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Cholesterol-based dimesogenic bidentate ligands and their Cu(II) and Pd(II) metallomesogens

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The synthesis and evaluation of the liquid crystalline properties of non-conventional liquid crystals, consisting of two non-identical mesogenic segments interconnected via a paraffinic chain spacer, are of considerable current interest. In particular, chiral dimesogens possessing a cholesteryl ester unit as the chiral entity joined to other aromatic mesogens through a polymethylene spacer have shown unique and interesting thermal behaviour. In continuation of our investigations on this topic, here we present the synthesis and characterization of the first examples of cholesterol-based unsymmetrical dimesogenic bidentate ligands and their Cu(II) and Pd(II) metal-organic systems (metallomesogens). Our studies reveal that the dimesogenic bidentate ligands exhibit multiple mesophases, whereas their metal complexes stabilize only the mesophase.

1. Introduction

Of all the non-conventional low molar mass thermotropic mesogens known to support liquid crystal behaviour, the dimesogens possessing either two structurally identical (symmetrical) or non-identical (unsymmetrical) mesogenic segments connected by a central spacer such as a polymethylene or an oligo(oxyethylene) or oligosiloxyl group, are attracting much attention [1]. This is because they are regarded as model compounds for polymeric liquid crystals and also because of their unusual properties in comparison with conventional liquid crystals. Remarkable differences have also been noted in the behaviour of symmetrical and unsymmetrical dimesogens [2–6].

Recently, chiral dimesogens [2], especially unsymmetrical dimesogens consisting of a cholesteryl ester unit as a chiral segment covalently connected to different mesogenic moieties, namely Schiff's base, azo, stilbene [3], tolane [4], biphenyl [5, 6], etc., via a polymethylene unit, have been studied extensively owing to their quite different and interesting thermal behaviour. For instance, Hardouin *et al.* reported that by linking a cholesteryl ester unit with a Schiff's base mesogenic segment through a *n*-pentyl spacer leads to the observation of a rich polymorphic sequence including an incommensurate smectic A (SmA) mesophase [3*b*]. Further studies on similar types of compound showed that the length of the spacer and the molecular structure of the non-cholesteryl mesogenic segment are more critical for the occurrence

of an incommensurate phase than for the appearance of other mesophases, viz. the blue phases (BP), the twist grain boundary (TGB) phase and the chiral smectic C (SmC*) phase [3*c–e*].

In order to explore the possibility of obtaining similar mesophases and to understand the structure–property relations in such types of dimesogen we have attached different types of chiral or achiral Schiff's base entity to the cholesteryl ester unit through a *n*-pentyl spacer and found that they exhibit SmA, TGB and chiral nematic (N*) mesophases [7]. If the Schiff's base linkage is linked to either a chiral or an achiral tolane entity, the resulting dimesogens have stabilized SmA [8] and N* [4] mesophases, respectively, over wide temperature ranges, indicating the sensitivity of the mesomorphic behaviour to the structure of the non-cholesteryl segment in these systems. Other investigations have also supported the fact that the mesomorphic behaviour in these systems is sensitive to the parity of the spacer and molecular structure of the non-cholesteryl segment [5, 6].

On the other hand, metal-containing mesogens, either organometallic systems (involving metal–carbon or metal– π bonds) or metal-organic systems (involving metal–heteroatom bonds) commonly termed metallomesogens, have also been attracting attention in their own right [9]. These molecules exhibit a variety of interesting phenomena, such as paramagnetism [10], ferroelectric properties, one-dimensional electrical conductivity [11], optical effects [12] such as dichroism, non-linear optical behaviour and electro-optical [13] properties.

