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Copper-containing dendromesogens: the influence of the metal on the mesomorphism

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The synthesis and liquid crystalline behaviour of the first and second generations of a dendrimeric structure based on poly(propyleneimine) (DAB-dendr$(NH_2)_x$) are reported. 4-(4-*n*-Alkoxybenzoyloxy)salicylaldehydes are used as mesogenic moieties attached at the peripheral amino groups of the dendrimers giving rise to dendromesogens with four and eight mesogenic branches. From these dendromesogens, considered as organic ligands, were prepared six metal-containing dendrimers which incorporate two or four copper atoms in their structures. All the dendrimeric ligands and three of the metal-containing dendrimers exhibit liquid crystalline properties which were studied by optical microscopy, DSC, X-ray diffraction and EPR spectroscopy.

1. Introduction

In recent years, dendrimers have become one of the most attractive subjects of research in the fields of Materials and Supramolecular Chemistry [1]. The generation of macrostructures showing a regular structural growth and the capability of modulation of the properties of the dendrimeric materials by introducing new and different structural moieties in the dendrimeric architectures open a vast and exciting world of possibilities for their use in new applications [2].

Since 1988, when the liquid crystalline properties of molecular trees were first reported [3], many other systems have been described involving thermotropic liquid crystalline dendritic polymers [4] and hyperbranched polymers based on flexible branched mesogens [5]. Another approach to achieve dendritic architectures displaying liquid crystalline properties consists in the introduction of mesogenic moieties at the periphery of basic dendrimeric generations with reactive terminal functions. In this sense, the results reported by Shibaev [6], Frey [7], Lattermann [8], Meijer [9] and Goodby [10], and their co-workers, are remarkable. Several mesogenic units are linked at the periphery of a functionalized dendrimer forming a liquid crystalline shell around the central nucleus.

As far as metal-containing dendromesogens are concerned, two examples have been reported to date: a ferrocene-containing liquid crystalline dendrimer [11] with six ferrocene units exhibiting an enantiotropic smectic A mesophase over a broad range of temperature, and several metal complexes derived from the first and second generations of poly(ethyleneimine) dendrimers [12]. In this case, a hexagonal columnar mesophase was detected for a Cu(II) complex. The interest of these materials incorporating transition metal atoms comes from the possibility of obtaining specialized materials which may combine the properties of liquid crystals with those due to the presence of metal atoms, such as electric, magnetic, catalytic or non-linear optical (NLO) properties.

In this paper we present the synthesis and properties of new dendritic liquid crystal materials from two generations of organic dendrimers, as well as their corresponding copper-containing derivatives (see figure 1). The influence of the copper atoms in the dendrimeric structure on the mesogenic properties of the materials is evaluated and a model is proposed to explain the results obtained for the mesophase parameters by X-ray diffraction studies. An EPR study of the copper-containing dendrimers in the different phases has also been carried out.

