actual metallomesogens as reported in the literature.[1-6]

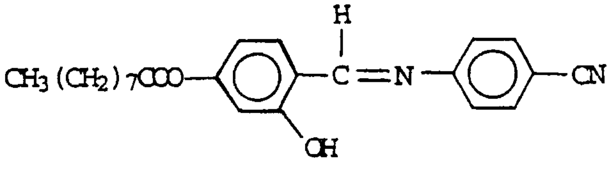
In this paper, we report a systematic attempt towards the synthesis and characterization of some diorganotin-Schiff's base complexes aiming at the establishment of potential metallomesogenic material. The Schiff's bases used in this study and their abbreviations are as follow:



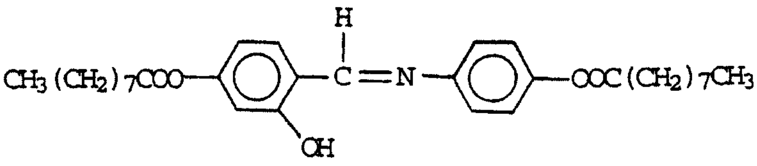
OVA-4CN



SAL-PEA



TFDBENZ(NCL)-4CN



TFDBENZ(NCL)-4NCL

The investigation was carried out by putting emphasis on the coordination and the geometry around the central tin atom in the crystalline phase. The compounds thus synthesized were characterized by microanalytical, spectroscopy (^{1}H and ^{13}C NMR) and X-ray single crystal diffraction analysis. The preliminary results pertaining to the transition temperature using differential scanning calorimetry are also reported.

EXPERIMENTAL

The purity of all products was checked by elemental analysis (C, H, N) and the results are listed in Table I. The identification of products was carried out by the 500-MHz ^{1}H and ^{13}C NMR. The NMR spectra (Tables II and III) were recorded on a JEOL JNM-GX-500 spectrometer. Whilst DMSO-d_6 was used as the solvent, the tetramethylsilane (TMS) was used as internal standard. Transition temperatures and enthalpies were measured by differential scanning calorimetry with Perkin-Elmer DSC-10 operated at a scanning rate of 10 °C/min on heating.

CRYSTALLOGRAPHY

Crystal structure determination on P2OVA-4CN and B2SAL-PEA was carried out on CCD area detector diffractometer (Siemens SMART system) and four-circle diffractometer (Rigaku5 system), respectively. The procedure in the structure determination and solution for both crystals are almost similar with each other and the structure determination on P2OVA-4CN is described as an example.

TABLE I Microanalytical data

Compound	% Calculated			% Found		
	C	H	N	C	H	N
OVA-4CN	71.41	4.80	11.10	71.40	4.80	11.15
M2OVA-4CN	43.26	3.85	5.93	43.20	3.84	5.91
P2OVA-4CN	54.40	3.73	4.03	54.57	3.73	4.68
SAL-PEA	79.96	6.72	6.21	79.93	6.70	6.22
B2SAL-PEA	60.49	6.42	3.71	60.50	6.42	3.70
M2SAL-PEA	45.88	4.77	3.15	45.86	4.75	3.12
TFDBENZ-4CN	70.58	4.24	11.75	70.64	4.20	11.78
M2TFDBENZ(NCL)-4CN	59.03	6.00	5.73	59.11	6.02	5.74
P2TFDBENZ(NCL)-4CN	63.28	5.69	5.09	63.31	5.70	5.06
TFDBENZ-4OH	68.11	4.85	6.11	68.12	4.84	6.13
M2TFDBENZ(NCL)-4NCL	54.34	6.79	1.92	54.39	6.74	1.88

Intensity data for the crystal were measured at room temperature on a CCD diffractometer, Siemens SMART system, fitted with graphite monochromated Mo-K• radiation, $\lambda=0.71073$ Å. The θ-2θ scan was employed to measure a total of 7093 reflections such that $\theta_{max} < 31°$. The crystal of P2OVA-4CN is monoclinic with the space group $P2_1/n$ and the cell dimensions were determined as a=14.070(1), b=13.531(1), c=15.008(1) Å, and β=116.13(1)°. No significant decomposition occurred during the data collection. Lattice parameters were derived by a least-squares treatment of the setting angles for 19633 reflections.

The structure was solved by direct method and refined by full-matric least-squares refinement on F with anisotropic displacement parameters for the non-H atoms. The positions of the H atoms were found on the different Fourier maps and refined using isotropic displacement parameters.

