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Mesomorphic dithiocarbamate complexes

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Abstract—Complexes of 4-(4'-alkyloxyphenylethyl)piperidine dithiocarbamates with nickel, palladium, copper and zinc have been formed. The nickel and copper complexes are mesomorphic showing smectic phases S_C and crystal B mesophases. Copyright © 1996 Elsevier Science Ltd

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Metal-containing liquid crystals are of great interest [1]. With such systems it is possible to introduce desirable properties inherent in metal complexes, such as high electronic polarisability, colour and paramagnetism, into liquid crystalline systems. This combination of novel electronic and magnetic molecular properties with the macroscopic supramolecular ordering of a mesophase is likely to lead to a variety of new and interesting effects. Many such modifications to these physical properties would be extremely difficult to achieve in purely organic materials.

Although the first metallomesogens were reported over 80 years ago [2] it is only recently that this field has attracted more serious and systematic study. The advent of this more focused research followed reports of the now classic nickel dithiolene complexes of Giroud and Mueller-Westerhoff (Fig. 1) [3]. Since these first compounds, relatively few liquid-crystalline sulfur coordination complexes have been synthesised and studied. Ohta [4] and ourselves [5] have reported the liquid crystalline behaviour of some 4-alkyl-





oxydithiobenzoate complexes (Fig. 2), while Ohta also reported derivatives of the dithiolenes above (Fig. 3) which showed columnar mesophases [6]. More recently, Hoshino-Miyajima [7] demonstrated for the first time mesomorphism in complexes of piperazine dithiocarbamates (Fig. 4).

We too have turned our attention to 1,1-dithiolato systems. Simple dithiocarbamate complexes have been extensively studied [8] and thus have a well-developed chemistry, offering great synthetic flexibility. We report here on the synthesis and characterisation of some new piperidine dithiocarbamate complexes of nickel, palladium, copper and zinc. We describe the observed mesomorphism and try to rationalise this behaviour with respect to the ligand and to the effect of the metal centre. In-mesophase EPR studies of these complexes have already been reported [9].



Fig. 1. Mesomorphic dithiolenes.





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Fig. 4. Hoshino-Miyajima's mesomorphic dithiocarbamates.

RESULTS AND DISCUSSION

The mesogenic complexes, 3, were prepared by the multistep synthesis outlined in Scheme 1. The 4-alkyloxy-4'-stilbazoles are mesomorphic, and were synthesised by a procedure we have described previously [10]. Catalytic hydrogenation of the butyloxy and hexyloxy stilbazole derivatives with platinum(IV) oxide (Adams catalyst) gave the 4-substituted piperidine (1; n = 4, 6). Deprotonation of these secondary amines and subsequent reaction with carbon disulfide gave the sodium salt of the dithiocarbamate ligand (2; n = 4, 6), the reaction of which with an appropriate divalent metal salt yielded the complexes (3; M = Ni, Pd, Cu, Zn; n = 4, 6). These complexes were sparingly soluble in most organic solvents and the palladium derivatives tended to decompose in chlorinated solvents. By analogous synthetic procedures, we have also made a variety of other simple piperidine dithiocarbamate complexes (Fig. 5) 4-7 (the unsubstituted piperidine derivative), 5 (4-phenylpiperidine), 6 (4-nonylpiperidine) and 7 (3-octyloxypiperidine). We include these non-mesomorphic materials because they make for a useful comparison with our mesomorphic complexes, 3, and those complexes of Hoshino-Miyajima [7]. They also give an indication of the large differences in melting points that simple structural modifications of dithiocarbamate metal complexes can afford.

The mesomorphism of these materials was studied by optical microscopy and differential scanning calorimetry. The phases and the transition temperatures were assigned on the basis of the microscopy and are given in Table 1.