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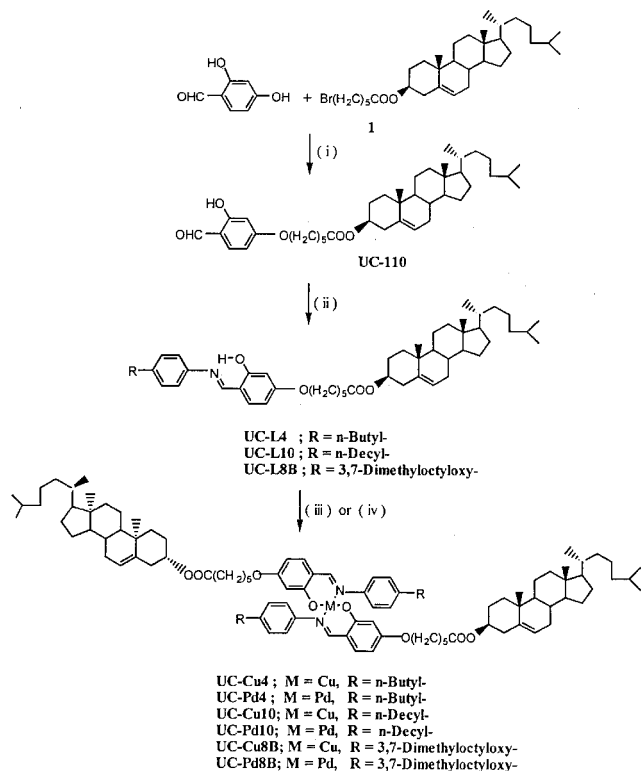
After the first report [14] of mesogenic behaviour in metal-containing liquid crystals, several guidelines have been suggested for mesophase formation in low molar mass monomeric metallomesogens and subsequently extended to polymers (high molar mass systems) [15]. Over the years, main chain [16], side group [17] and crosslinked [18] polymeric metallomesogens have been reported with a focus on molecular design and synthesis. But it is interesting to note that only a few reports are available on the intermediate structures, namely the oligomeric metallomesogens. Further, all the reported systems are organometallics [19, 20]. On the other hand, to the best of our knowledge, metal-organic oligomeric liquid crystals and in particular, cholesterol-based bidentate dimesogenic ligands and their metal-organic metallomesogens have not been reported to date.

As part of our investigations on the molecular design, synthesis and evaluation of the thermal behaviour of cholesterol-based oligomeric liquid crystals [4, 7, 8, 21] we initiated synthetic work to introduce a metal atom into these materials to evaluate the structure-property relations and to furnish the first examples of cholesterol-based unsymmetrical dimesogenic bidentate ligands as well as their metal-organic systems. It was also reasoned that owing to the presence of a chiral (cholesteryl ester) unit in these systems they may exhibit ferroelectric properties. In this Communication we report the synthesis and characterization of cholesterol-based unsymmetrical dimesogenic ligands and their Cu(II) and Pd(II) metallomesogens.

2. Experimental

Schiff's bases, in particular salicylaldehydes derived from substituted salicylaldehydes are versatile bidentate ligands that form (N–O) chelates with many metals. Due to the diversity of substituents that can be introduced, a variety of stable metallomesogens have been reported [22]. A literature survey on metallomesogens indicates the increasing number of mesogens containing Cu(II) and Pd(II) metal atoms, and underlines the versatility of the square-planar coordinate geometry which is typical of these atomic species exhibiting nematic (N), smectic and columnar (Col) mesophases [9]. Thus, in our present studies the molecular design incorporates a salicylaldehyde segment covalently connected to a cholesteryl ester entity via a *n*-pentyl spacer to form a mesogenic bidentate ligand which chelates to Cu(II) and Pd(II) and so furnishes the novel metal-organic systems.

The synthetic pathway to the dimesogenic ligands and their Cu(II) and Pd(II) complexes is depicted in the scheme (see also the Appendix). The key intermediate with cholesteryl and salicylaldehyde moieties, **UC-110**, was obtained by the *O*-alkylation of 2,4-dihydroxybenzaldehyde with cholesteryl 6-bromohexanoate (**1**)



Scheme. Synthetic route to cholesterol-based unsymmetrical dimesogenic bidentate ligands and their metal complexes. Reagents and conditions: (i) KHCO_3 , acetone, reflux, 48 h; (ii) 4-substituted anilines, EtOH, AcOH, reflux, 2 h, quantitative; (iii) $\text{Cu}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, $\text{MeOH}-\text{C}_6\text{H}_6$, reflux, 2 h, 75–88% yield; (iv) PdCl_2 , CH_3CN , K_2CO_3 , reflux, 24 h, 45–70% yield.

