Correlation between magnetic properties and molecular structure of some metallo-mesogens

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The behaviour of a large number of paramagnetic metallo-mesogenic molecules with Cu and VO in different mesophases in a magnetic field was investigated by EPR techniques and magnetic susceptibility measurements. The investigation of the angular dependence of the EPR spectra enabled conclusions to be reached concerning the molecular orientation in the external magnetic field. Temperature dependence magnetic susceptibility measurements were carried out in order to obtain information about the overall susceptibility anisotropy. The good agreement between experimental results and calculated data based on the known increment scheme is obvious. It is shown that the direction of orientation of the molecules in a magnetic field is predetermined by the sum of the anisotropy of the phenyl ring and the chelate core in the molecular structure.

1. Introduction

Liquid crystalline materials containing various paramagnetic metals have recently received appreciable attention. As may be expected, the combinations of the liquid crystal properties of organic mesogens with the magnetic properties of metal ions will enable the creation of some novel anistropic materials that may be useful for magnetic and non-linear optics [1, 2]. In some theoretical considerations, it is suggested that a liquid crystal ferromagnet may exist due to the presence of the mesophase [3] (especially in smectic C* phases [4]) and the magnetic ordering.

Up to the present time, a large number of metallo-mesogens having diverse structures has been synthesized. In particular, we obtained for the first time paramagnetic complexes of Cu and VO with Schiff's bases with different molecular structures possessing smectic A, C and nematic phases [5–8].

However, the number of papers devoted to the systematic investigation of the physical properties for such liquid crystals, especially the paramagnetic ones, is extremely small [9, 10]. However, the magnetic properties and structural organization of some substances synthesized in this research group have been examined in details by means of EPR [11] and magnetic susceptibility measurements [12, 13].

The problem of correlation of molecular constitution and mesophase structure with the behaviour of metallo-mesogens in an external magnetic field is of great interest, but almost unexplored in a systematic fashion up to now. We have tried here to study particular aspects of this problem by means of EPR investigations of various metallo-mesogens with different structures of the ligands, different kinds of central metal ion and various types of mesophase (structures I and II, figure 1). Susceptibility measurements of representative compounds are also included.

2. Experimental

The methods of synthesis are described in previous papers [5–8]. Chiral derivatives were obtained using as starting materials commercial (−) 2-butanol, (−) 2-octanol and (−) 2-methylbutylamine. The composition and structure of all compounds reported in tables 1–3 were confirmed by elemental analysis, NMR, IR and

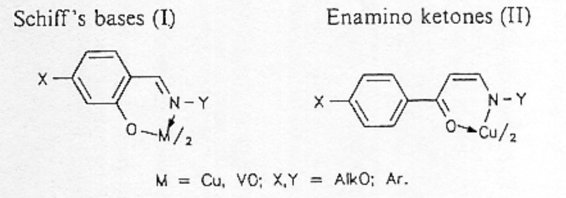
Schiff's bases (I)
Enamino ketones (II)

Figure 1. Structures of the investigated Schiff's bases complexes I and the enaminoketone derivatives II.

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Table 1. Phase transition temperatures, calculated magnetic susceptibility anisotropies and orientations relative to the magnetic field of copper complexes with Schiff's bases (structure **I** for M = Cu in figure 1).