The simple piperidine derivative, 4 melted at 306°C with decomposition. Addition of the phenyl group in the 4-position, 5, raised the melting point to 333°C (with decomposition), while further substitution by a nonyl group in the 4-position of the phenyl ring, 6, decreased the melting point to 238°C. However, most impressive was the reduction in the melting point to 68°C if 3-octyloxy substitution was employed. (This material, 7, is not strictly comparable, because it is a mixture of two enantiomers and another diasterioisomer; consequently there may be a considerable depression in melting point with respect to a single. pure component.) That simple substitution gives such a large range of crystal stabilities suggests that with suitable molecular design, mesomorphic behaviour may be attainable.

An interesting comparison can be made between our nickel complex 6 (m.p. 238° C) and a similar compound of Hoshino-Miyajima [7], namely the bis(4octylpiperazine-l-dithiocarbamato) complex of palladium(II). This complex exhibited an enantiotropic nematic phase, melting at 209° C and clearing at 237° C. Since palladium derivatives tend to melt at a few degrees above their nickel congeners, we attribute this difference in phase behaviour to the difference in the ring structures. Our piperidine derivative is rigid, and inversion of the nitrogen in the 1-position is not possible since it is conjugated through the sulfur to the metal. This rigidity of the piperidine ring is supported by the NMR data for all our substituted



Scheme 1. Reagents and conditions : (i) H_2 , PtO_2 in AcOH; (ii) NaOH, CS_2 in EtOH; (iii) $Pd_3(AcO)_6 NiCl_2 \cdot 6H_2O$, $CuSO_4 \cdot 5H_2O$ or $Zn(AcO)_2$ all in EtOH and H_2O .



Fig. 5. Non-mesomorphic dithiocarbamate nickel complexes.

Table 1. The mesomorphism of the dithiocarbamate complexes : Transition temperatures are given in $^{\circ}$ C. Enthalpies, Δ H, in parentheses, are given in kJ mol⁻¹; monotropic phase transitions are indicated in parentheses; ^a signifies the transition was accompanied by thermal decomposition

Complex	Phases and Transition Temperatures						
	К	K′	Κ″	K″′	B	S _C	1
3 Ni4	• 110	• 303ª				•	
	{9.2}	{46.8 }					
3 Ni6	• 65	• 148	• 241	• 256	• 291 ^a	• 295 ^a	•
	{7.5}	{7.1}	{13.7}	{15.6}	{15.9}	{24.7}	
3 Pd4	• 75	• 321ª					•
3 Cu4	• 155	• 244			• (242)	• 248 ^a	•
	{16.5}	{29.5}					
3 Cu6	• 145	• 216			• (201)	• 241 ^a	•
	{4.6 }	{27.6}					
3 Zn6	• 203						•
	<i>{62.9}</i>						
4 Ni	• 306 ^a						•
5 Ni ph	• 225	• 333ª					•
		{32.9}					
6 Ni9	• 110	• 238					•
		{43.0}					
7 Ni8	• 68	()					•
	{37.5}						

derivatives, in which axial and equatorial protons are non-equivalent and the couplings are well resolved. However, Hoshino-Miyajima reported the piperazine derivatives in solution and at room temperature to have equivalent axial and equatorial protons. The mechanism for this is quite clearly rapid inversion of the nitrogen in the 4-position, on an NMR timescale, causing a conformational interconversion between chair forms, in which the 4-substituent always remains equatorial. It is this inversion that destabilizes the crystal and does not appear to be detrimental to the mesomorphism, revealing a nematic phase which cannot be seen in the more rigid piperidine complex [6].

Of the mesogenic complexes, **3**, only the nickel and copper derivatives showed liquid-crystalline behaviour, the palladium and zinc complexes being nonmesomorphic. Both the nickel and copper complexes (3; M = Ni, Cu; n = 6) showed similar phase behaviour. On cooling from the isotropic liquid (3; M = Ni, Cu; n = 6) a highly birefringent, schlieren texture of a S_C phase was observed. This phase was quite viscous and cohesive and no two brush schlieren could be seen. Further cooling saw a transition to a crystal B phase, in which a mosaic texture and a few focal conic domains were observed. That it was possible to focus well on the texture would seem to preclude the possibility of identification as an S₁ phase.

