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

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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
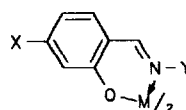
Schiff's bases (I)   Enamino ketones (II)
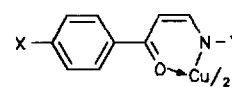
M = Cu, VO; X,Y = AlkO; Ar.

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

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EPR spectroscopy. The transition temperatures and mesophase types were determined by polarizing microscopy, supported in some cases by DSC.

The orientation in the mesophase in the external magnetic field was investigated by means of Q-band (RE1306) and X-band (RE1308) EPR spectrometers. The substances possessing only a smectic phase were initially heated until isotropic and then cooled to the smectic phase in the presence of a 1·4 T magnetic field. Such a magnetic field is usually sufficient for the orientation of molecules at the isotropic–smectic phase transition point. The substances possessing nematic and fluid smectic phases were oriented initially in the nematic phase and then cooled slowly to the smectic phase; the orientation of the molecules was unchanged. The $\chi(T)$ data for some complexes of Cu with Schiff's bases (compounds 2 and 12 in table 1) were recorded using a Faraday-type magnetometer. For the measurements presented, an improved system compared to that of Merz and Haase [14] was used (computer controlled Cahn D-200 microbalance, Bruker B-MN 200/60 power supply). The applied field was 1·2 T. The magnetic susceptibilities of the metallo-mesogens in the temperature range 300 K to 500 K were measured in the heating mode of this installation, modified for this range. Diamagnetic corrections of the molar magnetic susceptibilities were applied using Pascal's constants [15]. The $\chi(T)$-fits were performed with the IBM 3090-200E VF computer of the TH Darmstadt. The function minimized was $\Sigma(|\chi_{exp} - \chi_{calc}|/\chi_{exp})$. Magnetic moments were obtained from $\mu_{eff}/\mu_B = 2\cdot828(\chi T)^{(1/2)}$.

3. Results

All the substances of structure I (tables 1 and 2) are complexes with Schiff's base ligands. Besides these substances, we have investigated some derivatives of enamino-ketones (II) (see table 3) which have a different kind of coordination site. In tables 1 and 2, a temperature in parenthesis relates to a transition to a monotropic mesophase formed on cooling the isotropic phase produced from the crystalline phase at the temperature recorded in the column headed I. The variety of substances provides a wide range of mesophases including those that are chiral and gives us an opportunity to investigate the behaviour of metallo-mesogens in a magnetic field.

For copper complexes in the smectic phase, exchange narrowed EPR spectra consisting of two lines were observed (see figure 2). Bikchantaev *et al.* [16], showed that the spectral line with lower g-factor (2·053, $g_\perp$ for all copper complexes with Schiff's bases results from molecules with their long axes directed along the direction of the external magnetic field. The g-factor value of the second line (2·082) is equal to the mean between g-factors ($g_\parallel$ and $g_\perp$) and is connected with the short axes of the

complexes (see figure 3). For copper complexes, $g_\parallel$ is directed along the normal to the chelate plane; $g_\perp$ lie in the plane of the chelate core. The value of $g_\parallel$ is larger than $g_\perp$ for copper complexes, whereas for vanadyl complexes, $g_\parallel$ is lower than $g_\perp$.

For complexes with enamino-ketones containing copper, the g-factors of the two above mentioned lines are, respectively, 2·056 and 2·110. The averaging of the short axes g-factors is the result of the joint effect of two mechanisms: rapid rotation of the molecules around their long axes and spin exchange between molecules with randomly distributed short axes (long axes being partially oriented). It should be noted that the isotropic g-factor calculated from the smectic phase spectrum is 2·072 (2·092 for enamino-ketone derivatives), close to the isotropic g-factor determined from the position of the single line of the spectrum for the isotropic phase ($g = 2\cdot08$).

The g-factor values of the spectra for the isotropic, nematic and smectic phases correspond to those of square planar complexes of copper with a trans-configuration of the chelate core [17].

Investigation of angular dependences in the EPR spectra allowed us to reach conclusions concerning the molecular orientation in the external magnetic field. If the molecular long axes are oriented along the magnetic field, then the spectral line related to the long axis of the complexes has to be of maximal intensity for the initial orientation. This line has a minimal intensity after rotation of the sample by 90° relative to the magnetic field direction. When the molecules are oriented perpendicular to the magnetic field, one should observe the inverse picture [18]. Therefore, angular dependence EPR-measurements are a valuable tool for estimating molecular orientation in an external magnetic field.