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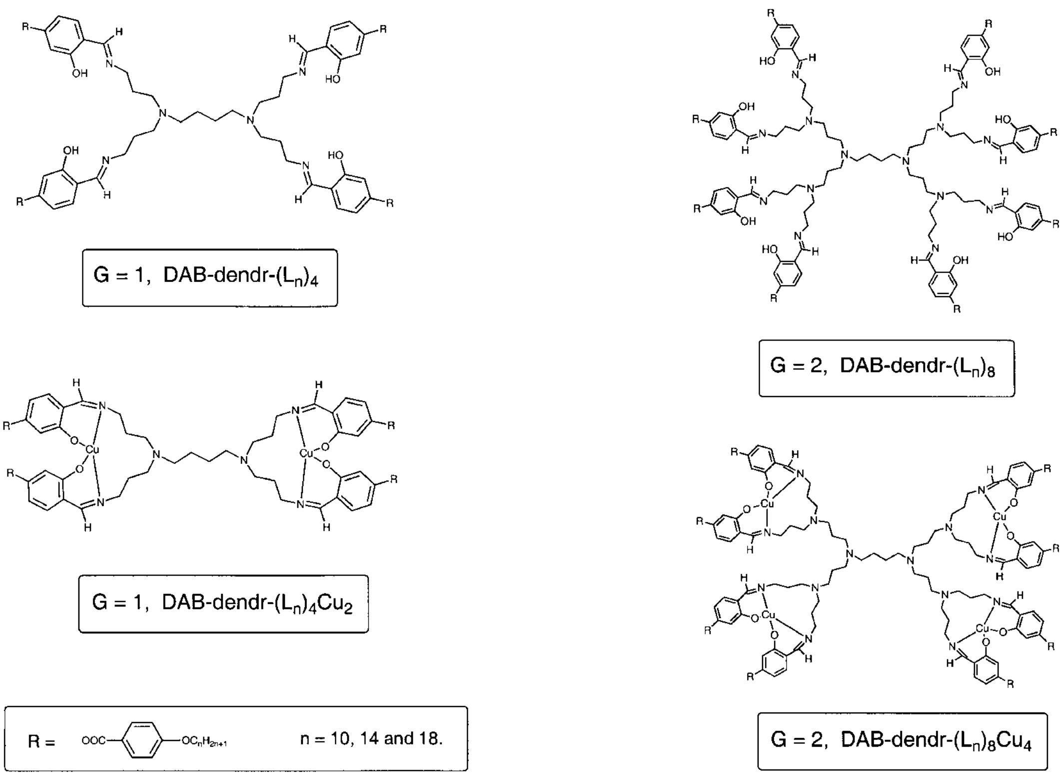


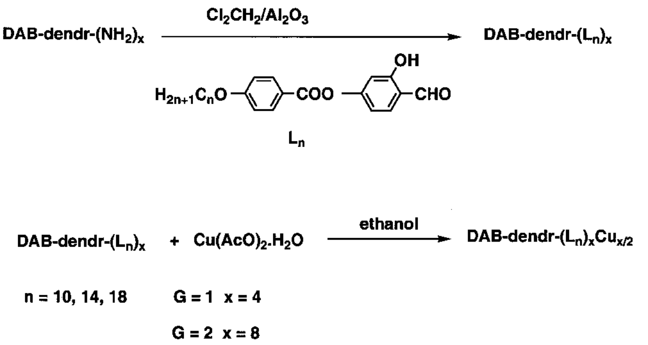
Figure 1. Structures of the dendrimeric ligands and the copper-containing dendrimers obtained therefrom.

2. Experimental

2.1. *Synthesis*

The organic dendrimers were prepared by condensation of the corresponding 4-(4-alkoxybenzoyloxy)salicylaldehyde with the first and second generations (G) of poly(propyleneimine) dendrimers functionalized with terminal NH_2 groups (DAB-dendr-$(NH_2)_x$). The dendrimeric ligands obtained thereby react with $Cu(OAc)_2$ H_2O to yield the desired metal-containing dendromesogens (scheme 1).

All dendromesogens were isolated as air-stable solids (yellow in the case of the ligands and green for the copper complexes), soluble in solvents such as dichloromethane and tetrahydrofuran and insoluble in ethanol.



Scheme 1.

2.2. *Characterization*

The structures of the new dendrimeric ligands have been established on the basis of ^1H and ^{13}C NMR and IR spectroscopy, FAB^+ and MALDI-TOF mass spectrometry and elemental analysis. ^1H and ^{13}C NMR spectroscopy have proved very useful in confirming the structure and to assess the purity of these materials. Evidence for the condensation reaction is provided by the absence of the signal at 195 ppm in the ^{13}C NMR spectrum (corresponding to the carbonyl group of the aldehyde) and by the total absence of the NH_2 signal of the starting dendritic polyamine in both ^1H NMR and IR spectra.

The structures of the copper complexes were confirmed by elemental analysis and FAB^+ and MALDI-TOF mass spectrometry. The data obtained for the characterization of the organic and the copper-containing dendrimers are given in tables 1, 2, and 3.