This similarity in phase behaviour of the nickel and copper derivatives is not wholly unsurprising, as typically they adopt essentially isostructural square planar geometries. However, in the solid state, the copper dithiocarbamates tend to associate as weakly bound

dimers, so as to give each of the copper centres a square pyramidal geometry. That this is a weak interaction is indicated by the fact that dissolution in polar solvents invariably generates the monomeric species. We envisage that at the temperatures of the mesophase there is more than sufficient energy to break the dimer, and this is supported by the remarkable similarity to the mesomorphism of monomeric nickel derivative. This square planar geometry, leaves large uncoordinated areas above and below the plane, which are potentially free for dynamic, lateral intermolecular metal/ligand (sulfur) and metal/metal interactions. Originally we had considered the possibility that such interactions might promote the formation of the observed smectic phases, however the observation of a nematic phase in the dithiocarbamate complexes of Hoshino-Miyajima [7] means that this cannot be the case. Thus, the observed smectic behaviour is more likely to be due simply to the alternate areas of high and low polarisability present in the structure.

The palladium derivative (3; M = Pd; n = 4) was expected to adopt a similar structure to the nickel congener. However that no mesomorphism was observed was probably due simply to the alkyl chain not being sufficiently long to depress the melting point sufficiently to uncover the phase behaviour. No monotropic phases were observed as upon melting, thermal and chemical decomposition occurred. In the zinc derivative (3; M = Zn, n = 6), no mesomorphism was observed, rather a simple melting into an isotropic state. Simple zinc dithiocarbamates have a great propensity to form dimers in the solid state, which at least in the case of the dithiobenzoate complexes which we studied, persist into the mesophase. Thus, it is not entirely clear why these systems are not mesomorphic.

EXPERIMENTAL

Microanalyses were performed at the Universities of Sheffield and Leeds. IR spectra were recorded as KBr discs on a Perkin-Elmer 1600 Series FTIR. UV spectra were recorded on a Philips PU 8720 UVvis scanning spectrophotometer. Proton NMR were recorded on a Bruker ACL250 spectrometer; proton chemical shifts are quoted relative to internal CDCl₃ or CD₂Cl₂, all proton couplings are in Hz; for structural assignments refer to Fig. 2. Mass spectra were recorded on a Kratos MS25 instrument with a DS55 data system. The mesomorphism was studied by polarising optical microscopy using a Carl Zeiss Labpol microscope equipped with a Linkam TH600 hot stage and a PR600 temperature controller, and by differential scanning callorimitry with a Perkin-Elmer DSC7 instrument. The transition temperatures and phase types were assigned on the basis of the microscopy studies. All chemicals were used as received unless otherwise specified.

4-(4'-Butyloxyphenethyl)piperidine (1; n = 4)

To a solution of trans-4-butyloxy-4'-stilbazole (1.51 g, 5.95×10^{-3} mol), in glacial acetic acid (100 cm³), platinum(IV) oxide (147 mg, 6.48×10^{-4} mol) was added. The mixture was placed under a hydrogen atmosphere, stirred vigorously and the uptake of hydrogen monitored. After 4 equivalents of hydrogen had reacted, the reaction was stopped. The acetic acid was distilled off under high vacuum, the residue was taken into dichloromethane (150 cm³), washed with water $(5 \times 30 \text{ cm}^3)$, and saturated brine solution $(1 \times 20 \text{ cm}^3)$. The organic phase was dried over anhydrous magnesium sulphate, filtered and the solvent removed under reduced pressure. Crystallisation from methanol gave the colourless, crystalline product 4-(4'-butyloxyphenethyl)-piperidine (0.307 g, 21%). m.p. 91.6°C; (Found: C, 77.7; H, 10.4; N, 5.1. $C_{17}H_{27}ON$ requires C, 78.1; H, 10.4; N, 5.4%); δ_{H} (250 MHz; CDCl₃) 0.97 (3H, t, ³J_{AB} 7.3, H^A), 1.10-1.30 (4H, m br, H^{Ja} and H^B), 1.40–1.60 (4H, m br, H^{Je} and H^H), 1.60-1.80 (3H, m, H^C and H^J), 1.91 (2H, t br, ${}^{2}J_{KaKe} = {}^{3}J_{KaJa}$ 11, H^{Ka}), 2.55 (2H, m, H^{G}), 2.90 (1H, s, H^L), 2.97 (2H, d, ²J_{KeKa} 11, H^{Ke}), 3.93 (2H, t, ${}^{3}J_{DC}$ 6.5, H^D), 6.81 (2H, AA'XX', ${}^{3}J_{FE}$ 8.5, J 2.5, H^E), 7.07 (2H, AA'XX', ³J_{EF} 8.5, J 2.5, H^F).

