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Preliminary communication

The synthesis of liquid crystalline lanthanide complexes of Schiff's base ligands: *N*-(4-*n*-alkoxysalicylidene)-4′-*n*-alkylanilines

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The reaction of *N*-(4-*n*-alkoxysalicylidene)-4′-*n*-alkylanilines with freshly prepared lanthanide salts leads to mesomorphic terbium and dysprosium complexes exhibiting the smectic A phase.

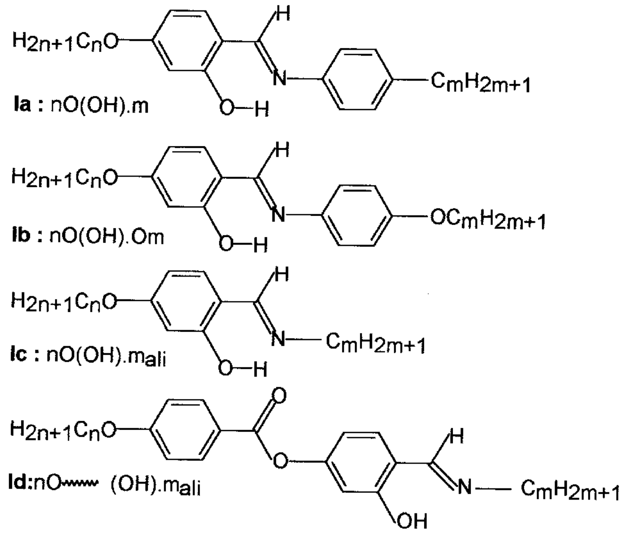

Figure 1. Molecular structures of Schiff's base ligands studied previously for complexation.

Metal-containing liquid crystals, popularly known as metallomesogens, are derived either from rod-like molecules or disc-like molecules, which may or may not themselves exhibit liquid crystalline behaviour, incorporated with a metal atom [1]. These metallomesogens exhibit various mesophases that are also formed by pure organic materials: nematic, smectic, columnar and cubic liquid crystalline phases. Since the introduction of a metal into liquid crystalline compounds possessing coordinating atoms may induce novel properties, interest is growing rapidly in the field of metallomesogens. Several review articles have been published in recent years describing the characteristics of metallomesogens [2]. The family of Schiff's bases exhibiting liquid crystalline behaviour offers wide scope [3–7] with great possibilities of using multifaceted substituents that can be introduced in various positions; thereafter the incorporation of a metal centre yield metallomesogens exhibiting novel phases. Introduction of the *o*-hydroxy group into *N*-(4-*n*-alkoxybenzylidene)-4′-*n*-alkylanilines has led to the possibility of bidental coordination of O and N with metals such as Cu, Ni, Pd, Re, Mn etc. Of the various ligands, *N*-(4-*n*-alkoxysalicylidene)-4′-*n*-alkylanilines [^{n}O(OH).^{m}] (**Ia**), *N*-(4-*n*-alkoxysalicylidene)-4′-*n*-alkoxyanilines [^{n}O(OH).O^{m}] (**Ib**), *N*-(4-*n*-alkoxysalicylidene)-4′-*n*-alkylamines [^{n}O(OH).$^{m_{\text{ali}}}$] (**Ic**), or related materials with extended aryl moieties on one (or other) side of the central bridging imine group (**Id**), the molecules ^{n}O(OH).^{m}, ^{n}O(OH).O^{m} and ^{n}O(OH).$^{m_{\text{ali}}}$ are prominent candidates for coordination with several transition metals (see figure 1). However, efforts to coordinate f-block metals with the above ligands have met with little success except for the case of the *N*-(4-*n*-alkoxysalicylidene)-4′-*n*-alkylamines [^{n}O(OH).$^{m_{\text{ali}}}$] [8–10]. Any attempt at the coordination of metals of the lanthanide group with any of the ligands possessing an aryl moiety on the nitrogen atom presents a special experimental challenge [8]. Of particular importance, we attempted to experiment with the synthesis of the lanthanide complexes with ^{n}O(OH).^{m}, which may promote new molecular structures with possible extension of the molecular length with aryl or aliphatic moieties and different substituents. Our attempts proved to be successful, and in the present communication we report

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the synthesis and characterization of the first mesomorphic lanthanide complexes, in particular the dysprosium and terbium compounds of *N*-(4-*n*-heptoxy-2-hydroxybenzylidene)-4′-*n*-tetradecylaniline, 7O(OH).14.