3. Results and discussion

3.1. *Mesomorphic properties*

The thermal behaviour of the materials as revealed by optical polarizing microscopy and differential scanning calorimetry (DSC) is summarized in table 4. The data gathered in the table correspond to the second heating and cooling scans of the first and second generation organic dendrimers and the first heating scan of the first and second generations of the copper-containing

Table 1. Elemental analyses and infrared data for the dendromesogens.

Dendrimer	Elemental analysis/%						IR/cm^{-1}	
	C		H		N			
	Found	Calc.	Found	Calc.	Found	Calc.	COO	C=N
DAB-dendr-(L10)$_4$	73.2	73.2	8.2	8.3	4.5	4.6	1741	1629
DAB-dendr-(L14)$_4$	74.5	74.5	9.1	9.0	4.2	4.1	1740	1630
DAB-dendr-(L18)$_4$	75.1	75.6	9.6	9.5	4.0	3.7	1741	1633
DAB-dendr-(L10)$_8$	72.9	73.0	8.7	8.4	5.1	5.2	1734	1632
DAB-dendr-(L14)$_8$	74.2	74.3	8.2	8.1	4.7	4.6	1730	1633
DAB-dendr-(L18)$_8$	75.2	75.4	9.8	9.6	4.2	4.2	1737	1635
DAB-dendr-(L10)$_4$ Cu$_2$	68.6	68.6	7.5	7.5	4.3	4.3	1729	1633
DAB-dendr-(L14)$_4$ Cu$_2$	70.4	70.4	7.9	8.2	3.8	3.8	1730	1635
DAB-dendr-(L18)$_4$ Cu$_2$	71.7	71.8	9.1	8.9	3.5	3.5	1730	1635
DAB-dendr-(L10)$_8$ Cu$_4$	68.3	68.6	8.1	7.7	4.8	4.8	1728	1631
DAB-dendr-(L14)$_8$ Cu$_4$	70.4	70.1	8.6	8.4	4.4	4.4	1732	1633
DAB-dendr-(L18)$_8$ Cu$_4$	71.8	71.7	9.2	8.9	4.0	3.9	1730	1633

Table 2. Mass spectrometric data for the dendromesogens.

Dendrimer	Molecular mass		
	Calculated	FAB$^+$	MALDI-TOF
DAB-dendr-(L10)$_4$	1838.45	1838 [M$^+$]	1837.0 [M$^+$ − 1]
DAB-dendr-(L14)$_4$	2062.89		2064.3 [M$^+$ + 1]
DAB-dendr-(L18)$_4$	2287.32		2286.0 [M$^+$ − 1]
DAB-dendr-(L10)$_8$	3817.14	3817 [M$^+$]	3842.2 [M$^+$ + Na]
DAB-dendr-(L14)$_8$	4266.00		4272.9 [M$^+$ + 7]
DAB-dendr-(L18)$_8$	4714.86	4715 [M$^+$]	4715.9 [M$^+$ + 1]
DAB-dendr-(L10)$_4$ Cu$_2$	1961.50	1960 [M$^+$]	1962.7 [M$^+$ + 1]
DAB-dendr-(L14)$_4$ Cu$_2$	2185.95	2185 [M$_+$ − 1]	2188 [M$^+$ + 2]
DAB-dendr-(L18)$_4$ Cu$_2$	2410.38	2407 [M$^+$ − 3]	2411.7 [M$^+$ + 1]
DAB-dendr-(L10)$_8$ Cu$_4$	4063.27	4064 [M$^+$ + 1]	4066.6 [M$^+$ + 3]
DAB-dendr-(L14)$_8$ Cu$_4$	4488.10	4511 [M$^+$ + Na]	4335.5
DAB-dendr-(L18)$_8$ Cu$_4$	4960.98		4963.9 [M$^+$ + 3]

Table 3. ^{1}H NMR and ^{13}C NMR spectroscopic data for the dendromesogens. Data for one representative example of each type of compound are given.