which in turn was obtained by esterifying commercial cholesterol with 6-bromohexanoyl chloride. Schiff's bases **UC-L4**, **UC-L10** and **UC-L8B** were obtained by the condensation of **UC-110** with 4-substituted anilines in boiling ethanol containing traces of acetic acid; these were then treated in solution with $\text{Cu}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ or PdCl_2 to obtain the brown copper (**UC-Cu4**, **UC-Cu10** and **UC-Cu8B**) and yellow palladium (**UC-Pd4**, **UC-Pd10** and **UC-Pd8B**) metal-organic metallomesogens, respectively.

3. Results and discussion

The phase sequences and transition temperatures for all the ligands and their metal complexes were investigated using a polarizing optical microscope (Leitz DMRXP) and a differential scanning calorimeter (Perkin Elmer DSC7); the results are summarized in the table. The dimesogenic ligand **UC-L4** exhibits two mesophases; its copper complex **UC-Cu4** shows only one mesophase. However, a disappointing factor was the rather inconsistent thermal behaviour of the complex **UC-Cu4** which we now describe. For **UC-Cu4**, optical microscopy showed that during first heating, the crystal (Cr) melts

Table 1. Phase transition temperatures^a (°C) and enthalpies [J gm⁻¹] of dimesogenic bidentate ligands and their Cu(II) and Pd(II) metal complexes. Cr = crystal, SmC* = chiral smectic C phase; SmA = smectic A phase; TGB = twist grain boundary phase; N* = chiral nematic phase; I = isotropic liquid state; () = monotropic phase.

Compound	Phase transition sequence
UC-L4	Cr 130.1 [75.6] SmA ^b 74.9 [4.5] N* 203.0 [4.8] I
UC-Cu4	Cr 153.9 [35.8] SmA 231.3 [11.5] I
UC-Pd4	Cr 219.2 [35.5] SmA 252.2 [12.5] I
UC-L10	Cr 120.3 [54.1] SmC* 153.6 ^c SmA ^b 185.6 [1.3] N* 187.2 [4.2] I
UC-Cu10	Cr 182.1 [39.0] N* 189.5 [3.8] I
UC-Pd10	Cr 215.3 [44.8] N* 218.9 [2.9] I
UC-L8B	Cr 116.7 [23.5] SmC* 146.4 ^c SmA ^b 176.5 [2.1] N* 179.6 [4.4] I
UC-Cu8B	Cr 180.7 (46.7) (N* 173.8 [3.4]) I
UC-Pd8B	Cr 214.7 (51.3) (N* 201.8 [1.7]) I

^a Peak temperatures in the DSC thermograms obtained during heating cycles at 5°C min⁻¹.

^b A transient TGB phase was observed between SmA and N* for all the ligands.

^c The SmC* phase was observed using polarizing microscopy and was too weak to be recognised by DSC.

to the SmA phase, exhibiting the characteristic focal-conic texture on slides treated for planar orientation, and a dark field of view on slides treated for homeotropic orientation, which is retained till the isotropic (I) phase with a 10°C width for the transition. The width of the transition becomes broader (~20°C) in the cooling mode, but the compound remains in the SmA phase down to room temperature (rt). Both the melting and the SmA–I transitions were clear and reasonably sharp in the first DSC heating scans. However, subsequent scans showed only the SmA–I transition which became much broader and less clear with time. A noticeable drift in the clearing temperature (ct) was also observed indicating inconsistency in the thermal behaviour of the complex. The absence of a melting transition on second heating probably results from the formation of a glassy state originating from either metal–metal or metal–ligand interactions. Similar results were obtained for the palladium complex **UC-Pd4**. It appears that the inconsistent thermal behaviour of both **UC-Cu4** and **UC-Pd4** is because of the high ct value. Therefore it was reasoned that the transition temperatures could be reduced by softening the molecule. For this purpose a higher homologue of **UC-Cu4**, namely **UC-L10**, containing a *n*-decyl chain was synthesized and then converted to its metal complexes **UC-Cu10** and **UC-Pd10**.