The results concerning the orientation of the copper complexes by the magnetic field are reported in tables 1 and 3.

The spectra for the vanadyl compound 1 (see table 2) shown in figure 4 are typical for those complexes. 'Glass-like' EPR spectra were observed for the isotropic phase, because of the high viscosity of the melt. The parameters of the spectra are the following: $g_\parallel = 1\cdot946$, $g_\perp = 1\cdot987$, $A_\parallel = 181$ Oe, $A_\perp = 58$ Oe. In the mesophase, the 'perpendicular' spectral components decrease and the 'parallel' components increase when the sample is turned through 90° (see figure 4). Such a spectral feature results from the fact that the long axes of molecules are oriented along the magnetic field direction. This means that the long axes of all the vanadyl complexes investigated are oriented parallel to the magnetic field (see table 2).

4. Discussion

To explain the results obtained, we carried out calculations of the magnetic susceptibility tensors of the com-

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				Anisotropies of magnetic susceptibilities/10^{-6} cm^3 mol^{-1}			Orientation to H
			S_C	S_A	N	I	$-\Delta\chi_p$	$\Delta\chi_D$	$\Delta\chi_p+\Delta\chi_D$	
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	$C_7H_{15}O-Ph-COO-$	$(\pm)-CH(CH_3)(CH_2)_4CH_3$	—	—	(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 I for M=VO in figure 1).

Compound	X	Y	Temperature of phase transitions/°C			Anisotropies of magnetic susceptibilities/10^{-6} cm^3 mol^{-1}			Orientation to H
			S_A	N	I	$+\Delta\chi_p$	$\Delta\chi_D$	$\Delta\chi_p+\Delta\chi_D$	
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	196·0	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	—	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	∥

Table 3.   Phase transition temperatures, calculated magnetic susceptibility anisotropies and orientations relative to the magnetic field of copper complexes with enaminoketones (structure **II** in figure 1).

Com-pound	X	Y	Temperature of phase transitions/°C				Anisotropies of magnetic susceptibilities/10^{-6} cm^3 mol^{-1}			Orientation to **H**
			S_C	S_A	N	I	$-\Delta\chi_p$	$\Delta\chi_D$	$\Delta\chi_p + \Delta\chi_D$	
1	$C_9H_{19}O-$	$-Ph-OC_{12}H_{25}$	128·0	187·0	189·0	192·0	79·24	89·73	10·49	∥
2	$C_9H_{19}O-$	$-Ph-OC_8H_{17}$	139·0	—	—	198·0	77·73	89·73	12·00	∥
3	$C_{10}H_{21}-c-C_6H_{10}-$	$-i-C_{13}H_{27}$	107·0	109·0	122·0	130·0	92·69	30·50	−62·19	⊥

pounds under investigation. The magnetic susceptibility includes two contributions: the paramagnetic contribution from the metal ion and the diamagnetic contribution from the ligands. The paramagnetic contribution was calculated according to the Van Vleck formula:

$$\chi_i = \frac{N_L g_i^2 \mu_B^2}{3kT} S(S+1), \tag{1}$$

where S is the central metal ion spin, μ_B is the Bohr magneton, k is Boltzmann's constant, T is the mesophase temperature and the g_i are the g-tensor components.

