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F. R. Diaz; N. Valdebenito; J. L. Serrano; M. Marcos; J. I. Martinez; P. J. Alonso

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Smectic Cu(II), Pd(II) and VO(IV) complexes: synthesis, EPR and thermogravimetric studies

by F. R. DIAZ*, N. VALDEBENITO
Departamento de Química Orgánica, Facultad de Química,
Pontificia Universidad Católica de Chile, Casilla 306, Correo 22, Santiago, Chile

J. L. SERRANO, M. MARCOS, J. I. MARTÍNEZ and P. J. ALONSO
Instituto de Ciencias de Materiales de Aragón (ICMA),
Universidad de Zaragoza-Consejo Superior de Investigaciones Científicas,
Plaza S. Francisco s/n, 50009 Zaragoza, Spain

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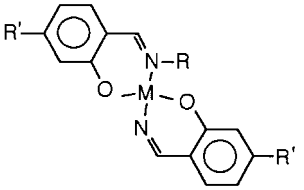
The octadecanoate of *N*-(4-hexyloxyphenyl)salicylaldimine and the corresponding Cu(II), Pd(II) and VO(IV) complexes were synthesized and studied. The compounds were characterized by IR, ^{1}H NMR, elemental and thermal analysis and polarized light microscopy. Thermogravimetric analysis and electronic spectra of the complexes are reported. Electron paramagnetic resonance (EPR) measurements were performed.

1. Introduction

The increasing number of investigations of metallomesogens can be attributed to the wide variety of chemical and physical properties presented by these compounds. The presence of metals in the organic structure gives rise to important effects on the physical properties of the compounds which make them interesting substances for technical applications [1–9].

Although the first mesogenic Schiff's base complex was reported in 1923 when Vorländer found that diarylmercury Schiff's bases formed smectic phases [10], only in the past 15 years have these compounds been receiving attention because of their liquid crystalline properties as well as their interesting magnetic properties.

In the literature, salicylaldimine complexes of various metals and organic moieties are found, having the following structure.



Most of this work has been carried out for $R = C_nH_{2n-1}$–O–C_6H–COO– [11–19], with only a few authors reporting complexes having aliphatic structures for *R* [3, 20, 21]. Sirigu *et al.* [3] synthesized copper and palladium complexes where $R' = R = C_nH_{2n-1}$–COO–, $n = 6$–12; all the compounds presented smectic C phases.

Similar complexes, with M = VO, $R = R' = C_nH_{2n-1}$–COO–, $n = 5$, 10 have been studied by Galyametdinov *et al.* [21], finding low viscosity SmC mesophases that can easily orientate in a magnetic field.

In addition to generating liquid crystalline materials we are interested in studying the orientation of the molecules in the mesophase and their thermal stability, which is an important requirement in finding applications for metallomesogens.

In the present paper, we report the synthesis, characterization and mesogenic properties of the iminoester, 4-[*N*-(4-hexyloxyphenyl)]salicyldaldimine octadecanoate and its Cu, Pd and VO complexes. The thermal degradation behaviour of the complexes was studied and EPR measurements of the paramagnetic (Cu and VO) complexes were performed at room temperature and in the fluid phases. Our results are explained with reference to phase structures.

2. Experimental

All chemicals and solvents were obtained from Aldrich and Merck Ltd. IR spectra were determined via KBr pellets, using a Perkin-Elmer model 567 spectrophotometer. ^{1}H NMR spectra were obtained with a Bruker AM-200 spectrometer. Elemental analyses were performed on a CH Heraeus Mikrostandart analyser.

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*Author for correspondence.

Thermal analyses were performed with a Perkin Elmer DSC-7 differential scanning calorimeter with a heating rate of 10°C min^{-1}. Phase textures were determined with an Olympus BH-2 polarizing light microscope, equipped with a Mettler hot stage, at a heating rate of 10°C min^{-1}. Thermogravimetric analyses were carried out with a Mettler TG-50 thermobalance equipped with a TC-10 microprocessor, using powdered samples heated under nitrogen at 20°C min^{-1}. EPR measurements were carried out with a Variant E 112 spectrometer working in X-band. Powdered samples of Cu-L_2 and VO-L_2 were examined at room temperature and in the mesophase.