Sodium 4-(4'-butyloxyphenethyl)piperidine dithiocarbamate (2; n = 4)

4-(4'-Butyloxyphenylethyl)piperidine (150 mg, 5.74×10^{-4} mol) and sodium hydroxide (34.2 mg, 8.55×10^{-4} mol) were dissolved in ethanol (10 cm³) and heated under reflux for 30 mins. Carbon disulfide (5.0×10^{-2} cm³, 8.5×10^{-4} mol) was added. This solution was cooled to room temperature over a period of 1 h. The product, sodium (4(4'-butyloxyphenethyl)) piperidine dithiocarbamate was not isolated but was used *in situ*.

Bis-[4-4'-butyloxyphenethyl]piperidine dithiocarbamatol nickel (II) (3; M = Ni; n = 4)

To the solution of sodium 4-(4'-butyloxyphenylethyl)piperidine dithiocarbamate $(2.8 \times 10^{-4} \text{ mol})$ in ethanol (10 cm³), a solution of nickel (II) chloride hexahydrate (33 mg, 1.4×10^{-4} mol) in water (2 cm³) was added. The green product precipitated immediately. The mixture was stirred for 1 hour, filtered, and the crude product washed with water, methanol, ethanol, pentane and hot acetone. Recrystallisation from dichloromethane yielded the product, bis[4-(4'*n*-butyloxyphenethyl)piperidine dithiocarbamato] nickel (II), (39 mg, 42%). (Found: C, 59.0; H, 7.2; N, 3.8. C₃₆H₅₂O₂N₂S₄Ni requires C, 59.1; H, 7.26; N, 3.8%); $\delta_{\rm H}$ (250 MHz; CDCl₃) 0.96 (6H, t, ³J_{AB} 7.2, H^A), 1.20 (4H, quart, ${}^{2}J_{J_{aJe}} = {}^{3}J_{J_{aKa}} = {}^{3}J_{Jal}$ 12.5, H^{Ja}), 1.35–1.70 (10H, m br, H^B, H^H and H^J), 1.73 (4H, quin, ${}^{3}J_{CD} = {}^{3}J_{CB} 7.0, H^{C}$, 1.83 (4H, d br, ${}^{2}J_{JeJa} 12.5, H^{Je}$),

2.50 (4H, t br, ${}^{3}J_{GH}$ 8.1, H^G), 2.92 (4H, dt, ${}^{2}J_{KaKe} = {}^{3}J_{KaJa}$ 13, ${}^{3}J_{KaJe}$ 3, H^{Ka}), 3.92 (4H, t, ${}^{3}J_{DC}$ 6.6, H^D), 4.48 (4H, d br, ${}^{2}J_{KeKa}$ 13, H^{Ke}), 6.78 (4H, AA'XX', ${}^{3}J_{FE}$ 8.5, H^F), 7.07 (4H, AA'XX', ${}^{3}J_{EF}$ 8.5, H^E).

The synthesis of all other derivatives was carried out in a similar manner to that described above.