We assumed axial properties for the g-tensor, with the
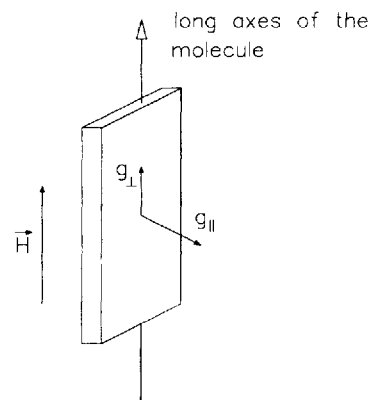
Figure 3.   Relative orientation of the axes of g-tensors in the rod-like molecules of the copper complexes ($g_\parallel > g_\perp$).
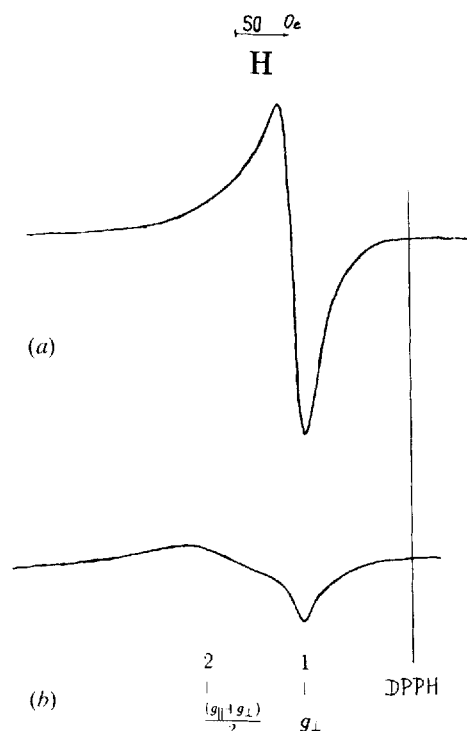
Figure 2. Q-band EPR spectra of copper compound **6** (see table 1) in the S_A phase: (*a*) initial orientation of sample; (*b*) after rotation through 90°.
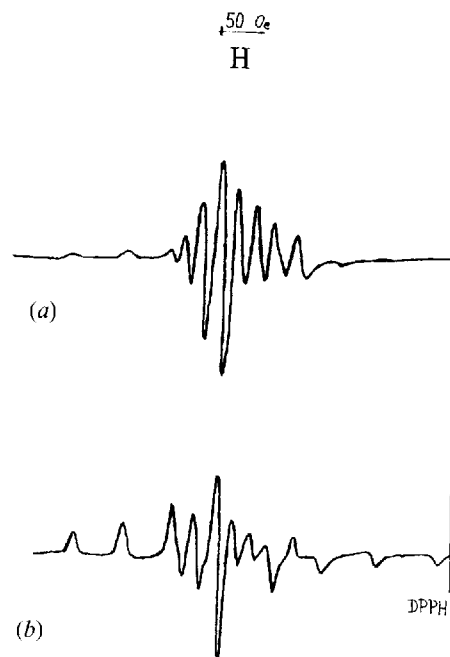
Figure 4. X-band EPR spectra of vanadyl complex **1** (see table 2) in the S_A phase: (*a*) initial orientation of sample; (*b*) after rotation through 90°.

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]: $g_{\parallel M} = 2\cdot235$, $g_{\perp M} = 2\cdot053$.

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.

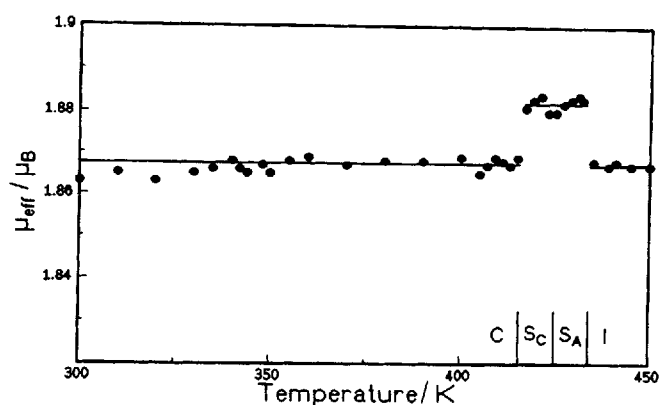The averaged (isotropic) susceptibility for a uniaxial phase is defined as

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.

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

while the magnetic anisotropy is given by

$$\Delta\chi = \chi_{\parallel} - \chi_{\perp}. \qquad (3)$$

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 $\mathbf{n}$, 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 $\mathbf{H}$ and the axis of maximum magnetic susceptibility χ_{max} is zero.

(a) When $\Delta\chi > 0 (\chi_{\parallel} = \chi_{max})$, the field causes a uniform orientation of the director $\mathbf{n}$ along $\mathbf{H}$, 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 $\mathbf{H}$, causes an increase in $\Delta\chi^{i \to m}$ from $\bar{\chi} = \frac{1}{3}(\chi_{\parallel} + 2\chi_{\perp})$ to χ_{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

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

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

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.

An increase in susceptibility associated with the field induced orientation of the smectic C and A phases was observed. We can conclude from our EPR results that compound **2** must be oriented with the molecular axis orthogonal to the magnetic field (i.e. $\Delta\chi < 0$), but for compound **12**, with the director **n** parallel to **H** ($\Delta\chi > 0$).