2.1. *Synthesis of N-(4-hexyloxyphenyl)-4-hydroxysalicylaldimine*

2,4-Dihydroxybenzaldehyde, 15·0 mmol and an equimolar quantity of 4-hexyloxyaniline were dissolved in 20 ml of toluene. A Dean–Stark trap was adapted to the flask and the solution was boiled for 4 h under reflux. The solvent was eliminated and the imine purified by dissolving in cold methanol and adding 10% of water. Yield 84%, m.p. 120°C. IR νcm^{-1}: 3373 (O–H, *para*); 2343–2368 (O–H, *ortho*); 1629 (C=N). ^{1}H RMN. δppm: 8·48 (s, H, N=C–H); 7·20 (d 3H arom); 6·90 (d, d 2H, arom); 6·4 (d, d 2H arom); 3·96 (t, 2H, –CH_2–O); 1·78 (m, 8H –CH_2); 0·95 (t, 3H, CH_3).

2.2. *Synthesis of 4-N(4-hexyloxyphenyl)salicylaldimine octadecanoate*

N-(4-Hexyloxyphenyl)-4-hydroxisalicylaldimine 2·20 mmol was dissolved in dry THF. The solution was cooled at 0°C and 2·20 mmol of octadecanoyl chloride was added dropwise. After stirring for 12 h, the solution was poured into methanol. The precipitated ester was purified by successive recrystallization with ethanol and hexane. M.p. 88°C. IR: 1754 (C=O); 1623 (C=N). ^{1}H RMN: 13·76 (s, H, O–H); 8·57 (s, H, N=CH); 7·34 (d, H, arom); 7·24 (d, 2H, arom); 6·92 (d, 2H, arom); 6·72 (d, H, arom); 6·66 (dd, H, arom); 3·96 (t, 2H, O–CH_2); 1·62 (m, 36H, –CH_2–); 2·55 (t, 2H, CO–CH_2); 0·88 (sext., 6H, 2 CH_3).

2.3. *Synthesis of Cu-L_2*

1·0 mmol of L and 0·5 mmol of $Cu(CH_3CO_2)_2$ were dissolved in 30 ml of ethanol and the solution was heated under reflux for 3 h. The product complex was filtered off, washed thoroughly with ethanol, and recrystallized from chloroform/methanol.

2.4. *Synthesis of VO-L_2*

0·35 mmol of $VOSO_4.5H_2O$ dissolved in 10 ml of ethanol and 0·1 ml of TEA was added to 0·7 mmol of L dissolved in 40 ml of methanol; the solution was heated under reflux for 3 h. The precipitated complex was filtered off and washed with methanol. L_2-VO was purified by recrystallization from ethylacetate/ethanol (1:3).

2.5. *Synthesis of Pd-L_2*

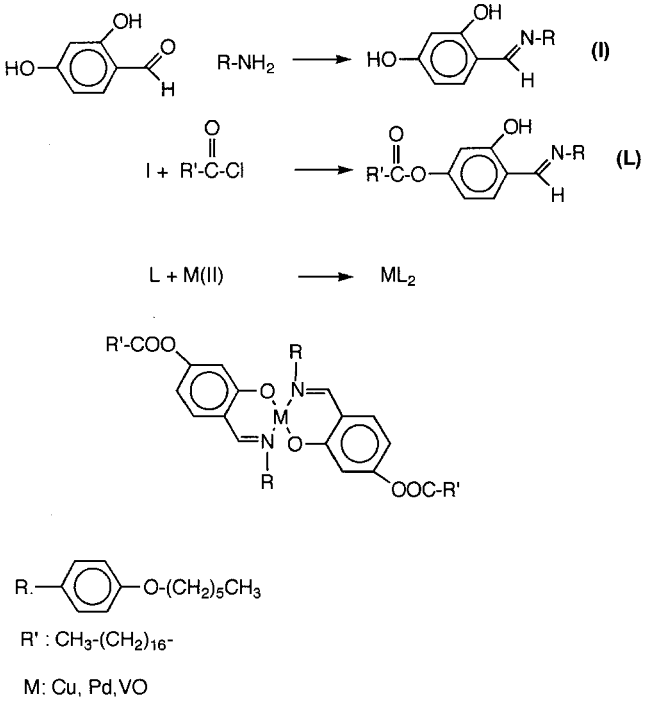
0·6 mmol of L was dissolved in 20 ml of warm ethanol, and 0·3 mmol of $Pd(CH_3CO_2)$ dissolved in cold ethanol was added. The solution was heated under reflux for 1 h and left at room temperature for 3 h. The precipitated complex was filtered off and purified by recrystallization from toluene/ethanol. ^{1}H RMN, δppm: 7·66 (s, H, CH=N); 7·17 (m, 3H, arom); 6·94 (d, 2H, arom); 6·29 (d, H, arom); 5·95 (d, H, arom); 4·01 (t, 2H, CH_2–O); 2·49 (t, 2H, CH_2–CO); 1·36 (m, 38H, CH_2).

