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Supplementary Material Available: Tables of ^{13}C and ^{1}H NMR chemical shifts and ^{1}H NMR NOE data and summaries of MS and IR data for kedarcidin chromophore (Figure 1), tables of ^{13}C and ^{1}H NMR data for methyl α-L-mycaroside (**1**), the methyl α- and β-glycosides of kedarosamine (**2**), and the 2′-chloroazatyrosyl naphthoamide fragment (**3**), computer-generated drawing of the X-ray structure of the 3-*p*-bromobenzoate derivative of the methyl β-glycoside of kedarosamine with atom numbering scheme, and crystallographic parameters (19 pages). Ordering information is given on any current masthead page.

Discotic Bimetallomesogens: Building Blocks for the Formation of New Columnar Arrangements of Transition Metals

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Liquid crystals incorporating transition metal complexes as their core groups (mesogens) promise to dramatically increase the range of properties currently exhibited by mesomorphic materials.[1] The development of bimetallic mesogens is an important step to the realization of the true potential of inorganic liquid crystals since these mesogens can exhibit ferromagnetism[2] and/or mixed oxidation states,[3] properties key to the formation of magnetic and conductive materials, respectively. However, this aspect of inorganic liquid crystals has been somewhat limited, and only a few bimetallic liquid crystals have been described.[1,4] We report herein our results on the development of new discotic dicopper liquid crystalline complexes and the use of molecular shape to create novel columnar superstructures.

We have synthesized and characterized a number of dicopper complexes[5] as shown in Scheme I. These complexes melt to give birefringent fluid phases with columnar superstructures as is often observed for disc-shaped molecules.[6] Although the monomeric structures of **II** and **IIIa,b** do not exhibit the disc-like shape which is typically a precondition for the formation of a columnar mesophase, dimeric structures of **II** and **IIIa,b** can display a disc-like shape similar to that of **I** if nearest neighbors in the columns are correlated, such as is shown in Scheme I. The columnar liquid crystalline phases of **I**, **II**, and **IIIa,b** are stable over a wide temperature range, but the stability of these phases is very sensitive to the number of side chains and to electronic effects. For example, liquid crystallinity is totally suppressed in derivatives of **I** and **II** substituted by 3,4-dialkoxyphenyl groups instead of 3,4,5-trialkoxyphenyls. Similar modification of **IIIa,b** still results in mesomorphism, although optical textures are suggestive of smectic phases rather than columnar phases. Substitution of the terminal methyl group of **II** for a trifluoromethyl group also destroys the liquid crystallinity by increasing the melting point. Presumably the increased affinity of the more electron-poor copper centers for axial ligands increases dative interactions between the neighboring complexes.

DSC analysis of **I** shows a large enthalpy (5–25 kcal/mol) for the crystal-to-liquid crystal transition at lower temperature (50–100 °C) and a low enthalpy (0.5–2.3 kcal/mol) for the liquid crystal-to-isotropic transition at higher temperatures (150–225 °C). The width of the temperature range of mesomorphism is roughly side chain independent at about 120 °C, and the melting and clearing points both decrease as the side chain length increases. The textures of **I** viewed under a polarizing microscope are best described as mosaic with wedge- and leaf-shaped disclinations. This texture combined with analysis of the directional nature of extinction brushes indicates a tilted rectangular columnar structure.[7] X-ray diffraction (Figure 1) confirms that the columns pack in a rectangular array with liquid-like order within the columns (i.e., D_{rd}). For **I** ($n = 8$) the distortion away from a hexagonal lattice is large,[7b,8] **a** = 57.0 Å and b = 27.1 Å, and for **I** ($n = 10$) we have found a lower distortion, a = 55.6 Å and b = 30.3 Å.

Many of the **II** and **IIIa,b** derivatives exhibit relatively high clearing points (200–250 °C) which are accompanied by some decomposition. However, a reduction of clearing points with increasing side chain lengths results in stable isotropic phases for **II** ($n \geq 10$) and **IIIb** ($n = 14$). DSC analysis reveals a very wide temperature range of mesomorphism (100–150 °C), which is constant for different derivatives of **II** and **IIIa**, with **IIIb** showing more complex behavior. The combined enthalpies of the crystal-to-crystal and/or crystal-to-liquid crystal transitions are large (10–20 kcal/mol), and the liquid crystal-to-isotropic transitions are of low enthalpy (0.5–1.2 kcal/mol). When cooled from their isotropic phases, **II** and **IIIa,b** display textures which are a mixture of pseudo focal conics and mosaic regions with linear birefringent defects, suggesting hexagonal columnar structures.[6] As is shown in Figure 1, X-ray diffraction of the mesophases of **II** and **IIIb** confirms a hexagonal columnar arrangement with liquid-like order in the columns (i.e., D_{hd}). The identical d-spacing of the (100) peaks supports the idea that dimerization of **II** and **IIIa,b** produces a similar shape (Scheme I). Hence, **IIIa,b** exhibits a novel antiparallel correlation within the columns (i.e., a D_{hd} antiphase), which results in a structure whereby nonequivalent metal centers stack in an alternating fashion. Indeed a crystal structure determination on **IIIb** ($n = 6$) shows such an alternating antiparallel columnar arrangement.[9] Although the lattice parameters of the