Just as for the lower homologue, while the ligand **UC-L10** shows multiple mesophases, the metal complexes **UC-Cu10** and **UC-Pd10** have only one mesophase. We

show (figures 1 and 2) the DSC scans in both the heating and cooling modes for the ligand **UC-L10** and the copper complex **UC-Cu10**. For **UC-Cu10**, the Cr–N* and N*–I transitions are seen (figure 2) to be sharp and clear in both the heating and cooling cycles. The N* phase itself was found to be thermally stable as evidenced by the good reproducibility of DSC thermograms (see inset in figure 2 for three cooling cycles), justifying our argument that the inconsistent thermal behaviour or thermal degradation of **UC-Cu4** was because of the higher ct. However, the palladium complex **UC-Pd10** was again found to undergo thermal degradation on heating to the isotropic phase. In order to confirm that lowering the ct improves the thermal stability of the

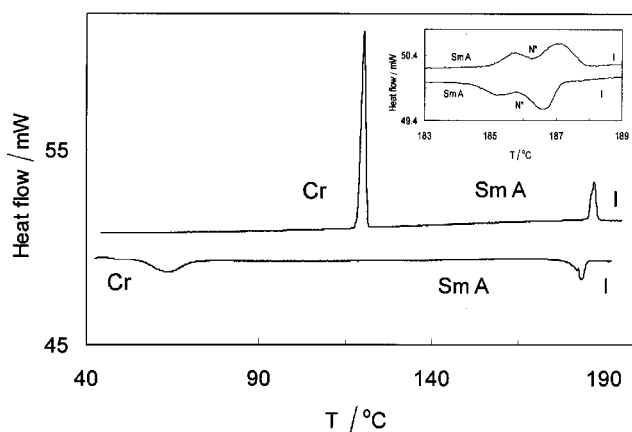


Figure 1. DSC thermograms showing both heating and cooling cycles (at 5°C min⁻¹) for the ligand **UC-L10**. The inset shows the peaks for the SmA–N* and N*–I transitions obtained during heating and cooling cycles at a slower rate of 1°C min⁻¹.

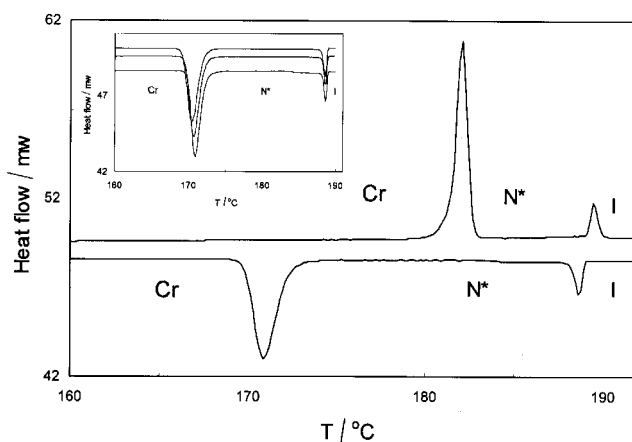


Figure 2. DSC thermograms showing both heating and cooling cycles (at 5°C min⁻¹) for the metal complex **UC-Cu10**. The inset shows the thermograms obtained during three successive cooling scans demonstrating the reproducibility of the transitions and the thermal stability of the complex.

system, we introduced a branched (3,7-dimethyloctyloxy) chain as the substituent in the 4-position of aniline and prepared the dimesogenic ligand **UC-L8B** and its corresponding complexes **UC-Cu8B** and **UC-Pd8B**. As anticipated, the branched chain does lead to a substantial reduction in the *ct*. The melting temperature is not altered much, and this leads to the N* mesophase becoming monotropic. It is again found that **UC-Cu8B** is thermally stable, while **UC-Pd8B** is not, suggesting that thermal degradation of the palladium complex is perhaps an inherent property of this type of molecular assembly.

As mentioned in the table, the dimesogenic bidentate ligands **UC-L10** and **UC-L8B** stabilize the SmC* phase. Preliminary electro-optic studies for these two compounds show ferroelectric switching with a typical response time of 250 μ s (response time is defined as the time for the intensity to increase from 10% to 90% of its maximum value). More detailed studies on ferroelectric properties such as measurements of spontaneous polarization, response time, etc., as functions of temperature are in progress.