3. Results and discussion

3.1. *Synthesis and characterization*

The ester L was synthesized (see the scheme) according to a procedure described previously [22], and characterized by IR, ^{1}H NMR spectroscopy and quantitative elemental analysis. The results were consistent with the proposed structure. Polarized light microscopy of the ester showed a smectic C mesophase between 89·6 and 111·4°C and a nematic phase between 111·4 and 118·1°C. The transition temperatures were obtained by differential scanning calorimetry (DSC).

The complexes were prepared as described previously [23–25] by the addition of an alcoholic solution containing the appropriate metallic salt to a hot solution



Scheme.

of the imine (see the scheme). The elemental analyses of the complexes are summarized in table 1 and are in accord with their structures. Table 2 gives the IR and visible spectroscopy data for the compounds.

All the complexes presented ν (C=N... metal) stretching at lower frequencies (1610 cm^{-1}) than the iminoester band (1623 cm^{-1}) in the IR spectra. The electronic spectra of the complexes (figure 1), show lower energy absorptions than the free ligand. Marcos *et al.* [26] found an absorption band between 645 and 670 nm for complexes possessing three aromatic rings in the ligand. The low absorption values obtained in the present work are attributed to the lower magnitude of the conjugation in the molecules of the Cu, Pd and VO complexes which separates the antibonding electronic levels so that higher energy is needed for the transition.

Table 1. Elemental analysis exp. (calc.) and yields of L and the complexes.

Complex	Yield/%	C/%	H/%	N/%
L	50	76·50 (76·74)	10·36 (9·91)	2·28 (2·41)
Cu-L$_2$	68	73·13 (72·78)	9·50 (9·24)	2·32 (2·29)
Pd-L$_2$	65	70·42 (70·31)	9·11 (8·93)	2·27 (2·21)
VO-L$_2$	71	73·51 (72·57)	9·67 (9·22)	2·37 (2·28)

Table 2. IR and visible spectroscopic data for L and its complexes.

	ν/cm^{-1}		
Complex	C=O[a]	C=N[b]	λ/nm[c]
L	1754	1623	358
Cu-L$_2$	1740	1610	387
Pd-L$_2$	1760	1610	415
VO-L$_2$	1750	1610	359

[a] Stretch band of carbonyl group.
[b] Stretch band of imine group.
[c] Absorption band.

3.2. *Mesogenic and thermal properties*

In order to assign the transition temperatures, calorimetric parameters were determined for the ligand L, and for the complexes. The results are summarized in table 3. The thermograms obtained for the compounds are gathered from the second heating or cooling scans.

The ligand showed nematic and smectic C phases detected by polarized light microscopy only. The mesophases shown by the complexes were identified as smectic A by their optical textures. The Cu-L$_2$ complex revealed a monotropic behaviour showing a smectic A phase during the cooling scan in the range 143–162°C.

An enantiotropic smectic phase was found for the VO-L$_2$ complex, with low transition temperatures and a range of stability of 45°C. This is probably due to the square pyramidal structure of the vanadyl centre increasing intermolecular distances and lowering the fusion temperature. Similar properties for other VO complexes have been reported [24, 27].