The synthesis of the ligand and the complex is described in the scheme. The ligand *N*-(4-heptoxysalicylidene)-4′-*n*-tetradecylaniline, 7O(OH).14, was synthesized following synthetic procedures well documented in the literature [4]. 4-*n*-Heptoxysalicylaldehyde was purified by column chromatography, eluting with hexane/chloroform (1/1), and the compound 7O(OH).14 was recrystallized from ethyl alcohol. The spectroscopic data for the ligand are in conformity with reported data.

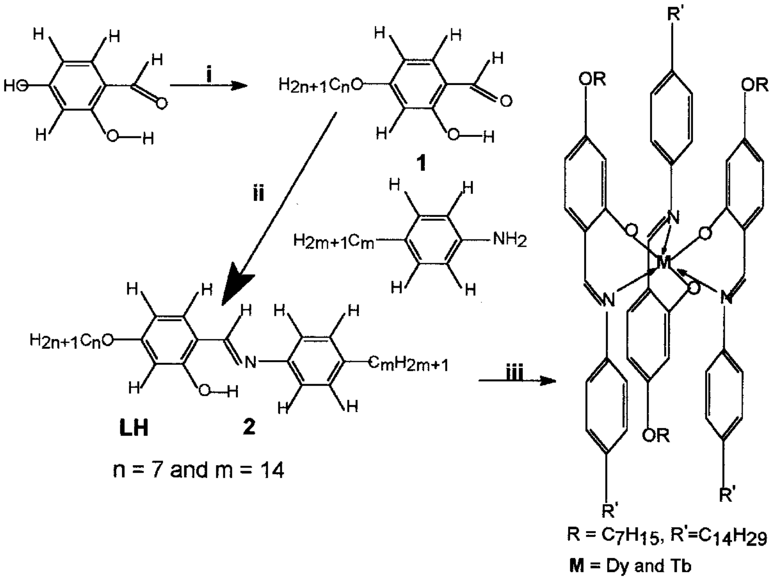
The synthesis of the terbium(III) and dysprosium(III) complexes is now described. Equimolar alcoholic solutions of freshly prepared terbium (or dysprosium) nitrate, prepared from their carbonates, and the ligand (7O(OH).14 = LH), were mixed and heated at reflux for 3 h at 80°C. The boiling solution became viscous, and was cooled and further stirred for an hour or more depending upon the appearance of a microcrystalline precipitate. Further precipitation of the complex was induced by the slow addition of acetonitrile. The precipitated complexes were filtered off, washed with ethanol/acetonitrile mixture, dried *in vacuo* and recrystallized from acetonitrile. The transition temperatures of the ligand and complexes are presented in the table.

Table. Transition temperatures (°C) for the ligand and its dysprosium and terbium complexes.

Compound	Transition temperatures
7O(OH).14 (LH)	$\mathrm{Cr} \underset{<30}{\overset{34.9}{\rightleftarrows}} \mathrm{SmF} \underset{58.6}{\overset{58.9}{\rightleftarrows}} \mathrm{SmC} \underset{70.1}{\overset{70.2}{\rightleftarrows}} \mathrm{SmA} \underset{95.7}{\overset{95.9}{\rightleftarrows}} \mathrm{I}$
$\mathrm{Tb(L)_3}$	$\mathrm{Cr} \underset{56}{\overset{60}{\rightleftarrows}} \mathrm{SmA} \underset{142}{\overset{142}{\rightleftarrows}} \mathrm{I}$
$\mathrm{Dy(L)_3}$	$\mathrm{Cr} \underset{62}{\overset{65.1}{\rightleftarrows}} \mathrm{SmA} \underset{148}{\overset{148.2}{\rightleftarrows}} \mathrm{I}$