4-(4'-Hexyloxyphenethyl)piperidine (1; n = 6)

$$\begin{split} &\delta_{\rm H} \ (250 \, \text{MHz}; \ \text{CDCl}_3) \ 0.90 \ (3\text{H}, \ t, \ {}^3\text{J}_{AB} \ 9.5, \ \text{H}^A), \\ &1.15 - 1.37 \ (8\text{H}, \ m \ \text{br}, \ \text{H}^{Ja} \ \text{and} \ \text{H}^B), \ 1.37 - 1.58 \ (4\text{H}, \ m \ \text{br}, \ \text{H}^{Je} \ \text{and} \ \text{H}^H), \ 1.58 - 1.83 \ (3\text{H}, \ m, \ \text{H}^C \ \text{and} \ \text{H}^I), \ 1.91 \ (2\text{H}, \ \text{t} \ \text{br}, \ {}^2\text{J}_{KaKe} = \ {}^3\text{J}_{KaJa} \ 10.4, \ \text{H}^{Ka}), \ 2.55 \ (2\text{H}, \ m, \ \text{H}^G), \\ &2.88 \ (1\text{H}, \ \text{s}, \ \text{H}^L), \ 2.97 \ (2\text{H}, \ \text{d}, \ {}^2\text{J}_{KeKa} \ 10.4, \ \text{H}^{Ke}), \ 3.92 \ (2\text{H}, \ \text{t}, \ {}^3\text{J}_{DC} \ 6.5, \ \text{H}^D), \ 6.81 \ (2\text{H}, \ \text{AA'XX'}, \ {}^3\text{J}_{FE} \ 8.4, \ \text{J} \ 2.5, \ \text{H}^E). \end{split}$$

Bis [4-(4'-hexyloxyphenethyl)piperidine dithiocarbamato] nickel (II) (3; <math>M = Ni; n = 6)

Analytical data: Found: C, 60.9; H, 7.6; N, 3.5. $C_{40}H_{60}O_2N_2S_4Ni$ requires C, 61.0; H, 7.7; N, 3.6%; NMR data as for the homologue above.

Bis [4-(4'-butyloxyphenethyl)piperidine dithiocarbamato] palladium (II) <math>(3; M = Pd; n = 4)

Analytical data: Found: C, 55.2; H, 6.7; N, 3.55. C₃₆H₅₂O₂N₂S₄Pd requires C, 55.47; H, 6.72; N, 3.59%; NMR data as for the homologue above.

Bis [4-(4'-butyloxyphenethyl)piperidine dithiocarbamatol copper (II) (3; <math>M = Cu; n = 4)

Analytical data: Found: C, 58.6; H, 7.2; N, 3.7. $C_{36}H_{52}O_2N_2S_4Cu$ requires C, 58.7; H, 7.1; N, 3.8%; λ_{max} (CH₂Cl₂)/nm 230 (ε /dm³ mol⁻¹ cm⁻¹ 27,500), 274 (43,300), 437 (14,000), 508sh (3800) and 610 (1200).

Bis [4-(4'-hexyloxyphenethyl)piperidine dithiocarbamato] copper (II) (3; <math>M = Cu; n = 6)

Analytical data: Found: C, 60.5; H, 7.3; N, 3.6; S, 15.8. $C_{40}H_{60}O_2N_2S_4Cu$ requires C, 60.6; H, 7.6; N, 3.5; S, 16.2%; λ_{max} (CH₂Cl₂)/nm 232 (ϵ /dm³ mol⁻¹ cm⁻¹ 23,800), 274 (44,500), 436 (14,100), 442sh (13,800), 505sh (4300) and 607sh (1300).

Bis [4-(4'-hexyloxyphenethyl)piperidine dithiocarbamato] zinc (II) (3; M = Zn; n = 6)

