

Synthesis of New Metallomesogens containing a Metal 4-Substituted-piperazine-1-dithiocarboxylate Core

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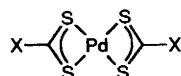
New metallomesogens, bis[4-(*n*-alkyl)- and bis[4-(4-*n*-alkoxyphenyl)-piperazine-1-dithiocarboxylato]metal(II) complexes, have been synthesized and shown to exhibit either a nematic or a smectic phase.

Metallomesogens¹ (also grouped as metal-containing liquid crystals,² or transition metal liquid crystals³) are a new class of materials of great potential. It is expected that the orientational controllability of an assembly of transition metal elements would impart interesting novel properties to molecular materials. The molecular aspect of these compounds would depend mostly on the ligand design, and various types of the ligand,² as well as different central metal atoms,³ have been tested for the mesogenic character of the resulting coordination compounds.

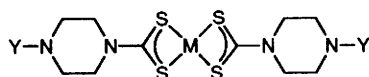
Sulfur donor ligands have so far been relatively less exploited, although the first report of 'contemporary' metallomesogen research was on a nickel(II) dithiolene complex.⁴ Metal dithiocarbamates, on the other hand, are a well-known

group of coordination compounds of rich chemistry for many applications⁵ and, with appropriate chemical modifications, it was felt that they should yield a new type of liquid crystalline material. We report here the results of our preliminary survey of mesomorphic complexes having a metal *N,N*-dialkyldithiocarbamate framework.

Synthetic routes, adapted from literature methods,⁶ to these newly prepared derivatives are shown in Scheme 1; the piperazine derivatives used for compounds **3** and **4** were prepared by known procedures for either *O*- or *N*-alkylation. Compounds **3** were obtained by metathesizing isolated sodium salt precursors, while for the other amines, potassium hydroxide and carbon disulfide were added and then subjected *in situ* to the reaction with Na₂[PdCl₄]. Compounds **2** and **3**



1-*n* X = N(C_nH_{2n+1})₂ (*n* = 6, 8)



2 M = Pd, Y = Ph
 3a-*n* M = Pd, Y = C₆H₄-OC_nH_{2n+1} (*n* = 10, 18)
 3b-*n* M = Ni, Y = C₆H₄-OC_nH_{2n+1} (*n* = 10, 18)
 3c-*n* M = Cu, Y = C₆H₄-OC_nH_{2n+1} (*n* = 10, 18)
 3d-18 M = Zn, Y = C₆H₄-OC₁₈H₃₇
 4-*n* M = Pd, Y = C_nH_{2n+1} (*n* = 6, 8)

were insoluble in most organic solvents and purified by recrystallizing from pyridine.† In contrast, compounds **1** and **4** are highly soluble in non-coordinating solvents such as acetone and halomethanes, allowing crystallization by adding ethanol to these solutions.† The materials thus prepared were characterized for the mesomorphism by polarizing microscopic observation and differential scanning calorimetry (DSC) with a scanning rate of 5 K min⁻¹.

The long chain derivatives of the piperazine-1-dithiocarbonylate complex, **3a**, **3b**, **3c** and **4**, proved to be mesomorphic. Table 1 shows the results of the DSC measurements‡ where K, S_c, N and I denote crystalline, smectic C, nematic, and isotropic liquid phases, respectively, and related non-mesogenic complexes, **1**, **2** and **3d**, are included for comparison.

From Table 1 several points become apparent concerning the ability of the metal dithiocarbamate species to show mesomorphic properties. Compounds **1** have low-melting temperatures, but the palladium chelate core appears to be insufficient for the liquid crystalline order to emerge.§ If the polymethylene chains are tied into a piperazine ring and a phenyl group is attached for some rigidity (**2**), the crystalline phase becomes far more stable than desired; the crystal exhibits no phase transition whatsoever before starting to decompose at a high temperature.

Placing flexible alkoxy tails at the 4-position, however, decreases the melting point by more than 60 °C, and a smectic liquid crystalline phase is now uncovered (**3a**). The phase behaviour persists if the palladium atom is replaced by nickel (**3b**). The melting points decrease if copper is employed (**3c**) but the chemical stability of the compounds is also lowered. The effect of alkyl chain elongation (**3-10** → **3-18**) on the melting point is more favourable in this case compared with those of the palladium and nickel compounds. The mesophase observed with these complexes has been tentatively assigned as smectic C based on the optical textures, which are 'sandy' for thick and Schlieren-like for thin preparations; X-ray diffraction measurements are in progress for confirmation.

