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Paramagnetic chiral mesophases of Shiff's base complexes of transition metals

W. Pyżuk[a]; Yu. Galyametdinov[ab]
[a] Laboratory of Dielectrics and Magnetics, Department of Chemistry, University of Warsaw, Warsaw, Poland [b] Kazan Physicotechnical Institute, Academy of Sciences, Kazan, Russia

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Paramagnetic chiral mesophases of Shiff's base complexes of transition metals

by W. PYŻUK* and YU. GALYAMETDINOV†
Laboratory of Dielectrics and Magnetics, Department of Chemistry,
University of Warsaw, 02–089 Warsaw, Al. Żwirki-Wigury 101, Poland

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Copper(II), nickel(II) and oxovanadium(IV) complexes of 4-(4-heptyloxybenzoyloxy)-*N*-(*S*)-2-methylbutylsalicylaldimine, as well as the parent ligand, were studied by optical and DSC methods. For the first two complexes, there exist between a tightly twisted chiral nematic phase and the isotropic liquid either some blue phases or novel-type amorphous phases, with their temperature ranges depending significantly on the metal centre. For the third complex, direct isotropization takes place.

It is a well known property of liquid crystals that strong disymmetry of molecules, resulting in their high twisting ability, can generate novel chiral mesophases [1]. Among them there are blue phases, existing between the chiral nematic (N*) phase and the isotropic liquid [2]. Most probably, a similar situation arises also in systems having a twist-grain-boundary smectic A* phase [3]. Recently, an intermediate phase (IP) formed by paramagnetic copper metallomesogens was reported and tentatively identified as a blue phase [4]. In this communication we confirm the existence of such paramagnetic IPs and compare their properties for different chelated metal ions.

Since complexation of a divalent transition metal ion by bidentate chiral ligands doubles the number of chiral centres within the resulting complex molecules, the twisting power of such complexes should become much higher than that of the parent ligand, and the helical pitch much tighter. The helical pitch is a major factor which controls the presence and temperature range of particular blue phases [5, 6]. For complexes, therefore, we expect an enhanced stability of these phases.

Complexes $7ML_2$ (formulae presented below), as well as their parent ligand, 7HL = 4-(4-heptyloxybenzoyloxy)-*N*-(*S*)-2-methylbutylsalicylaldimine, were chosen for our studies. Their syntheses were performed similarly to those reported in [7]. As a chiral substrate we used *S*(−)-2-methylbutylamine, $[\alpha]_D^{20}$-5·9°, obtained from Aldrich. Synthetic details, analytical data and magnetic properties will be described elsewhere. Besides an obvious paramagnetism for the copper and oxovanadium complexes, a weak paramagnetism is observed for the nickel analogue [8] (cf. [7] for properties of some related compounds).

All compounds, when studied microscopically, reveal the presence of a chiral nematic phase; no other mesophases were detected. For the ligand, a selective light reflection was observed, and so a helical pitch of 0·3–0·4 μm, in the temperature range

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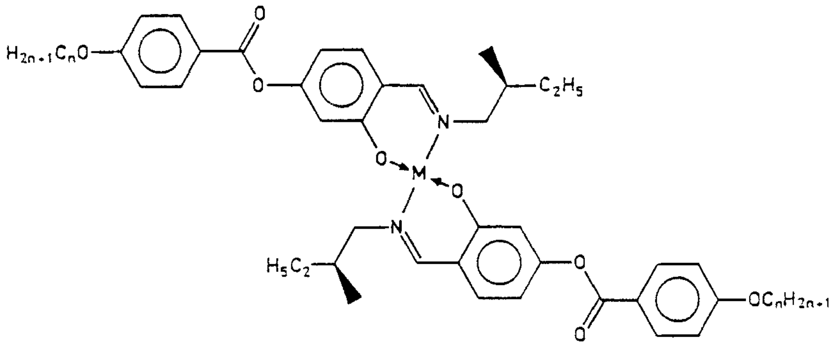
* Author for correspondence.

† Permanent address: Kazan Physicotechnical Institute, Academy of Sciences, Kazan, 420029, Russia.