The Pd-L$_2$ complex exhibited a monotropic smectic A phase with higher transition temperatures than those of other Pd(II) compounds reported in the literature [23, 28]. Pd(II) complexes have higher melting points and higher isotropization temperatures than their Cu and VO analogues, probably due to the short Pd–Pd distance between contiguous molecules, as observed by Sirigu and coworkers [3, 28] for similar compounds (R: $-C_6H_5-O-(CH_2)_5CH_3$; R': $CH_3(CH_2)_6-O-$).

All the complexes presented crystal–crystal transitions. Cu-L$_2$ and Pd-L$_2$ showed large entropic values for the crystal–smectic transition, showing that the crystal phases are very ordered. On the other hand, the VO-L$_2$ complex presented a large entropic change for the

Table 3. Optical and thermodynamic data for L and the complexes. I: isotropic, T: peak temperature, Cr: crystal, S: smectic.

Compound	Transition	T/K	Onset/K	ΔH/KJ mol^{-1}	ΔH/KJ mol^{-1}
L	Cr → SmC	361·0	357·6	63·98	178·89
(MW: 579·86)	SmC → N*	—	—	—	—
	N → I	393·1	385·5	5·71	14·81
Cu-L$_2$	I → SmA	434·9	436·4	−11·81	−27·06
(MW: 1257·29)	SmA → Cr$_2$	416·4	419·9	−44·35	−105·61
	Cr$_2$ → Cr$_1$	370·1	371·7	−22·45	−60·40
Pd-L$_2$	I → SmA	466·6	467·8	−6·42	−13·72
(MW: 1264·13)	SmA → Cr$_3$	454·3	457·1	−38·47	−84·15
	Cr$_3$ → Cr$_2$	364·5	366·2	−21·78	−59·48
	Cr$_2$ → Cr$_1$	346·4	347·5	−5·90	−16·98
VO-L$_2$	Cr$_1$ → Cr$_2$	360·2	356·5	40·73	114·24
(MW: 1224·65)	Cr$_2$ → SmA	380·6	377·8	13·13	34·76
	SmA → I	424·6	413·8	19·74	47·69

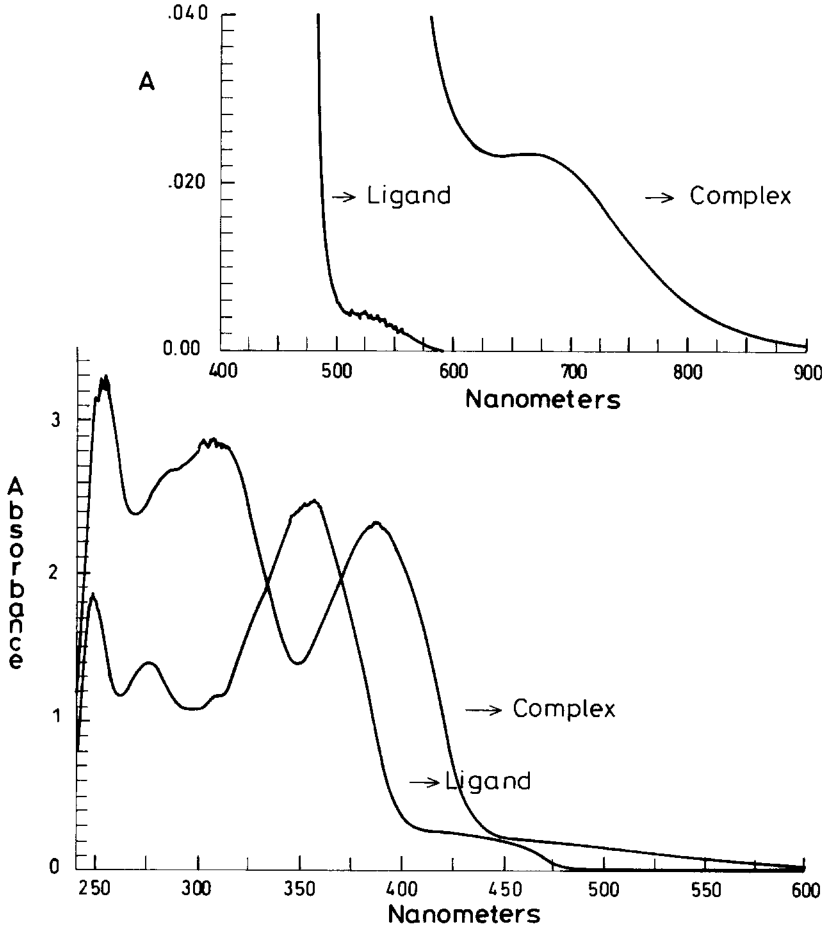


Figure 1. Electronic spectra of the ligand 4-*N*(hexyloxyphenyl)-salicyladimine octadecanoate, and the corresponding Cu(II) complex.