Compound	*X*	*Y*	Temperature of phase transitions/°C S_C	S_A	N	I	Anisotropies of magnetic susceptibilities/10^{-6} cm^3 mol^{-1} $-\Delta\chi_p$	$\Delta\chi_D$	$\Delta\chi_p+\Delta\chi_D$	Orientation to **H**
1	$C_7H_{15}O$-	-Ph-$OC_{12}H_{25}$	122·0	133·0	—	161·0	84·36	72·42	−11·92	⊥
2	$C_7H_{15}O$-	-Ph-$OC_{10}H_{21}$	125·0	146·0	—	160·0	84·55	72·42	−12·13 (−10·2)†	⊥
3	$C_7H_{15}O$-	-Ph-C_4H_9	(149·0)	—	—	149·6	86·60	63·76	−22·84	⊥
4	$C_7H_{15}O$-	-Ph-CN	—	—	(190·0)	202·0	79·07	49·30	−29·77	⊥
5	$C_7H_{15}O$-Ph-COO-	-$C_{12}H_{25}$	108·0	126·7	127·0	135·5	91·53	79·54	−11·99	⊥
6	$C_7H_{15}O$-	-Ph-c-C_6H_{10}-C_6H_{13}	237·0	263·0	—	285·0	65·52	55·62	−10·00	⊥
7	$C_7H_{15}O$-	-Ph-COO-Ph-$OC_{12}H_{25}$	208·0	—	217·0	238·0	74·72	117·00	42·28	∥
8	H-	-Ph-COO-Ph-$OC_{12}H_{25}$	—	—	176·0	184·5	81·54	124·49	42·95	∥
9	$C_7H_{15}O$-	-Ph-Ph-$OC_{12}H_{25}$	180·0	—	—	275·0	66·81	120·20	53·39	∥
10	H-	-Ph-Ph-$OC_{12}H_{25}$	182·0	—	—	186·5	79·70	127·68	47·98	∥
11	(+)$C_2H_5C^*H(CH_3)CH_2O$-	-Ph-OC_8H_{17}	—	127·0	—	139·6	88·70	72·42	−16·28	⊥
12	(−)$C_6H_{13}C^*H(CH_3)O$-	-Ph-Ph-$OC_{12}H_{25}$	143·0	—	152·0	161·0	86·14	120·20	34·06 (24·75)†	∥
13	(+)$C_2H_5C^*H(CH_3)CH_2O$-	-Ph-Ph-$OC_{12}H_{25}$	168·0	173·0	—	254·0	69·47	120·20	50·73	∥
14	(+)$C_2H_5C^*H(CH_3)CH_2O$-	-Ph-c-C_6H_{10}-C_6H_{13}	208·5	—	216·0	224·0	74·87	55·62	−19·25	⊥
15	$C_7H_{15}O$-Ph-COO-	(−)-$CH_2C^*H(CH_3)C_2H_5$	—	—	156·0	185·3	84·34	79·54	−5·80	⊥
16	$C_7H_{15}O$-Ph-COO-	(±)-$CH(CH_3)(CH_2)_4CH_3$	—	—	(33·0)	76·0	119·64	79·54	−40·10	⊥

†Experimental data obtained from magnetic susceptibility measurements.

Table 2. Phase transition temperatures, calculated magnetic susceptibility anisotropies and orientations relative to the magnetic field of vanadyl complexes with Schiff's bases (structure **1** for *M* = VO in figure 1).

Compound	*X*	*Y*	Temperature of phase transitions/°C S_A	N	I	Anisotropies of magnetic susceptibilities/10^{-6} cm^3 mol^{-1} $+\Delta\chi_p$	$\Delta\chi_D$	$\Delta\chi_p+\Delta\chi_D$	Orientation to **H**
1	$C_7H_{15}O$-	-Ph-OC_8H_{17}	151·0	—	176·8	16·82	72·42	89·24	∥
2	$C_7H_{15}O$-	-Ph-OCH_3	—	160·0	163·0	17·47	72·42	89·89	∥
3	$C_7H_{15}O$-Ph-COO-	-$C_{12}H_{25}$	102·0	—	121·0	19·20	79·54	98·74	∥
4	$C_7H_{15}O$-	-Ph-c-C_6H_{10}-C_6H_{13}	198·0	270·0	278·0	13·93	55·62	69·55	∥
5	(+)$C_2H_5C^*H(CH_3)CH_2O$-	-Ph-OC_8H_{17}	(145·0)	—	160·1	17·47	72·42	89·89	∥
6	(+)$C_2H_5C^*H(CH_3)CH_2O$-	-Ph-Ph-$OC_{12}H_{25}$	238·0	—	260·0	14·19	120·20	134·39	∥
7	(+)$C_2H_5C^*H(CH_3)CH_2O$-	-Ph-c-C_6H_{10}-C_6H_{13}	181·0	196·0	266·0	16·13	55·62	71·75	∥
8	$C_7H_{15}O$-Ph-COO-	(−)-$CH_2C^*H(CH_3)C_2H_5$		(132·0)	135·0	18·68	79·54	98·22	∥

axial axis ($g_{\parallel}$) directed along one of the short axes of the copper and vanadyl complexes. To calculate the contributions of the diamagnetic susceptibility tensors from different chemical bonds and groups according to the additive scheme, we used the procedure described by Ibrahim and Haase [19].

The contributions to the tensor of magnetic susceptibility form defined bonds and ligands have been calculated for some compounds using the geometrical parameters obtained by X-ray [20].

The resulting tensor of diamagnetic susceptibility was rotated towards those molecular axes along which the paramagnetic component was calculated and then the resulting tensor was averaged over the short axes of the complexes.

The contributions from the molecular fragments with isotropic susceptibilities (H, alkyl chains) were not taken into account (within the framework of this approach), hence the mean magnetic susceptibility is underestimated.

The mean susceptibility data calculated according to the Pascal scheme are in good agreement with experimental results, as can be seen in table 1.