Two salient features observed in the present investigations are:

- (1) On increasing the chain length the ligand shows a slightly richer polymorphism (compare **UC-L4** and **UC-L10**), but the metal complex interestingly shows a more disordered phase, namely N*, than for the lower homologue; this can be rationalized in terms of decreasing the possibility of metal-metal interactions.
- (2) The mesophase observed in the complexes is the same irrespective of the metal atoms used, which perhaps can again be attributed to the decreased metal-metal interactions. A systematic and exhaustive investigation is in hand in order to establish the correlation between the molecular structure of such cholesterol-based structurally unsymmetrical oligomeric metallomesogens and their mesophase behaviour.

4. Conclusion

In conclusion, we have synthesized the first examples of cholesterol-based structurally unsymmetrical dimesogenic bidentate ligands and their Cu(II) and Pd(II) metal complexes. Our studies reveal that the dimesogenic bidentate ligands are sensitive to small substitutional changes: a shorter chain length substitution stabilizes two mesophases, whereas a longer chain length give three mesophases. Interestingly, the metal complexes exhibit only one mesophase. Additionally, ferroelectric switching has been observed in two ligands. These novel

molecular assemblies may help in the better design of different metallomesogens suitable for many practical applications.

We are grateful to Prof. S. Chandrasekhar for encouraging interest in this work and to Dr S. Krishna Prasad, who initiated this work on cholesterol-based oligomeric metallomesogens, for many valuable discussions. We also wish to thank the referee for his useful suggestion.

Appendix

The detailed synthetic procedures will be reported elsewhere. The structures/properties of all the new ligands and metal complexes were authenticated by FTIR, NMR and MS. Selected data are now given for some of the materials.

UC-L10: IR (pellet): $\gamma_{\max}/\text{cm}^{-1}$ 2926, 2851, 1722, 1622, 1598 and 1566. ^1H NMR (400 MHz, CDCl_3): δ 13.94 (s, 1H, OH), 8.51 (s, 1H, CH=N), 7.24 (d, $J = 8.24$ Hz, 1H, Ar), 7.21 and 7.18 (AA'BB' pattern, 4H, $\Delta\gamma = 8.97$ Hz, $J = 8.67$ Hz, ArH), 6.47 (brs, 1H, Ar), 6.44 (d, $J = 2.4$, 1H, Ar), 5.37 (br d, $J = 4.8$, 1H, olefinic), 4.6 (m, 1H, CHOCH), 3.99 (t, $J = 6.36$, 2H, OCH_2), 2.61 (t, $J = 7.56$, 2H, ArCH_2), 2.32 (m, 4H, $2 \times$ allylic methylene), 2.02–0.90 (m, 51H, $6 \times \text{CH}$ $21 \times \text{CH}_2$ $1 \times \text{CH}_3$), 1.01 (s, 3H, CH_3), 0.91 (d, $J = 6.52$, 3H, CH_3), 0.86 (d, $J = 1.88$, 3H, CH_3), 0.85 (d, $J = 1.84$, 3H, CH_3) and 0.66 (s, 3H, CH_3). ^{13}C NMR (100 MHz, CDCl_3 , Spin Echo FT): δ 172.94 (CO), 164.02 (C), 163.27 (C), 160.5 (CH), 145.83 (C), 141.34 (C), 139.62 (C), 133.28 (CH), 129.26 (CH), 122.58 (CH), 120.73 (CH), 113.05 (C), 107.36 (CH), 101.56 (CH), 73.78 (CH), 67.77 (CH_2), 56.64 (CH), 56.10 (CH), 49.98 (CH), 42.27 (C), 39.69 (CH_2), 39.50 (CH_2), 38.12 (CH_2), 36.95 (CH_2), 36.55 (C), 36.16 (CH_2), 35.76 (CH), 35.48 (CH_2), 34.52 (CH_2), 31.88 (CH_2), 31.81 (CH), 31.49 (CH_2), 29.59 (CH_2), 29.49 (CH_2), 29.27 (CH_2), 28.74 (CH_2), 28.20 (CH_2), 27.98 (CH), 27.79 (CH_2), 25.53 (CH_2), 24.73 (CH_2), 24.25 (CH_2), 23.81 (CH_2), 22.8 (CH_3), 22.66 (CH_2), 22.54 (CH_3), 21.0 (CH_2), 19.28 (CH_3), 18.68 (CH_3), 14.1 (CH_3) and 11.82 (CH_3). FAB⁺ m/z 836.6 $[\text{M} + \text{H}]^+$ (calculated for $\text{C}_{56}\text{H}_{85}\text{NO}_4$).