transition smectic–isotropic, probably due to intermolecular axial interactions VO…VO, that are present in the mesophases.

The thermal stability of the complexes was studied by thermogravimetric analysis (figure 2). They showed about 2% decomposition after becoming isotropic, so the second scan DSC data are 1–2°C lower than the first scan. From table 4 it can be seen that the Pd complex shows higher decomposition at the isotropic temperature than do the VO and Cu complexes.

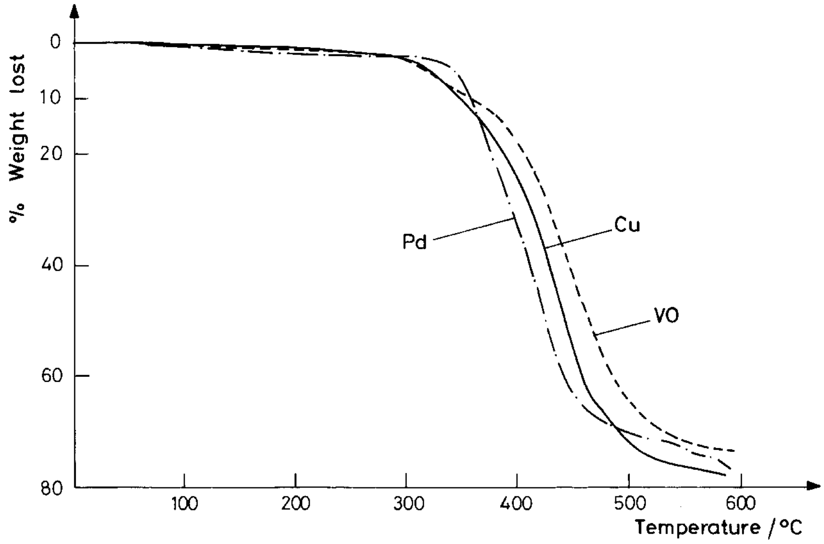


Figure 2. Thermogravimetric analysis of the complexes.

Table 4. Decomposition behaviour of the complexes.

	Cu-L$_2$	Pd-L$_2$	VO-L$_2$
Isotropic temp. T/°C	163	193	152
Wt loss at isotropic temp/%	1·00	1·95	0·90
Wt loss at 250°C/%	1·59	2·30	2·01
Temp. for 10% wt loss/°C	355	360	360

Furthermore, some authors have reported structural changes of the complexes without weight loss. Molecular geometry changes promoted by solution and temperature effects were reported: Sacconi and coworkers [29–31] found that Ni complexes change to tetrahedral structure in solution. Other authors [5] have observed that some planar molecules suffer tetrahedral distortion in the mesophase, so the phase appears heterogeneous, with tetrahedral molecules forming the isotropic sections of the texture.

All the complexes suffered 10% weight loss between 350 and 360°C; after this point decomposition becomes rapid.

3.3. *EPR measurements*

3.3.1. *Cu-L$_2$*

The EPR spectrum of Cu-L$_2$ powder samples measured at room temperature, figure 3 (*a*), is typical for this kind of compound [27, 32, 33]. It can be described using a spin Hamiltonian with only one Zeeman term.