TABLE II ^{1}H NMR

Compound	δ_{OH}	δ_{OH}	δ_{OH}	$\delta_{C:N}$	δ_{OCH3}	$\delta_{OC(CH2)7CH3}$
OVA-4CN	12.46	-	-	8.96	3.82	-
M2OVA-4CN	12.48	-	-	8.96	3.83	-
P2OVA-4CN	12.47	-	-	8.95	3.82	-
SAL-PEA	12.32	-	-	8.86	-	-
B2SAL-PEA	12.33	-	-	8.87	-	-
M2SAL-PEA	12.33	-	-	8.86	-	-
TFDBENZ-4CN	12.94	10.41	-	8.91	-	-
M2TFDBENZ(NCL)-4CN	12.94	-	-	8.92	-	2.17-0.83
P2TFDBENZ(NCL)-4CN	12.96	-	-	8.90	-	2.17-0.83
TFDBENZ-4OH	13.80	10.13	9.55	8.80	-	-
M2TFDBENZ(NCL)-4NCL	13.79	-	-	8.82	-	2.20-0.80

An empirical extinction correction was applied to Fc based on the Sachariasen's formula.[7] The refinement continued to final R=0.036 and Rw=0.031 for 6768 independent reflections. As for the weighing scheme, $1/\sigma(F)$ is used. The XTAL programs package [8] is used for structure solution and refinement.

RESULT AND DISCUSSIONS

The crystal structures and molecular structures of some diorganotin-Schiff's bases materials in the crystalline phase are presented according to the type of Schiff's bases.

TABLE III ^{13}C NMR

Compound	
OVA-4CN	165.46, 152.39, 150.44, 147.93, 133.60, 123.70, 122.39, 119.26, 118.82, 118.71, 116.17, 108.79, 55.90
M2OVA-4CN	165.89, 152.96, 133.65, 133.39, 123.78, 122.46, 122.44, 120.24, 119.28, 119.19, 118.89, 117.63, 113.45, 56.10, 55.97
P2OVA-4CN	166.06, 147.95, 134.66, 133.63, 133.37, 127.74, 127.23, 123.74, 122.42, 119.29, 119.16, 118.86, 118.73, 116.22, 113.42, 55.94
SAL-PEA	163.23, 148..20, 145.67, 144.19, 128.90, 121.70, 116.42, 114.17, 111.31, 105.32, 103.66, 52.13, 36.47
B2SAL-PEA	163.92, 148.54, 145.88, 145.78, 129.11, 124.54, 121..70, 116.42, 114.17, 111.31, 105.32, 52.14, 47.88, 42.31, 36.49, 35.65, 35.52
P2SAL-PEA	163.88, 148.82, 145.90, 144.43, 133.42, 133.78, 128.90, 125.09, 122.13, 121.70, 116.42, 114.17, 111.31, 105.32, 52.16, 36.50

(1) OVA-4CN

The molecular structure for P2OVA-4CN is shown in Fig. 1. Crystal data, fractional atomic coordinates and thermal parameters for both compounds are available upon requests from the authors.

The adduct P2OVA-4CN derived from the reaction of diphenyltin(IV) dichloride with OVA-4CN exhibits 1:1 (tin:ligand) stoichiometry (Table I) in which the geometry about the Sn atom is trigonal bipyramidal with Cl atom and the ipso-carbon atoms of the phenyl groups lying in equatorial plane (Fig. 1). The other Cl atom from Ph_2SnCl_2 moiety and O atom from the Schiff's base occupy *trans* apical sites.