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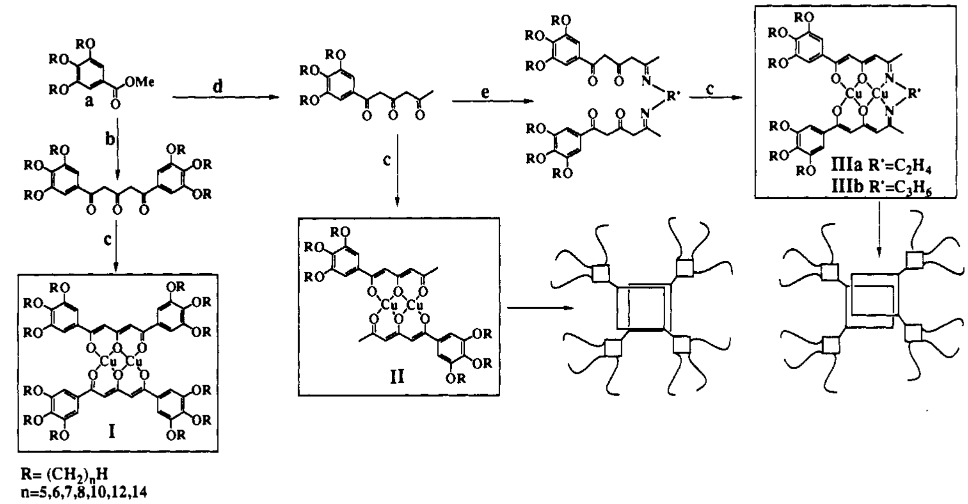
Scheme I[a]



[a] All reactions carried out under N_2; a. 1 eq. Methyl 3,4,5-trihydroxybenzoate, 3.3 eq. RBr, 7 eq. K_2CO_3, acetone reflux 3 days, ≈90%; b. 0.5 eq. acetone, 6 eq. NaH, DME reflux 24 hr., ≈85%; c. 1 e.q. $Cu(OAc)_2(H_2O)$, $CHCl_3$/EtOH (1/4), 70 °C, 1 hr., 95%; d. 1 eq. acetylacetone, 3 eq. NaH, DME reflux 24 hr., ≈75%; e. 0.5 eq. $H_2NC_2H_4NH_2$ or $H_2NC_3H_6NH_2$, EtOH, RT 12 hr., 90%.

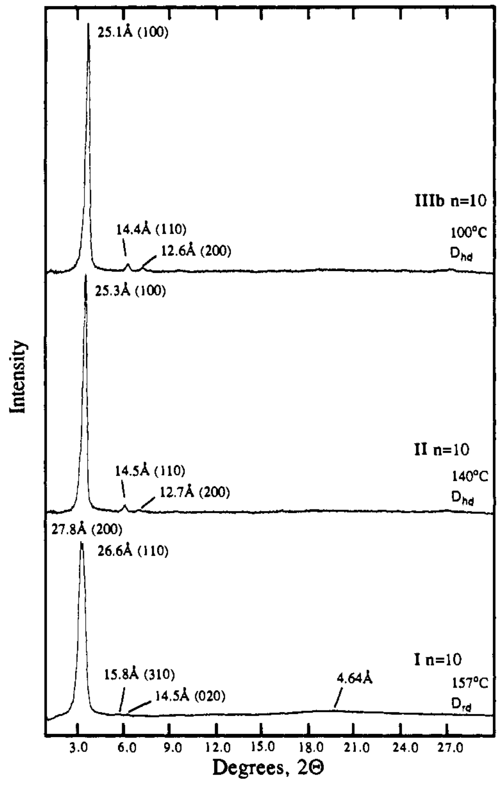


Figure 1. X-ray diffraction data for the liquid crystalline phases of **I**, **II**, and **IIIb** ($n = 10$).

D_{hd} phases of **II** and **IIIa,b** are the same, their dynamics are different. **II**'s texture shows a considerable reduction in the birefringence with increasing temperature, whereas **IIIa,b**'s textures show essentially constant birefringence. This is likely the result of precessional motion of the phenyl rings in **II**'s D_{hd} phase which is not possible for **IIIa,b** due to a higher density within the columns.

We have discussed our results on the dicopper complexes; however, the ligands reported display extensive coordination chemistry and represent versatile building blocks for the formation of a variety of materials with different transition metals.[5,10] Our future reports will describe related homo- and heteronuclear bimetallic liquid crystalline complexes as well as related trimetallic mesomorphic complexes.

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Supplementary Material Available: Tables of crystal coordinates, thermal parameters, bond distances, and bond angles and ORTEP diagrams of **IIIb** ($n = 6$) and graphs of phase transitions and tables of enthalpies of phase changes and elemental analysis data for all compounds reported (26 pages). Ordering information is given on any current masthead page.

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First Hydrogen Abstraction–Rearrangement Model for the Coenzyme B_{12}-Dependent Methylmalonyl-CoA to Succinyl-CoA Carbon Skeleton Rearrangement Reaction

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Coenzyme B_{12} is an obligatory cofactor in a remarkable series of 12 enzyme-catalyzed rearrangement reactions.[1] Of these, the three-carbon skeleton rearrangements in the series have been particularly intriguing because of the lack of precedent for such transformations among organic reactions.

The rearrangements are typified by the interconversion of methylmalonyl-CoA with succinyl-CoA (eq 1), in which the thioester migrates to the methyl carbon following hydrogen abstraction. Rearrangements in this series can be represented more

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