$$H = \mu_B (g_x B_x S_x + g_y B_y S_y + g_z B_z S_z)$$

where μ_B is the Bohr magnetron, B-vector the applied continuous magnetic field, S-vector the electronic spin of copper ($s = 1/2$) and, g_x, g_y and g_z the giromagnetic tensor eigenvalues. (X, Y, Z) is the principal frame of the g-tensor. We obtained from the spectrum the following eigen values: $g_x = 2{\cdot}04 \pm 0{\cdot}01$, $g_y = 2{\cdot}08 \pm 0{\cdot}01$, $g_z = 2{\cdot}21 \pm 0{\cdot}01$. These correspond to a copper entity in a quasi square planar environment. These values are a little different from those found for isolated molecules of similar compounds. Moreover, the hyperfine structure due to the copper nucleus is not observed, indicating that a long range magnetic exchange interaction is taking place [32, 33]. In such a case, g values obtained in concentrated samples usually differ from those of the molecule. These variations are due to loss of orientational correlation between molecules coupled by exchange. g values similar to those found in our case have been associated with a positional pre-smectic structure in the solid phase [33].

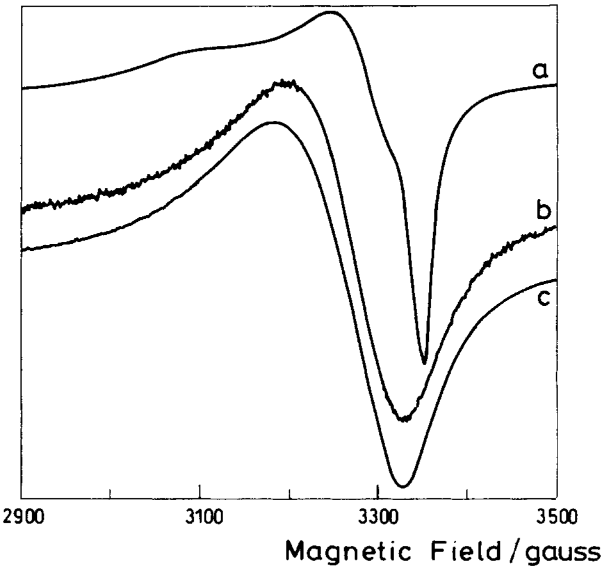


Figure 3. EPR spectrum of Cu-L$_2$: (*a*) at room temperature; (*b*) in the isotropic phase; (*c*) in the smectic phase.

No changes were found in the spectrum at different temperatures in the solid phase. The EPR of the isotropic liquid phase, figure 3 (*b*), showed only a broad signal centred at a field corresponding to $g = 2{\cdot}1$. The spectrum is due to exchange and motional averaging of g values in a sample with orientationally non-correlated molecules.

On cooling the sample, a monotropic SmA phase appears. Its EPR spectrum displays an asymmetric signal centred at about $g = 2{\cdot}11$. The asymmetry of this signal is related to some spatial correlation of the molecular axes in the mesogenic domain [32]. The spectrum of the sample solidified from the smectic phase is similar to that of the untreated sample.

Samples of Cu-L$_2$ in the SmA phase can be oriented by magnetic fields of about 1·5 T. The orientation is preserved in the solidified sample when it is cooled from the smectic phase in the presence of the magnetic field. In this case the EPR spectrum becomes anisotropic. It shows the same features as non-oriented sample spectra, but their relative intensities vary. The spectrum taken from the sample 'as frozen', that is, without any rotation after the freezing process, figure 4 (*a*), shows an increase in the intensity at low field. On the other hand, in the spectrum taken after rotating the sample 90° around an axis perpendicular to the magnetic field, the low field signal almost disappears, figure 4 (*b*). This indicates that Cu-L$_2$ in the smectic phase tends to orient with the director perpendicular to the magnetic field, as do copper complexes derived from 2,4-salicylaldimine. This behaviour differs from that of diamagnetic liquid crystals and is caused by the copper contribution to the susceptibility anisotropy [34].

3.3.2. *VO-L$_2$*

The EPR spectrum of a powder sample of VO-L$_2$ at room temperature displays a broad signal at about $g = 2{\cdot}0$ with many superimposed peaks (figure 5).