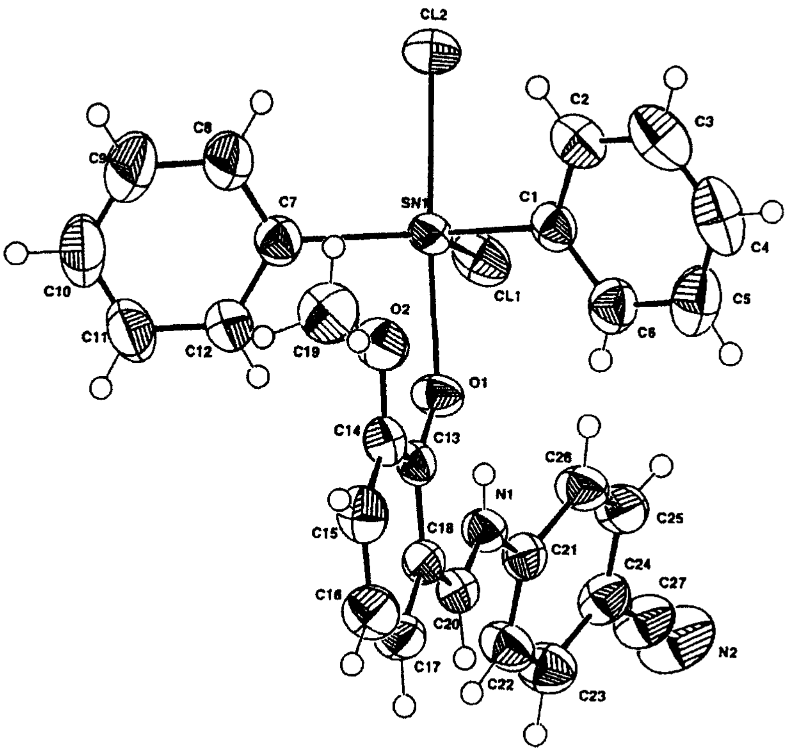


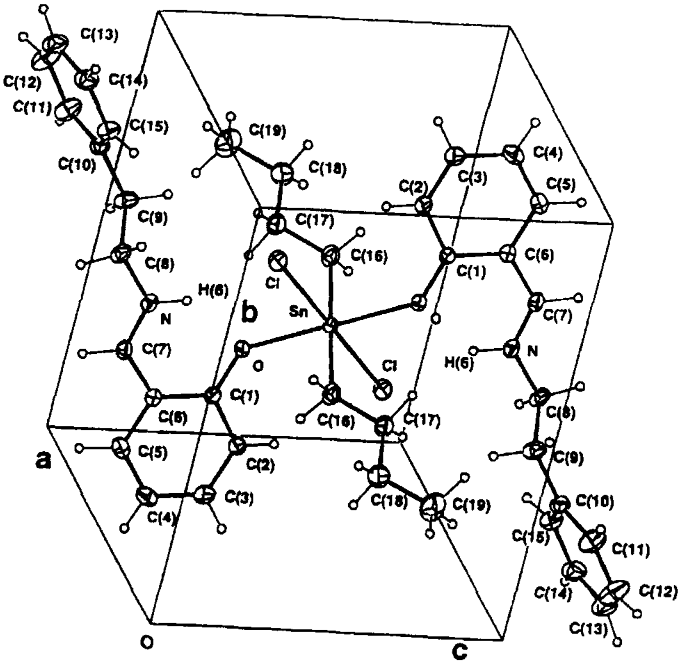
FIGURE 1 Crystal structure of P2OVA-4CN.

Inspection from the ^1H NMR spectrum of P2OVA-4CN shows that a sharp peak ascribed to the azomethine proton at δ=8.96 ppm appears to be almost unaltered in comparision with the spectrum of the uncoordinated Schiff's base. Broadening of the O-H and the strenthening of the N-H bond. This indicates the participation of O atom in the coordination to the Sn atom. Further evidence regarding the participation of phenolic oxygen in the coordination to the tin atom can be inferred from ^{13}C NMR in which the peak owing to the carbon bonded to the phenolic oxygen atom is shifted by 0.6 ppm. A peak which appears at δ=-48.56 ppm in the ^{119}Sn NMR spectrum (not tabulated) is located within the range of chemical shifts as reported for the five-coordinate complexes.[9]

(2) SAL-PEA

The molecular structure for PB2SAL-PEA is shown in Fig. 2. Crystal data, fractional atomic coordinates and thermal parameters for both compounds are available upon requests from the authors.

FIGURE 2 Crystal structure of B2SAL-4CN.