The CHN analysis results were consistent with a stoichiometry with the empirical formula [$\mathrm{LnL_3}$] (Ln = Tb or Dy) data here given under. $\mathrm{C_{102}H_{156}N_3O_6Tb}$: calc. C 72.95, H 9.36, N 2.50; found C 72.85, H 9.86, N 2.60%; $\mathrm{C_{102}H_{156}N_3O_6Dy}$: calc. C 72.80, H 9.34, N 2.50; found C 72.95, H 9.84, N 2.65%. However it is difficult to differentiate between the compositions of [$\mathrm{LnL_3}$] and [$\mathrm{Ln(LH)_3(NO_3)_3}$] or [$\mathrm{Ln(LH)_2L(NO_3)_2}$] from CHN microanalysis alone. The FAB mass spectrum of the complex $\mathrm{TbL_3}$, recorded using a JEOL SX 102 mass spectrometer, is shown in figure 2. The molecular ion peak of the complex [$\mathrm{LnL_3}$] appeared at an m/z value of 1680, followed by a peak at 1172 [$(\mathrm{ML_2})^+$], suggesting the loss of one unit of ligand (L) upon fragmentation. Further fragmentation does yield the molecular base peak of the ligand at $m/z = 508$.

The compound 7O(OH).14, on cooling, exhibits a smectic phase, at 95.7°C, with focal-conic fan textures and predominant homeotropic regions characteristic of a smectic A phase. On further cooling, the sample exhibits either broken focal-conic groups or a schlieren texture below 70.1°C, characterizing the phase as a smectic C phase. On further cooling, the sample exhibited another transition at 58.6°C to a broken focal-conic fan texture characteristic of a smectic F phase and



Scheme. Synthesis of the lanthanide complexes. Reagents and conditions: i $\mathrm{C}_n\mathrm{H}_{2n+1}\mathrm{Br}$, $\mathrm{KHCO_3}$, Kl, acetone heat 3 h; ii EtOH, AcOH (catalytic amount); iii $\mathrm{M(NO_3)_3 \cdot }x\mathrm{H_2O}$, EtOH reflux 3 h.

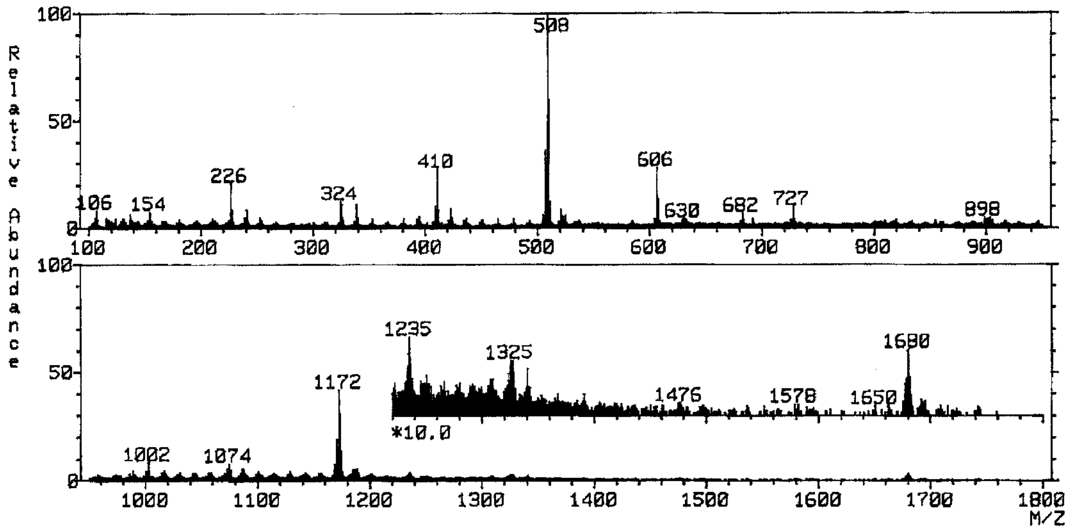


Figure 2. FAB mass spectra of TbL_3.

resembling the texture for the ^{n}O.^{m} compounds [11]. The terbium (60 to 142°C in a heating cycle) and dysprosium (65.1 to 148.2°C) complexes exhibited only one phase which was characteristic of the smectic A phase, with typical focal-conic textures or bâtonnets or homeotropic regions. The homeotropic regions are characteristic of the smectic A phases exhibited by many compounds possessing long alkyl chains in the ^{n}O(OH).^{m} series. The mesophases are highly viscous, as is evident from the shearing behaviour above the melting point. Further, a large decrease in viscosity is apparent from the increase in fluidity in the vicinity of the clearing temperature.