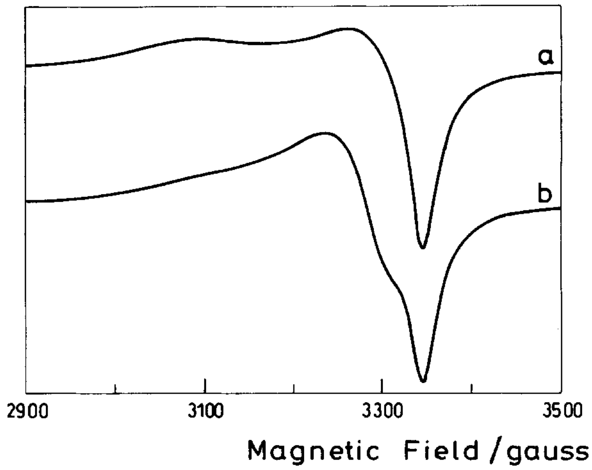


Figure 4. EPR spectra of Cu-L_2 solidified in the presence of a magnetic field: (*a*) sample with the oriented field parallel to the measuring field; (*b*) sample rotated 90°.

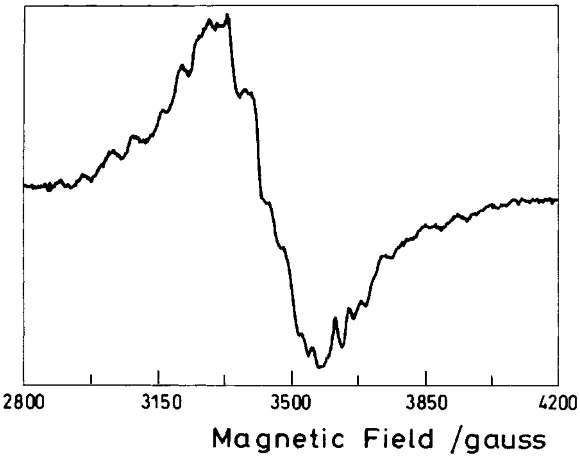


Figure 5. EPR spectrum of VO-L_2 measured at room temperature.

Other similar vanadyl complexes [27, 35] show a peak structure because of the hyperfine structure of the vanadium nucleus ($I = 7/2$) but in our case more peaks are seen than would correspond to such an interaction. We found that the spectrum is compatible with the existence of pairs of VO-L_2 molecular complexes coupled by strong magnetic interaction. On the other hand, the structure in the spectrum implies the absence of a strong long range exchange interaction.

In the spectra obtained in the solid phase at higher temperatures, the peaks corresponding to the vanadium hyperfine structure increase in relative intensity in such a way that, when the SmA phase is reached, only these peaks are visible and the spectrum can be assigned to VO complexes without any exchange interaction, as in other similar compounds [27] (figure 6). The spacing between peaks decreases when the sample is heated in the mesophase. This is attributed to the motional averaging of the molecule hyperfine tensor.

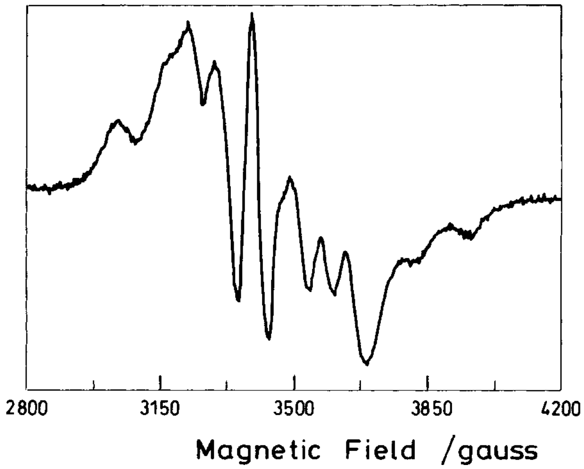


Figure 6. EPR spectrum of VO-L_2 in the smectic phase.

The sample is not oriented in the mesophase by magnetic fields up to 1·5 T. The spectrum of the solidified sample is the same as that for the untreated sample.

4. Conclusions

We conclude that all the complexes described in this paper presented smectic A phases. The VO-L_2 complex showed an enantiotropic behaviour with low transition temperatures and a wide range of stability. VO-L_2 is not oriented by a magnetic field in the mesophase.

The copper complex has a wider mesophase range and lower transition temperatures than the palladium compound. The Cu-L_2 smectic phase is oriented with the director perpendicular to the magnetic field, as occurs with other Cu complexes derived from 2,4-salicyladimine.

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