DAB-dendr-(L10)$_4$	^{1}*H NMR* 14.02 (s, 1H), 8.28 (s, 1H), 8.08 (d, $J = 8$ Hz, 2H), 7.20 (d, $J = 8$ Hz, 1H), 6.92 (d, $J = 9$ Hz, 2H), 6.76 (d, $J = 2$ Hz, 1H), 6.66 (dd, $J = 9$ Hz, $J = 2$ Hz, 1H), 4.0 (t, 2H), 3.57 (t, 2H), 2.49 (t, 2H), 2.4 (m, 1H), 1.79 (m, 4H), 1.4–1.1 (m), 0.86 (t, 3H). ^{13}*C NMR* 164.42, 164.22, 163.56, 163.52, 154.15, 132.30, 132.04, 121.30, 116.48, 114.26, 112.16, 110.58, 68.28, 56.77, 53.89, 51.30, 31.86, 29.52, 29.34, 29.29, 29.06, 28.38, 25.94, 25.07, 22.65, 14.10.
DAB-dendr-(L10)$_8$	^{1}H NMR 13.9 (s, 1H), 8.25 (s, 1H), 8.05 (d, $J = 9$ Hz, 2H), 7.17 (d, $J = 8$ Hz, 1H), 6.91 (d, $J = 9$ Hz, 2H), 6.74 (d, $J = 2$ Hz, 1H), 6.64 (dd, $J = 9$ Hz, $J = 2$ Hz, 1H), 4.0 (t, 2H), 3.55 (t, 2H), 2.45 (m), 1.76 (m), 1.54–1.25 (m), 0.86 (t, 3H). ^{13}*C NMR* 164.37, 164.23, 164.45, 154.13, 132.28, 132.06, 121.30, 116.47, 114.24, 122.15, 110.54, 68.28, 56.83, 52.11, 51.37, 29.52, 29.35, 29.28, 29.06, 28.42, 25.94, 24.51, 22.64, 14.08.

dendrimers. As can be observed, the dendrimeric ligand of the first generation with terminal chains of ten carbon atoms displays an enantiotropic nematic phase as well as a monotropic smectic C phase. All the other dendrimeric ligands of the first and second generations show enantiotropic smectic mesophases of the types indicated. Three of the six copper-containing dendrimers synthesized exhibit mesomorphic properties; two of them belong to

Table 4. Phase transition temperatures and associated enthalpies and entropies of dendrimeric ligands[a] and metal-containing dendrimers.

Dendrimer	Transition	T/°C	ΔH/kJ mol^{-1}	ΔS/J mol^{-1} K^{-1}
DAB-dendr-(L10)$_4$	Cr–N	99.5	66.0	177.2
	N–I	115.8	3.5	9.0
	N–SmC	86.9[c]	0.3	0.8
	SmC–Sm[b]	75.3[c]	0.5	1.4
DAB-dendr-(L14)$_4$	Cr–SmC	113.3	68.3	176.8
	SmC–I	122.6	10.7	27.0
	SmC–Sm[b]	94.4[c]	0.4	1.1
DAB-dendr-(L18)$_4$	Cr–SmC	57.9	61.8	186.8
	SmC–SmA	84.4	1.7	4.8
	SmA–I	116.2	4.4	11.3
DAB-dendr-(L10)$_8$	Cr–SmC	65.2	73.3	216.7
	SmC–SmA	91.9	3.6	9.9
	SmA–I	100.8	25.2	67.4
DAB-dendr-(L14)$_8$	Cr–SmC	49.1	46.6	144.7
	SmC–SmA	91.5	5.1	14.0
	SmA–I	112.1	17.8	46.2
DAB-dendr-(L18)$_8$	Cr–SmC	60.7	159.6	478.3
	SmC–SmA	125.3	2.4	6.0
	SmA–I	135.1	18.1	44.4
DAB-dendr-(L10)$_4$ Cu$_2$	Cr–I	179.2	62.4	138.0
DAB-dendr-(L14)$_4$ Cu$_2$	Cr–SmC	163.2	41.1	94.2
	SmC–I	196.9	14.9	31.7
DAB-dendr-(L18)$_4$ Cu$_2$	Cr–SmC	166.6	27.5	62.6
	SmC–I	187.3	3.2	7.0
DAB-dendr-(L10)$_8$ Cu$_4$	Cr–I	110[d]		
DAB-dendr-(L14)$_8$ Cu$_4$	Cr–I	80[d]		
DAB-dendr-(L18)$_8$ Cu$_4$	Cr–SmC	35.3	18.9	61.3
	SmC–I	107.7	4.1	10.8