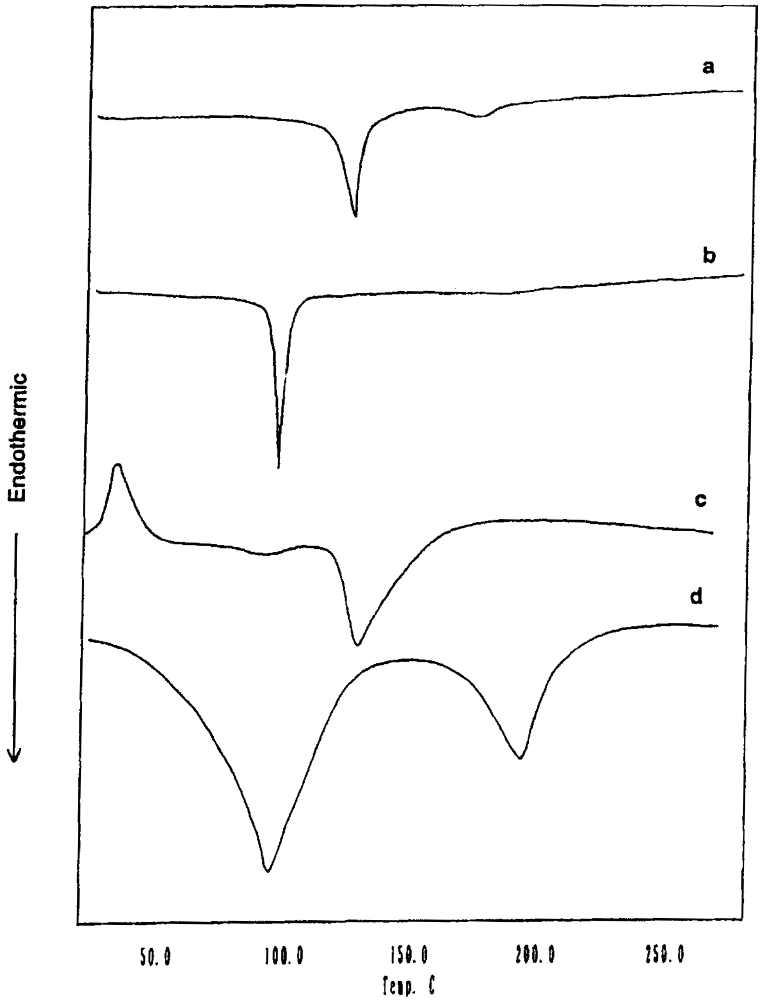


FIGURE 3 DSC thermograms for (a) P2OVA-4CN, (b) B2SAL-PEA, (c) M2TFDBENZ(NCL)-4CN, and (d) M2TFDBENZ(NCL)-4NCL on heating at 10°C min^{-1}.

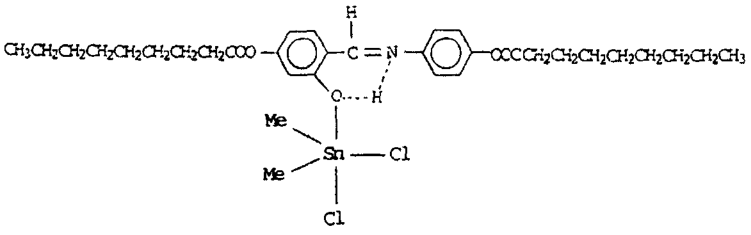
The thermal behaviour of B2SAL-PEA as observed in the DSC curves (Fig. 3) shows only one endotherm, which can be ascribed to the melting temperature (96.5 °C). Apparently B2SAL-PEA do not show mesogenic behaviour. This can be attributed to the lack of planarity particularly along the long axis of the Schiff's base which hinders good molecular packing as that observed in the *ortho*-metallated palladium-imine system.[10]

From Fig. 2, it is clearly shown that the planes of the phenyl rings of the ligand are almost perpendicular with each other. It is different from that observed in the aromatic Schiff's bases in which the planes of the phenyl rings are almost coplanar owing to the bridging by C=N bond.[11-13]

In addition, the Sn atom in B2SAL-PEA is coordinated in octahedral configuration with two equivalent and identical Sn-O bonds. As in P2OVA-4CN, the proton from the phenolic group of the ligand molecule has migrated to the exocyclic imine N atom.

(3) TFDBENZ(NCL)-4NCL

The microanalytical data for M2TFDBENZ(NCL)-4NCL suggests that the ligand TFDBENZ(NCL)-4NCL which possesses long alkoxylic chain at the lateral position is coordinated to Sn atom in tin-ligand molar ratio of 1:1. The ^{1}H NMR spectral data show that the two peaks at δ=10.13 and 9.55 ppm assignable to both hydroxyl (OH) groups at the lateral positions of both aromatic rings of the ligand are absent in the adduct. This piece of evidence strongly suggests that the lateral OH in both aromatic rings were alkoxylated except the OH which lies at the *ortho* position. The peaks owing to the protons in the aliphatic carbon chain were observed within the chemical shift range of δ=2.20-0.80 ppm. The observation from the ^{1}H NMR spectral data strongly suggests that the molecular structure of M2TFDBENZ(NCL)-4NCL can be postulated as structure **I**.