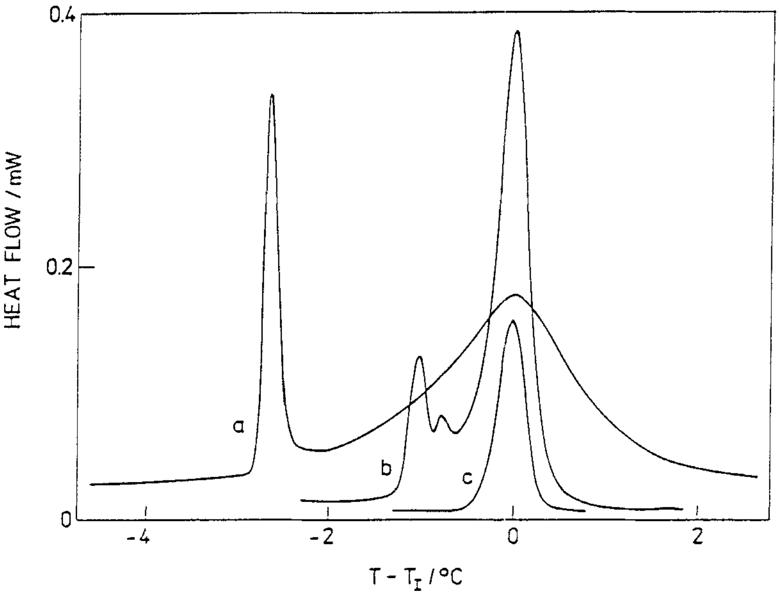
nML_2 : M = Cu, Ni, VO, Pd

50–40°C, was estimated. For the complexes, selective light reflection was observed only for samples diluted by achiral metallo-mesogens or conventional nematics, which proves that the pure chiral complexes are rather tightly twisted. Their helix was found to be right-handed by applying the contact method, using cholesteryl chloride (RH) and propionate (LH) as standards. Such handedness is in agreement with the empirical SED rule [9].

Since a high twist can generate blue phases with a short lattice constant, the question arises as to whether such phases are present in the complexes under study. Our approaches to detecting them by means of observation of selective light reflection or a transmission dip in the UV spectra have failed. On the other hand, the strong optical absorption of the samples, and not the absence of these phases, might be the decisive factor here. To elucidate the situation, we used differential scanning calorimetry (DSC). This method, if carefully applied, sometimes detects blue phases unobservable in the visible range [10].

Using a Perkin–Elmer DSC-7 and optimizing all the experimental parameters involved, we obtained good quality thermograms for all the compounds. For the ligand, above its melting temperature, a typical λ-shaped isotropization peak is observed, confirming the lack of blue phases. The thermograms of the complexes are distinctly different (see fig). The most simple occurs in the case of $7VOL_2$, for which only a signal for a phase transition to an isotropic liquid is present. However, the absence of pre-transitional anomalies in the specific heat, as well as an extremely low enthalpy change for the phase transition, should be noticed. The corresponding entropy change is only 0·095 R. Such behaviour would correspond, in terms of the Landau–de Gennes model, to a small value of the pre-transitional coefficient, a, in the free energy expansion for the system. There is also a simple interpretation of the DSC data for $7NiL_2$ for which the thermogram corresponds fully to the response of a system having a chiral nematic phase and blue phases. Two small peaks corresponding to transitions relating to intermediate phases are overlapped on one side of the isotropization peak. Furthermore, typical for blue phases are the temperature ranges of the phases (0·28°C and 0·81°C) and the transition enthalpies (see table).

In contrast to these complexes, for the copper analogue, some non-typical, but nevertheless reproducible, thermograms were recorded. The isotropization peak is diffuse over a broad temperature range. This broadening is more likely to result from specific heat pre-transitional anomalies and is certainly not connected with contamination of the samples. The thermograms were confirmed for samples synthesized independently in two laboratories and they do not change after subsequent recrystalliz-



DSC curves for 4-(4-heptyloxybenzoyloxy)-*N*-(*S*)-2-methylbutylsalicylaldimine complexes: (*a*) 7CuL$_2$ (sample 6·1 mg, scan 1°C min^{-1}); (*b*) 7NiL$_2$ (6·1 mg, 1°C min^{-1}); (*c*) 7VOL$_2$ (4·9 mg, 2°C min^{-1}). At the abscissa, the distance from the maximum temperature of the isotropization peak is marked off.