Analytical data : Found : C, 60.6; H, 7.5; N, 3.6; S, 16.2. $C_{40}H_{60}O_2N_2S_4Zn$ requires C, 60.5; H, 7.6; N, 3.5; S 16.1%; δ_H (250MHz; CDCl₃) 0.90 (6H, t, ${}^{3}J_{AB}$ 7.3, H^A), 1.25–1.65 (22H, m br, H^{Ja}, H^B, H^H and H^J), 1.77 (4H, quin, ${}^{3}J_{CD} = {}^{3}J_{CB}$ 7.0, H^C), 1.88 (4H, d br, ${}^{2}J_{JeJa}$ 13, H^{Je}), 2.59 (4H, t br, ${}^{3}J_{GH}$ 7.5, H^G), 3.11 (4H, dt ${}^{2}J_{KaKe} = {}^{3}J_{KaJa}$ 13, ${}^{3}J_{KaJe}$ 2.3, H^{Ka}), 3.92 (4H, t, ${}^{3}J_{DC}$ 6.5, H^{D}), 4.98 (4H, d br, ${}^{2}J_{KeKa}$ 13, H^{Ke}), 6.82 (4H, AA'XX', ${}^{3}J_{FE}$ 8.4, J 2.5, H^{F}), 7.07 (4H, AA'XX', ${}^{3}J_{EF}$ 8.4, J 2.5, H^{E}); FAB mass spectrum *m*/*z* 736 (M⁺, 25%), 459 (9), 306 (100), 288 (52), 273 (5), 241 (8) and 195 (9).

Bis [piperidine dithiocarbamato] nickel (II) (4; M = Ni)

Analytical data: Found : C, 37.9; H, 5.4; N, 7.4; S, 33.4. $C_{12}H_{20}N_2S_4Ni$ requires C, 38.0; H, 5.3; N, 7.4; S, 33.4%; δ_H (250MHz; CDCl₃) 1.65 (12H, br m, H^B and H^C), 3.71 (8H, br t, H^A).



Bis [4-phenylpiperidine dithiocarbamato] nickel (II) (5; M = Ni; n = Ph)

Analytical data : Found : C, 54.1 ; H, 5.5 ; N, 5.2 ; S, 23.7. $C_{24}H_{30}N_2S_4Ni$ requires C, 54.2 ; H, 5.3 ; N, 5.3 ; S, 24.1% ; δ_H (250MHz, CDCl₃) 1.74 (4H, d quart, ²J_{JaJe} = ³J_{JaI} = ³J_{JaKa} 13, ³J_{JaKe} 5, H^{Ja}), 1.98 (4H, br d, ²J_{JeJa} 14, H^{Je}), 2.85 (2H, t t, ³J_{IJa} 15, ³J_{He} 3.4, H^I), 3.03 (4H, d t, ²J_{KaKa} = ³J_{KaJa} 13, ³J_{KaJa} 3, H^{Ka}), 4.74 (4H, br d, ²J_{KeKa} 14, H^{Ke}), 7.20-7.35 (6H, m, H^A, H^B and H^C).



Bis [4-nonylpiperidine dithiocarbamato] nickel (11) (6; M = Ni; n = 9)

Analytical data : found : C, 57.0 ; H, 8.8 ; N, 4.5 ; S, 20.2. $C_{30}H_{56}N_2S_4Ni$ requires C, 57.0 ; H, 8.9 ; N, 4.4 ; S, 20.3% ; λ_{max} (CH₂Cl₂)/nm 244 (ϵ /dm³ mol⁻¹ cm⁻¹ 37,800), 328 (37,600), 383sh (6500), 394 (6900), 429sh



Fig. 6. The assignment of protons for the NMR of 1; n = 4, 6, and 3; M = Ni, Pd, Zn; n = 4, 6.

(1400) and 476sh (200); $\delta_{\rm H}$ (250MHz; CDCl₃) 0.88 (6H, t, ${}^{2}J_{AB}$ 6, H^A), 1.07–1.40 (16H, br m, H^B and H^{Ja}), 1.55 (2H, m, H¹), 1.78 (4H, br d, ${}^{2}J_{JeJa}$ 14, H^{Je}), 2.89 (4H, d t, ${}^{2}J_{KaKe} = {}^{3}J_{KaJa}$ 13, ${}^{3}J_{KaJe}$ 3.8 H^{Ka}), 4.52 (4H, br d, ${}^{2}J_{KeKa}$ 13, H^{Ke}).

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