[a] The data given for dendrimeric ligands correspond to the second heating cycle.
[b] Unidentified smectic mesophase.
[c] Monotropic transition.
[d] Transition detected by optical microscopy.

the first generation and one to the second generation. The melting temperatures observed decrease for both ligands and complexes with increasing the generation, as observed previously by Lattermann [8].

From the thermal studies performed on samples of all the materials, the differences observed in the transitional behaviour of the dendrimers of the first and second generations (both organic and copper-containing derivatives) are remarkable. The first generation dendrimers behave as typical low molecular mass mesogens, the thermograms registering neat peaks corresponding to the melting and clearing transitions. However, the second generation dendrimers present a thermal behaviour similar to that of typical amorphous polymers. In the first heating scan, the peak associated with the melting transition is observed, whereas on cooling from the isotropic liquid, the materials do not crystallize, but solidify into a glassy state which maintains the preceding mesophase texture.

A comparison of the thermal data for the first generation organic and copper-containing dendrimers demonstrates the dramatic increase in the melting temperatures of the metal complexes with respect to their organic analogues. This indicates the occurrence of an important change in the molecular structure which increases the intermolecular interactions in the case of the metal-containing dendrimers. However, this phenomenon is not observed when comparing the thermal data for the second generation dendrimers. In this case, the presence of copper atoms in the dendrimeric structure causes the disappearance of the liquid crystalline properties in the materials with terminal chains of 10 and 14 carbon atoms. The dendrimer with terminal C-18 alkoxy chains, however, shows a SmC mesophase in a temperature interval similar to that observed for the corresponding organic ligand.

Regarding the appearance of the mesophases under the microscope, the nematic phase corresponding to DAB-dendr-(L10)$_4$ shows a typical schlieren texture. The smectic C mesophases show both blurred schlieren and schlieren textures, and the smectic A mesophases were identified by the homeotropic texture observed when a mechanical shear was applied to the sample.

3.2. *X-ray diffraction studies*

All the compounds in both series (dendrimeric ligands and copper-containing dendrimers) were studied by X-ray diffraction in their high temperature mesophases. For these studies, the samples were loaded into Lindemann glass capillaries and irradiated at the appropriate temperature. The diffraction patterns were collected on photographic film. The photographs at high temperatures are characteristic of liquid crystal phases and confirm the microscopic observations in all cases. They show one or two sharp rings in the small angle region and a diffuse broad halo in the wide angle region. When two small angle rings are present, their reciprocal spacings are in the ratio 1 : 2. This kind of pattern is characteristic of a smectic structure; the small angle maxima correspond to the first and second order reflections from the smectic planes, whereas the wide angle halo indicates the existence of only short range order (liquid-like order) within the layers. These results are consistent with either a smectic A or a smectic C mesophase. There is only one exception to this behaviour and this relates to the nematic mesophase observed for compound DAB-dendr-(L10)$_4$ for which the small angle ring is diffuse, as expected from the absence of long range order along the molecular axes. The measured distances are gathered in table 5.