The results support the formation of lanthanide complexes with salicylideneimine-based *N*-arylamines. Moreover a large SmA phase range of about ~80°C, but at low temperatures, is observed in comparison with the complexes $[Ln(LH)_2(L)](NO_3)_2$, (where LH = 7O(OH).18^{ali}), for which the isotropization temperatures are around 150°C with either a small SmA (3°C) phase range (Tb complex) or no liquid crystalline phase (Dy complex) [10*a*]. This suggests that the *N*-arylamine derivatives are better candidates than their aliphatic counterparts. Reported observations for other terbium complexes of the homologues are a monotropic SmA in $[Tb(LH)_2(L)(NO_3)_2]$ (LH = 7O(OH).14^{ali} and 7O(OH).16^{ali} [10*b*]), a 2–3°C enantiotropic phase in $[Tb(LH)_2(L)(NO_3)_2]$ (LH = 7O(OH).18^{ali} [10*a*]), and an approx. 52°C enantiotropic phase in $[Tb(LH)_2(L)(NO_3)_2]$ (LH = 12O(OH).18^{ali} [10*c*, *d*]). Even when the counter ion is changed from NO_3 to dodecylsulphate $[Tb(LH)_3(DOS)_3]$ (LH = 14O(OH).18^{ali} [10*c*, *d*]) to promote liquid crystalline behaviour at low temperatures, it is only partially successful with a decrease in the transition temperatures, but also a decrease in the SmA phase range (60–81°C) [5*a*]. The difference between the complexes of the two homologous series $[LnL_3]$ (Ln = Tb, L = 7O(OH).14) and $[Tb(LH)_2(L)(NO_3)_2]$ (LH = 7O(OH).^{n}^{ali}; $n = 14$, 16 or 18 and 12O(OH).18^{ali}), is only the *N*-aromatic ring, which promotes enhanced mesomorphic behaviour because of strong intermolecular interactions. Hence both ends of the salicylaldimine core can be extended with aromatic cores for complexation with rare earth metals, which can be explored for practical purposes. Further work is in progress with other homologues and different counter ions to study the mesomorphism, the nature of the binding of the coordinating atoms and the effect of the size of the metal atom.

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References

[1] (*a*) Serrano, J. L. (editor), 1996, *Metallomesogens, Synthesis, Properties and Applications* (Weinheim: VCH); (*b*) Cabezon, B., Nicolau, M., Barbera, J., and Torres, T., 2000, *Chem. Mater.*, **12,** 776; (*c*) Hatsusaka, K., Ohta, K., Yamamoto, I., and Shirai, H., 2001, *J. mater. Chem.*, **11,** 423.

[2] (*a*) Giroud-Godquin, A. M., and Maitlis, P. M., 1991, *Angew. Chem. int. Ed. Engl.*, **30,** 375; (*b*) Espinet, P., Esteruelas, M. A., Oro, L. A., Serrano, J. L., Sola, E., 1992, *Coord. Chem. Rev.*, **117,** 215; (*c*) Hudson, S. A., and Maitlis, P. M., 1993, *Chem. Rev.*, **93,** 861; (*d*) Polishchuk, A. P., and Timofeeva, T. V., 1993, *Russ. Chem. Rev.*, **62,** 291; (*e*) Bruce, D. W., 1996, in *Inorganic Materials*, 2nd Edn, edited by D. W. Bruce and D. O'Hare (Chichester: Wiley), p. 429; (*f*) Hoshino, N., 1998, *Coord.*

Chem. Rev., **174,** 77; (*g*) Donnio, B., and Bruce, D. W., 1999, *Struct. Bond.*, **95,** 193; (*h*) Collinson, S. R., and Bruce, D. W., 1999, in *Transition Metals in Supramolecular Chemistry*, edited by J. P. Sauvage (New York: John Wiley), p. 285.