Concerning the estimation of the paramagnetic anisotropy $\Delta\chi_p$, the g-factors obtained from copper EPR spectra are not real g-factors of discrete molecules. They are a result of partial averaging over all the molecules owing to some disordering of the long axes of the complexes. A measure of such an angular disordering is the order parameter $\bar{P}$ and the averaging mechanism is the spin exchange between copper complexes. This is not true for the vanadyl complexes, because spin exchange does not take place in the mesophase, and so the experimentally obtained values of the g-factors represent non-averaged molecular parameters. The real non-averaged molecular g-factors of the copper complexes were obtianed from EPR spectra of frozen solutions of the complexes in toluene [8]: $g_{\parallel M} = 2{\cdot}235$, $g_{\perp M} = 2{\cdot}053$.

Calculated values of the anisotropies of the paramagnetic and diamagnetic susceptibilities, as well as their sums, are reported in tables 1 to 3. The sign of the anisotropy of the total magnetic susceptibility determines the manner of orientation of the complexes in the magnetic field. The good agreement between experimental results and calculate data is obvious. It should be emphasized that EPR measurements such as those presented here can confirm only the sign of $\Delta\chi_p + \Delta\chi_d$, but not the magnitude.

In the framework of our investigations, we have carried out temperature dependence magnetic susceptibility measurements of selected compounds (**2** and **12**, table 1) in order to obtain information about the overall susceptibility anisotropy in a rather qualitative sense.

The averaged (isotropic) susceptibility for a uniaxial phase is defined as

$$\bar{\chi} = \frac{1}{3}(\chi_{\parallel} + 2\chi_{\perp}), \tag{2}$$

while the magnetic anisotropy is given by

$$\Delta\chi = \chi_{\parallel} - \chi_{\perp}. \tag{3}$$

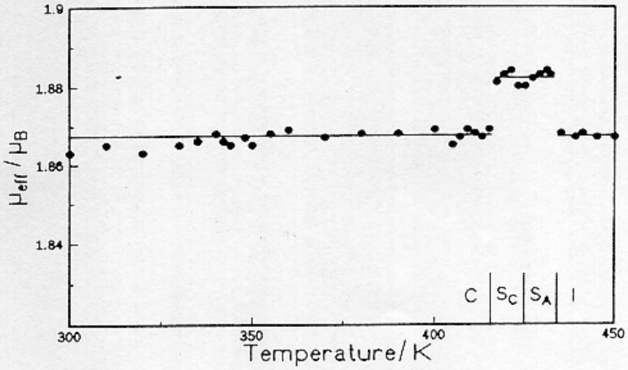

Figure 5. Effective magnetic moments versus temperature for compound **12**, (see table 1). C = crystalline, S_C = smectic C, S_A = smectic A and I = isotropic phases.

It must be pointed out that the directions of the axes '$\parallel$' of the χ-tensor and the g-tensor are different. In [2, 3], the axes '$\parallel$' correspond to the direction along the director **n**, and '$\perp$' is any direction perpendicular to this axis.

A necessary condition for a molecule to become oriented in a static homogenous magnetic field is that it should possess a magnetic anisotropy. In the special case of an axial χ tensor, the alignment torque vanishes if the angle between **H** and the axis of maximum magnetic susceptibility $\chi_{\max}$ is zero.

(*a*) When $\Delta\chi > 0 (\chi_{\parallel} = \chi_{\max})$, the field causes a uniform orientation of the director **n** along **H**, and $\chi_{\parallel}$ will be measured for the oriented mesophase.

(*b*) In the case $\Delta\chi < 0 (\chi_{\perp} = \chi_{\max})$, the molecular long axis is oriented orthogonal to the direction of the magnetic field and in the oriented phase, $\chi_{\perp}$ will be measured.

In both cases, the orientation of the sample in the crystalline state, with the axis of maximum susceptibility parallel to **H**, causes an increase in $\Delta\chi^{i \to m}$ from $\bar{\chi} = \frac{1}{3}(\chi_{\parallel} + 2\chi_{\perp})$ to $\chi_{\max}$ associated with the phase transition isotropic liquid to mesophase. Therefore we can calculate the magnitude of $\Delta\chi$, including orientational behaviour, from EPR data about the sign of $\Delta\chi = (\chi_{\parallel} - \chi_{\perp})$ using

$$\Delta\chi > 0; \quad \Delta\chi = \frac{3}{2}\Delta\chi^{i \to m}, \tag{4 a}$$

$$\Delta\chi < 0; \quad \Delta\chi = -3\Delta\chi^{i \to m}. \tag{4 b}$$

The results of temperature dependence magnetic susceptibility measurements for compounds **2** and **12** in table 1, are displayed together with the phase transition temperatures in figures 5 and 6.

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