It has been shown [6 *b*] that in mesomorphic dendrimers, smectic mesomorphism is promoted when the molecules are elongated along a preferred direction, whereas columnar mesomorphism is favoured when the dendrimer molecules adopt a more spherical geometry. We have found that in the smectic mesophases exhibited by a series of PAMAM-derived dendromesogens [13], the dendrimer molecules adopt a conformation such that the mesogenic units are parallel to each other, extending up and down from the molecule centre. In accordance with this, from the *d* values in table 5 it can be seen that in the present series the layer thickness increases as the terminal alkoxy chain is lengthened. However, the increase in the layer thickness is much lower than expected from an extended conformation of the hydrocarbon chain. Indeed, an increase in the molecular length of about 10 Å would be predicted on passing from (L10) to (L14) or from (L14) to (L18) if the hydrocarbon chains adopted an all-*trans*-conformation (each C–C bond in a zig-zag arrangement contributes 1.25 Å). This indicates that there is a high degree of conformational freedom involving not only the terminal alkoxy chains, but also the central poly(propylenimine), as revealed by the very low values obtained for the layer thickness compared with the molecular length *L* estimated from Dreiding stereomodels assuming an all-*trans*-conformation of the poly(propylenimine) dendrimer and alkoxy groups (table 5). This high conformational disorder was also observed by us for the above-mentioned PAMAM dendromesogens [13]. However, in the DAB-derivatives described in the current work, a comparison between the smectic layer thickness measured in the free ligands and in the corresponding copper complexes provides additional information concerning the molecular packing in the mesophase.

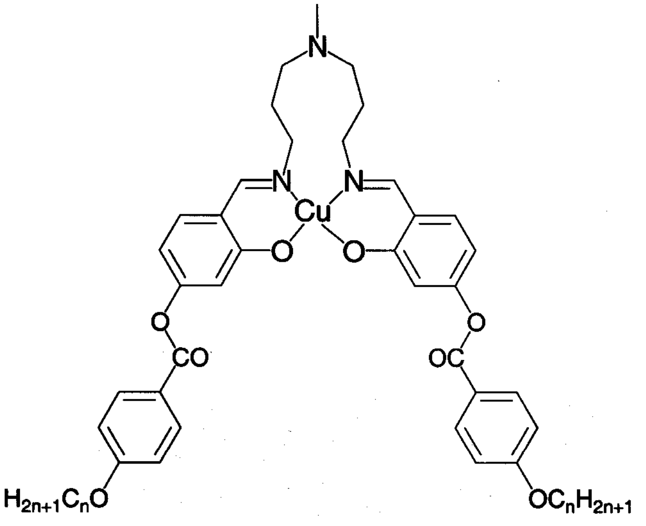
It is noteworthy that the smectic layer thickness is much smaller in the complexes than in the corresponding ligands. This fact cannot be accounted for only on the basis of conformational freedom of the flexible groups (observe the large difference between the experimentally measured spacings and the molecular length *L*, estimated from Dreiding stereomodels in table 5). A more plausible explanation is the existence of an interdigitated

Table 5. X-ray diffraction data, molecular cross-sectional areas calculated from these data, and molecular lengths estimated from Dreiding stereomodels.