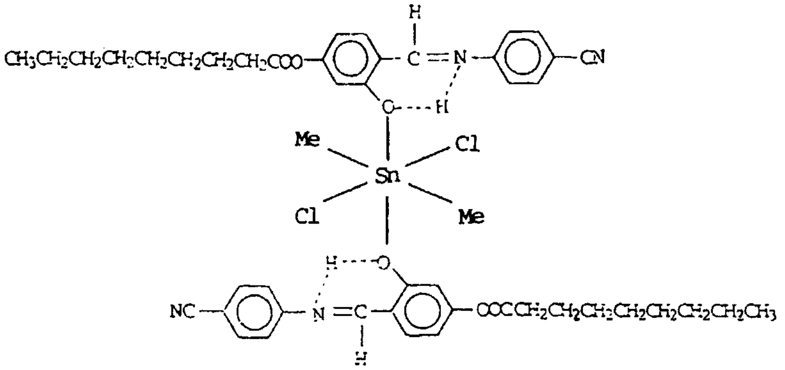
I

The DSC heating curve of M2TFDBENZ(NCL)-4NCL is characterized by the presence of two main endothermic transitions (Fig. 1). The first endotherm is somewhat broadened on the low temperature side and corresponds to the melting process. The maximum is centered at 92.6 °C and the apparent enthalpy is 140.5 kJ/mol.

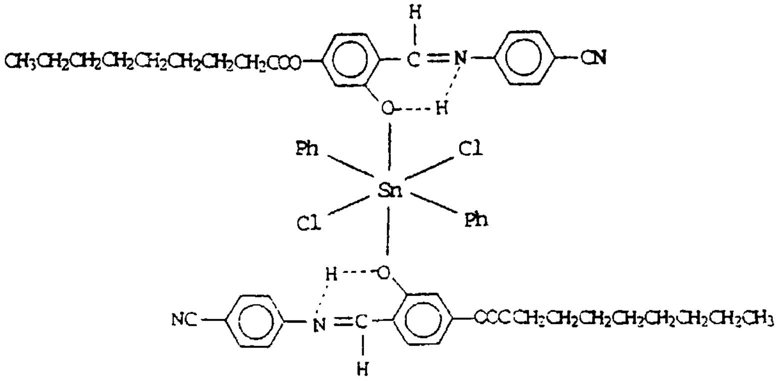
The second transition corresponding to the isotropization transition (T_i= 199.9 °C) is also broad. This piece of evidence strongly suggests the existence of a wide liquid crystal/isotropic liquid biphasic region.

(4) TFDBENZ(NCL)-4CN

The microanalytical data for the adducts derived from the reactions of Me_2SnCl_2 and Ph_2SnCl_2 with TFDBENZ(NCL)-4CN (Table I) are in accordance with the formulations M2TFDBENZ(NCL)-4CN and P2TFDBENZ(NCL)-4CN, respectively. These data also indicate that the Schiff's bases are coordinated to Sn atom in tin:ligand molar ratio of 1:2. The ^1H NMR spectral data (Table II) shows that a peak at δ=10.41 ppm which is assignable to the hydroxyl (OH) proton at the lateral position was absent upon adduct formation with Me_2SnCl_2 and Ph_2SnCl_2. However, the peak which can be ascribed to the *o*-hydroxyl group at δ=12.94 ppm was broadened. This observation suggests a similar coordinative behaviour of TFDNENZ(NCL)-4CN as those OVA-4CN and SAL-PEA in which the phenolic O atom at the *ortho* position from each ligand is coordinated to Sn atom. The peaks which appear within the chemical shift (δ) of 2.17-0.83 ppm in the ^1H NMR spectra of M2TFDBENZ(NCL)-4CN and P2TFDBENZ(NCL)-4CN can be ascribed to the protons in the aliphatic carbon chain which lie at the lateral position of the aromatic ring. With the microanalytical and ^1H NMR data, the molecular structures of M2TFDBENZ(NCL)-4CN and P2TFDBENZ(NCL)-4CN can be postulated as **II** and **III**, respectively.



II



III

A representative DSC curve for the structure **II** shows that the melting process was composed of exothermic and endothermic transitions as shown in Fig. 3-c. One of the reasons accounting for the emergence of the exotherm is the cold-crystallization of amorphous or defective regions. The upper temperature transitions was due to the melting of the most stable crystalline phase.

The further investigation upon the liquid crystalline phase is in progress and the results will be reported elsewhere.

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