UC-Cu10: IR $\gamma_{\max}/\text{cm}^{-1}$ 2926, 2850, 1734, 1610, 1588 and 1522. FAB⁺ m/z 1754.9 $[\text{M} + \text{Na}]^+$ (calculated for $\text{C}_{112}\text{H}_{168}\text{N}_2\text{O}_8\text{Cu}$).

UC-Pd10: IR (pellet): $\gamma_{\max}/\text{cm}^{-1}$ 2926, 2850, 1734, 1609, 1592 and 1518. ^1H NMR (CDCl_3 , 400 MHz): δ 7.56 (s, 2H, CH=N), 7.22 and 7.19 (AA'BB' pattern, 8H, $\Delta\gamma = 10.72$ Hz, $J = 8.45$, Ar), 7.01 (d, $J = 8.84$, 2H, ArH), 6.12 (dd, $J = 8.74$, $J = 2.28$, 2H, Ar), 5.53 (d, $J = 2.2$, 2H, Ar), 5.38 (br d, $J = 4.8$, 2H, olefinic), 4.6 (m, 2H, $2 \times$ CHOCH), 3.76 (t, $J = 6.16$, 4H, $2 \times \text{OCH}_2$), 2.63 (t, $J = 7.64$, 4H, $2 \times \text{ArCH}_2$), 2.3 (m, 8H, $2 \times$ allylic methylene), 2.05–0.90 (m, 102H, $12 \times \text{CH}$, $42 \times \text{CH}_2$, $2 \times \text{CH}_3$), 1.01 (s, 6H, $2 \times \text{CH}_3$), 0.91 (d, $J = 6.6$, 6H,

$2 \times \text{CH}_3$), 0.87 (d, $J = 1.8$, 6H, $2 \times \text{CH}_3$), 0.85 (d, $J = 1.72$, 6H, $2 \times \text{CH}_3$) and 0.67 (s, 6H, $2 \times \text{CH}_3$). ^{13}C NMR (100 MHz, CDCl_3 , Spin Echo FT): δ 172.91 (CO), 166.86 (C), 164.79 (C), 160.89 (CH), 147.41 (C), 140.67 (C), 139.63 (C), 135.34 (CH), 127.82 (CH), 124.66, 122.60 (CH), 114.63 (C), 106.46 (CH), 101.93 (CH), 73.78 (CH), 67.16 (CH_2), 56.65 (CH), 56.10 (CH), 49.99 (CH), 42.28 (C), 39.70 (CH_2), 39.49 (CH_2), 38.13 (CH_2), 36.97 (CH_2), 36.54 (C), 36.16 (CH_2), 35.77 (CH), 35.58 (CH_2), 34.52 (CH_2), 31.91 (CH_2), 31.83 (CH), 29.67 (CH_2), 29.56 (CH_2), 29.42 (CH_2), 28.74 (CH_2), 28.20 (CH_2), 27.98 (CH), 27.8 (CH_2), 25.6 (CH_2), 24.76 (CH_2), 24.25 (CH_2), 23.81 (CH_3), 22.80 (CH_3), 22.68 (CH_2), 22.54 (CH_3), 21.01 (CH_2), 19.30 (CH_3), 18.69 (CH_3), 14.12 (CH_3) and 11.83 (CH_3). FAB^+ m/z 1799.0 $[\text{M} + \text{Na}]^+$ (calculated for $\text{C}_{112}\text{H}_{168}\text{N}_2\text{O}_8\text{Pd}$).

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