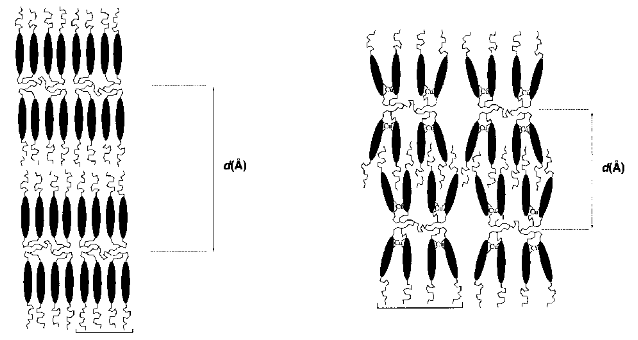
Compound	Temperature/ °C	Phase	Layer spacing *d*/Å	Molecular area/Å^2	Area per mesogenic unit/Å^2	Fully-extended molecular length *L*/Å
DAB-dendr-(L10)$_4$	95	N	45[a]	68	34	70
DAB-dendr-(L14)$_4$	110	SmC	52	66	33	80
DAB-dendr-(L18)$_4$	75	SmC	67	57	28.5	90
	100	SmA	57	67	33.5	
DAB-dendr-(L10)$_8$	70	SmC	52	122	30.5	80
	95	SmA	53	120	30	
DAB-dendr-(L14)$_8$	60	SmC	59	120	30	90
	80	SmC	59	120	30	
	100	SmA	58	122	30.5	
DAB-dendr-(L18)$_8$	100	SmC	61	128	32	100
	129	SmA	58	135	34	
DAB-dendr-(L10)$_4$ Cu$_2$	—	—	—	—	—	70
DAB-dendr-(L14)$_4$ Cu$_2$	180	SmC	38.5	94	47	80
DAB-dendr-(L18)$_4$ Cu$_2$	170	SmC	43	93	46.5	90
DAB-dendr-(L10)$_8$ Cu$_4$	—	—	—	—	—	80
DAB-dendr-(L14)$_8$ Cu$_4$	—	—	—	—	—	90
DAB-dendr-(L18)$_8$ Cu$_4$	55	SmC	45	183	46	100

[a] Diffuse maximum, order extends only to short distances.

structure favoured by the copper complexation. Indeed, coordination of the two salicylaldimine groups to the copper atom in a *cisoid* arrangement forces them to adopt a non-coparallel orientation. A few examples of liquid crystalline complexes are known in which a *cisoid* arrangement of salicylaldimine groups is forced to occur by linking two 5-substituted salicylaldehyde units to ethylenediamine [14]. X-ray analysis shows that in these salicylidenediamine complexes the hydrocarbon chains in the 5-position of the aromatic rings are colinear [15]; however, it is deduced that when the substituents are attached to the 4-position of the salicyl rings, the molecule must adopt a bent geometry (scheme 2). This would generate an empty space between the two mesogenic branches capable of accommodating a mesogenic branch from a molecule of a neighbouring layer (figure 2). In turn, the non-parallel arrangement of the mesogenic units would explain the poorer mesomorphic properties of the complexes compared with the free ligands.



Scheme 2.



DAB ligands:
Simplified view of the smectic structure

DAB copper complexes:
Simplified view of the interdigitated smectic structure

Figure 2. Schematic representation of the smectic structure for the organic dendrimers and the interdigitated smectic structure for the copper complexes.

In order to obtain further insight into this point, some calculations can be made in terms of density estimations and measured layer spacings. The molecular volume can be estimated from the molecular mass and the density. From the molecular volume, the molecular cross-sectional area in Å^2 can be deduced as

$$Area = V/d$$

where d is the measured layer spacing in Å. Table 5 lists the deduced molecular areas assuming that the density of these materials must be close to 1 g cm^{-3}. The table also lists the area per mesogenic unit for an up-and-down arrangement of the mesogenic units. In this structural model [13], the DAB moiety occupies the central slab of the smectic layer and the mesogenic units extend statistically on both sides. Thus, the area per mesogenic unit is the ratio between the cross-sectional area calculated with the formula shown above and half of the number of mesogenic units. It is interesting to note that in the free DAB ligands, the molecular areas obtained are approximately proportional to the number of mesogenic units, which is consistent with their parallel arrangement and supports the up-and-down model. The area per mesogenic unit ranges from 28.5 to 34 Å^2 and is consistent with typical chain areas in smectic mesophases [16].

It is also noteworthy that the layer thickness measured for the smectic C mesophase is similar to or larger than that for the smectic A mesophase in the same material. This unusual behaviour can be explained by a low tilt angle together with a lower degree of chain melting in the SmC mesophase compared to the SmA phase. The same phenomenon has been found in a series of palladium complexes containing four hydrocarbon chains [17], and this behaviour was explained by a loss of conformational freedom as the temperature decreases. In this situation, the disposition of the chains in a more extended conformation is able to compensate the effect of tilting.