† Elemental analyses were consistent for all of the complexes as formulated (unsolvated). The onset of very sharp melting transitions on the DSC thermograms supported their purity. ¹H and ¹³C NMR spectra of compound **4-6** in CDCl₃ confirmed its structure and indicated equivalence of two protons each in the 2- or 3-position of the piperazine ring executing rapid conformational interconversion.

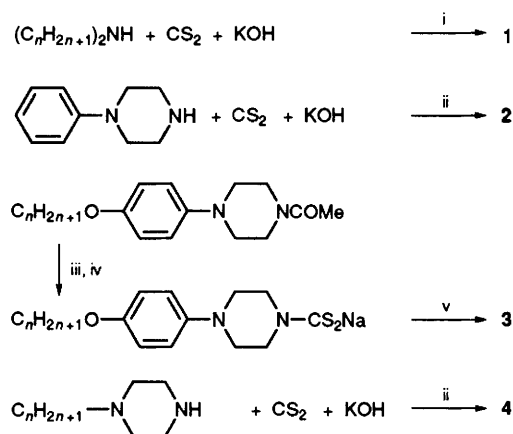
‡ Some of the values determined with the obtained crystals are approximate. Polymorphism of **3a-18**, **3b** and **3c-18** was indicated by somewhat split DSC peaks, but lengthy thermal treatment at high temperatures to obtain single phase specimens was avoided. The melting temperature of the K₁ phase of **3b**, as an exception, was assigned the higher one of two separate peaks.

§ Molten **1-8** may transform into a crystal smectic variation, since an exothermic process occurring 3 °C below its melting point accounts for only a quarter of the melting enthalpy.

Table 1 Mesomorphic transition temperatures (*T*/°C) and enthalpies^a (Δ*H*/kJ mol⁻¹)

Compound	K ₂	K ₁	S _c	N	I
1-6		65.8 (35.2)			
1-8		35.6 (54.0)			
2		326 ^b			
3a-10		258.5 (36.5)	330 ^b		
3a-18	120 (34) ^e	265.1 (18.2)	321 ^b		
3b-10		254.1 (19) ^f	334 ^c		
3b-18	120 (37) ^e	257.3 (19) ^f	315 ^c		
3c-10		230.0 (32.5)	247 ^c		
3c-18	117.0 (32.6)	208 (32) ^e	234 ^c		
3d-18		114.5 (85.0)	246.7 (61.2)		
4-6		103.0 (5.2)	232.1 (27.4)	252.0 ^d (1.6)	
4-8		64.1 (18.3)	208.9 (24.0)	237.3 (1.6)	

^a Values in parentheses. ^b Onset of exothermic decomposition. ^c Onset of endothermic decomposition. ^d Recorded during the first heating cycle. ^e Integrated over a split peak. ^f Summed for a pair of separated peaks (see footnote ‡).



Scheme 1 Reagents and conditions: i, Na₂[PdCl₄], in EtOH (aq); ii, Na₂[PdCl₄], in H₂O; iii, HCl (aq), reflux; iv, NaOH, CS₂, in H₂O; v, Na₂[PdCl₄], NiCl₂·6H₂O, CuSO₄·5H₂O, or ZnCl₂, in MeOH and/or H₂O

It turned out that the *p*-phenyleneoxy group is not essential for the mesomorphism (**4**), but the phase is nematic here. The optical textures were of marble type on heating but a Schlieren pattern with four brushes was also observed in part on cooling. Thus, the bis[dithiocarbonylate]palladium(II) core with added cyclic amine residues constitutes a sufficiently anisotropic moiety to form a mesophase.

It should be noted that the compounds **4** are 'nonaromatic' metallonematogens. Materials of this type with paramagnetic metal ions would be of interest from a magnetic field orientation viewpoint and allow an approach to the problem of magnetic anisotropy of metallomesogens.⁷

Synthetic efforts to modify the amine unit will also be useful. It should be noted that the compounds **3-18** undergo strongly endothermic solid-solid phase transitions. The K₂ →

K_1 transition enthalpy amounts to nearly twice the melting enthalpy in the cases of **3a-18** and **3b-18**. These K_1 phases are so designated because of the lack of fluidity, but could well be of a crystal smectic type. Further modifications of the molecular design would lead to the formation of a true liquid crystalline phase.

Another octadecyl homologue **3d-18** is distinct in its very large enthalpy changes upon phase transitions. While the rest of present compounds are more or less likely to have a crystal structure involving tetragonal association of square planar bis-chelates,⁵ this zinc complex could be in a dimeric, bridged tetrahedral form as in the cases of simpler dialkyldithiocarbamates of zinc(II).⁸ However, it appears to undergo an extensive structural transformation before melting. Appropriate ring substituents may be useful here again in adjusting the phase behaviour. Further research along these lines will be reported in due course.

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