[3] (*a*) Ciriano, M. A., Espinet, P., Lalinde, E., Ros, M. B., and Serrano, J. L., 1989, *J. mol. Struct.*, **196,** 327; (*b*) Ros, M. B., Ruiz, N., Serrano, J. L., and Espinet, P., 1991, *Liq. Cryst.*, **9,** 77; (*c*) Barbera, J., Espinet, P., Lalinde, E., Marcos, M., and Serrano, J. L., 1987, *Liq. Cryst.*, **6,** 833.

[4] (*a*) Ghedini, M., Morrone, S., Bartolino, R., Formoso, V., Francescangeli, O., Yang, B., Gatteschi, D., and Zanchini, C., 1993, *Chem. Mater.*, **5,** 876; (*b*) Ghedini, M., Morrone, S., Francescangeli, O., and Bartolino, R., 1994, *Mol. Cryst. liq. Cryst.*, **250,** 323; (*c*) Ghedini, M., Morrone, S., Gatteschi, D., and Zanchini, C., 1991, *Chem. Mater.*, **3,** 752; (*d*) Rao, N. V. S., Singha, D., Das, M., and Paul, M. K., 2002, *Mol. Cryst. liq. Cryst.* (in the press).

[5] (*a*) Van Deun, R., and Binnemans, K., 2001, *Liq. Cryst.*, **28,** 621; (*b*) van Deun, R., and Binnemans, K., 2000, *J. alloys Compd.*, **303–304,** 146; (*c*) Binnemans, K., Lodewyckx, K., van Deun, R., Galyametdinov, Y. G., Hinz, D., and Meyer, G., 2001, *Liq. Cryst.*, **28,** 279.

[6] (*a*) Guillevic, M., Danks, M. J., Harries, S. K., Collinson, S. R., Pidwell, A. D., and Bruce, D. W., 2000, *Polyhedron*, **19,** 249; (*b*) Guillevic, M., Light, M. E., Coles, S. E., Gelbrich, T., Hursthouse, M. B., and Bruce, D. W., 2000, *J. chem. Soc., Dalton Trans.*, 1437; (*c*) Martin, F., Collinson, S. R., and Bruce, D. W., 2000, *Liq. Cryst.*, **27,** 859.

[7] Binnemans, K., Bruce, D. W., Collinson, S. R., van Deun, R., Galyametdinov, Y. G., and Martin, F., 1999, *Proc r Soc A*, **357,** 3063.

[8] (*a*) Binnemans, K., Bruce, D. W., Collinson, S. R., van Deun, R., Galyametdinov, Yu. G., and Martin, F., 1999, *Phil. Trans. r. Soc. A*, **357,** 3063; (*b*) Binnemans, K., 1999, *Mater. Sci. Forum*, **315–317,** 169.

[9] Binnemans, K., van Deun, R., Bruce, D. W., and Galyametdinov, Y. G., 1999, *Chem. Phys. Lett.*, **300,** 509.

[10] (*a*) Galyametdinov, Y. G., Ivanova, G. I., Ovchinnikov, I. V., Prosvirin, A., Guillon, D., Heinrich, B., Dunmur, D. A., and Bruce, D. W., 1996, *Liq. Cryst.*, **20,** 831; (*b*) Galyametdinov, Y. G., Athanassopoulou, M. A., Griesar, K., Kharitonova, O., Bustamante, E. A. S., Tinchurina, L., Ovchinnikov, I., and Hasse, W., 1996, *Chem. Mater.*, **8,** 922; (*c*) Turanov, A. N., Ovchinnikov, I. V., Galyametdinov, Y. G., Ivanova, G. I., and Goncharov, V. A., 1999, *Russ. Chem. Bull.*, **48,** 690; (*d*) Galyametdinov, Y. G., Ivanova, G. I., Ovchinnikov, I. V., Binnemans, K., and Bruce, D. W., 1999, *Russ. Chem. Bull.*, **48,** 385; (*e*) Binnemans, K., Galyametdinov, Yu. G., Collinson, S. R., and Bruce, D. W., 1998, *J. mater. Chem.*, **8,** 1551.

[11] Rao, P. B., Rao, N. V. S., and Pisipati, V. G. K. M., 1991, *Mol. Cryst. liq. Cryst.*, **206,** 9.