Phase transition† temperatures (°C) and, in parentheses, enthalpies (J g^{-1}) for the ligand, 7HL = 4-(4-heptyloxybenzoyloxy)-*N*-(*S*)-2-methylbutylsalicylaldimine, and its Cu(II), Ni(II) and VO(IV) complexes.

Compound	C		N*		IP$_\alpha$		IP$_\beta$		I
7HL	●	57·4 (64·7)	●		—		—	51·0 (1·1)	●
7CuL$_2$	●	156·0 (59·6)	●	154·2 (0·27)	●		—	156·9 (1·3)	●
7NiL$_2$	●	154·7 (52·8)	●	187·6 (0·20)	●	187·9 (0·03)	●	188·7 (2·5)	●
7VOL$_2$	●	131·6 (44·1)	●		—		—	142·0 (0·36)	●

† Phases: C, crystal; N, nematic; I, isotropic liquid; IP, intermediate phase; ●, the phase exists; —, the phase does not exist.

ations. Moreover, the low temperature peak, corresponding to the N*–IP transition, is very sharp. This phase transition is obviously first order (a small hysteresis in the phase transition temperature is also observed) with an unexpectedly high transitional enthalpy and no pre-transitional effects. In general, the thermogram is, *toutes proportions gardées*, similar to those observed for some smectic A* systems with an amorphous phase of unknown structure [3].

Although the presence of the BPIII alone is expected for short pitched chiral nematogens [11], the existing experimental data do not suffice to prove that the intermediate, 2·7°C wide, mesophase of 7CuL$_2$ is this blue phase. Besides optical studies (difficult to perform with an inherent light absorption), phase diagram studies also appeared unrealistic. Construction of detailed binary phase diagrams, with reference substances, was too subtle a task, bearing in mind both the narrow temperature range involved and the low enthalpy of the N*–BPIII transition for the standards. The intermediate phase, because of its unusual thermal properties, might even be an entirely novel phase which exhibits a near-continuous phase transition to an isotropic liquid. To study the molecular organization of the phase, NMR analysis is inappropriate because of its paramagnetic properties. EPR studies could be more promising; this method has proved to be applicable to some chiral systems [12].

A tentative DSC examination of the diamagnetic analogues, $12NiL_2$ and $12PdL_2$, also reveals the presence of intermediate phases. In addition, the phase for the palladium(II)-complex is detectable optically; it appears as a fog-like texture.

In comparing the thermal stabilities of the complexes, we find that both the isotropization temperatures and the enthalpies are ranged in the sequence $NiL_2 > CuL_2 > VOL_2$. We checked that this sequence holds for Shiff's base complexes having normal as well as α- and β-branched *N*-alkyl substituents. This fact points to the role of the metal centre as a factor determining molecular shape (through the coordination geometry) and molecular interactions. In contrast, it is difficult to explain why the temperature range of the intermediate phases is wider for CuL_2 than for NiL_2. Phase transitions in chiral systems are determined by the chirality, $\kappa = q_0 (K_1\ a/b^2)^{1/2} (2a)]$, rather than simply by the inverse helical pitch, $p_0^{-1} = q_0/2\pi$. As yet, not much is known about the additional elastic (K) and free energy (a, b) constants for complexes. However, in view of our DSC results, a relatively low chirality, resulting from a small value of the a factor, might be responsible for the absence of any intermediate phases for the $7VOL_2$ compound. This effect might be connected with the marked non-planarity of oxovanadium complexes.

To summarize, for these metal complexes specified and having two chiral centres, mesophases intermediate between the nematic and isotropic liquids exist, in contrast to the parent, chiral ligand. The rôle of the metal centre, which influences the occurrence, temperature range and type of these phases, is not clear at present.

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