From the experimental value $\Delta\chi^{i\to m} = \chi_m - \chi_i(\Delta\chi^{i\to m}$ $= 3\cdot4 \times 10^{-6}\,cm^3\,mol^{-1}$ for compound **2**, $\Delta\chi^{i\to m} = 16\cdot5$ $\times 10^{-6}\,cm^3\,mol^{-1}$ for **12**), we can calculate the overall magnetic anisotropy $\Delta\chi = \Delta\chi_p + \Delta\chi_d$ based on equation (4 *b*) for compound **2** ($\Delta\chi < 0$ according to the EPR data) and equation (4 *a*) for compound **12** ($\Delta\chi > 0$). The results are $\Delta\chi = -10\cdot2(\pm 3\cdot3) \times 10^{-6}\,cm^3\,mol^{-1}$ and $\Delta\chi = +24\cdot8(\pm 3\cdot3) \times 10^{-6}\,cm^3\,mol^{-1}$ respectively.

Because of some disordering of the molecular long axes, these values are the result of partial averaging of the molecular magnetic anisotropies calculated above and are connected to the latter by the factors P (the order parameter). Thus, from a comparison of the experimental and calculated magnetic anisotropies (table 1), we have estimated the order parameters $0\cdot84(\pm 0\cdot2)$ and $0\cdot77(\pm 0\cdot1)$ for compounds **2** and **12**, respectively.

For copper metallomesogens (figure 1 (*a*), structure **1**), the manner of orientation (sign of $\Delta\chi$) depends on the number of phenyl rings in the molecule. Borchers and Haase [13] investigated *bis*[4-(4-hexyloxybenzoyloxy)-*N*-(4-butylphenyl)salicylaldiminato] copper(II) dissolved in 4-cyano-4′-pentylbiphenyl. Parallel orientation was observed, provided by the six phenyl rings present in the molecule of complex. The value of $\Delta\chi = +38\cdot5 \times 10^{-6}\,cm^3\,mol^{-1}$ is close to the results exhibited in this work for compounds with an equal number of phenyl rings (table 1, compounds **7** and **10**). In accordance with the data obtained, we can assume that the orientation of copper metallomesogens is with the long axes parallel to the magnetic field, when the number of phenyl rings is more than four.
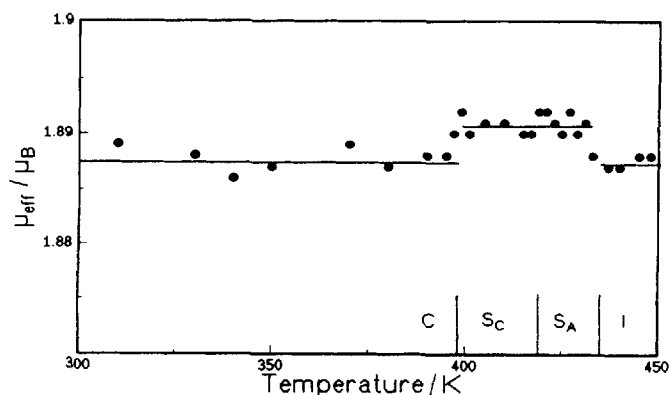
5. Conclusions

Magnetic susceptibility measurements, EPR data and calculations using an incremental scheme are in good agreement. As might be expected, the value of the total magnetic susceptibility, as well as its sign, depends mainly on: (1) the central metal ion; (2) the number of phenyl rings in the molecule; (3) the type of coordination site (presence or absence of the enamino-ketons chelate ring).

The direction of orientation of the molecules in a magnetic field is predetermined only by the sign of the total susceptibility anisotropy rather than by the mesophase type. The presence of chiral centres does not produce especial changes in the magnetic behaviour of metallo-mesogens as was predicted by Katz and Lebedev [3] and Buivydas [4].

The signs of the paramagnetic and diamagnetic anisotropies are opposite for the Cu complexes studied. If the number of phenyl rings, including enamino-ketone rings, in the molecular structure is greater than four, then the diamagnetic anisotropy exceeds the paramagnetic anisotropy and the molecular long axes align parallel to the magnetic field. Otherwise the long axes of copper complexes orient perpendicular to the field.

For VO complexes, the signs of the paramagnetic and diamagnetic anisotropies are the same (positive), and therefore the molecular long axes of these complexes are oriented along the magnetic field, independent of ligand structure. This means that alignment of VO complexes in a magnetic field is easy compared with Cu derivatives.

Figure 6.   Effective magnetic moments versus temperature for compound **2**, (see table 1). C = crystalline, S_C = smectic C, S_A = smectic A and I = isotropic phases.

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