For the copper complexes, the estimated area per mesogenic unit ranges from 46 to 49.5 Å^2. These high values, compared with those found for the metal-free homologues (28.5 to 34 Å^2), give additional support to the above-mentioned interdigitated structure. Indeed, if the hydrocarbon chains from neighbouring layers are imbricated, the molecular cross-sectional area must increase compared with that for the parent ligands.

3.3. *EPR studies*

Two copper-containing dendromesogens, DAB-dendr-(L18)$_4$Cu$_2$ and DAB-dendr-(L18)$_8$Cu$_4$, have been studied by electron paramagnetic resonance (EPR) spectroscopy. They are complexes with two and four copper atoms, respectively, with a similar square planar environment.

The EPR characterization has been made both on toluene solutions and on neat samples.

The X-band spectra recorded for both samples in toluene solution are given in figure 3. For DAB-dendr-$(L18)_4Cu_2$ (figure 3, curve A) a very broad band ($\Delta H_{pp} \approx 13$ mT) single signal centred in a g value of 2.10 is obtained. A trace of a very broad peak at a lower magnetic field ($g_{ef} \approx 2.28$) could also be present. The spectrum recorded for a solution of DAB-dendr-$(L18)_8Cu_4$ in toluene and frozen at liquid nitrogen temperature (figure 3, curve B) shows a well resolved structure which corresponds to the typical axial powder EPR spectrum of an isolated copper centre in this type of complex [18], with the following spin Hamiltonian parameters:

$$g_{\parallel} = 2.25 \pm 0.01 \qquad A_{\parallel} = 4.65 \pm 10 \text{ MHz}$$

$$g_{\perp} = 2.09 \pm 0.01 \qquad A_{\perp} < 60 \text{ MHz}$$

The signal obtained is broader than others detected for isolated copper complexes, especially in the perpendicular feature.

Those results are related to the interaction among the copper atoms in the complex. A strong dipolar interaction would be expected when the copper centres are close to each other. In this sense, the signal obtained for DAB-dendr-$(L18)_8Cu_4$ should be broader (with worse resolved features) than that obtained for DAB-dendr-$(L18)_4Cu_2$. The opposite effect is observed, so that the signal for DAB-dendr-$(L18)_4Cu_2$ must be affected by an additional broadening mechanism.

Another possible interaction is a magnetic exchange between copper centres. If the exchange energy is low compared with the spin Hamiltonian, an additional broadening would occur. With a large exchange, a pair spectrum would be displayed [18]. The spectrum of DAB-dendr-$(L18)_4Cu_2$ does not exhibit any exchange-coupled pair feature. In fact, the single signal detected may be due to a copper centre with the same parameters as DAB-dendr-$(L18)_8Cu_4$ and an additional broadening. In such a case, the trace at $g \approx 2.28$ would correspond to one of the parallel hyperfine structure peaks. Therefore, a weak intramolecular exchange interaction takes place in this compound. This exchange interaction is related to a weak bonding of paramagnetic species. This can explain its occurrence in DAB-dendr-$(L18)_4Cu_2$ whereas it has no effect for DAB-dendr-$(L18)_8Cu_4$ in which the closest copper centres are only very indirectly bonded.

It might appear surprising that two copper centres so close together give just a weak exchange coupling, since other copper complexes have shown a great tendency to form strong exchange-coupled systems. In these cases, the copper centres are at similar distances but in an axial direction which is perpendicular to the coordination plane. For the copper-containing dendrimers studied here, the approach of the copper centres in the in-plane direction seems to be less efficient for exchange coupling. The spectra obtained for neat samples are represented in figures 4 and 5, and can be interpreted in a similar way.

The spectrum recorded for DAB-dendr-$(L18)_4Cu_2$ shows no differences with respect to that obtained in solution. On heating the solid phase, the spectrum is not modified. When the smectic mesophase is reached, however, the EPR signal shifts to higher magnetic fields and a peak corresponding to the parallel hyperfine structure can be distinguished (figure 4, curve B). This can be understood as an effect of the motional modes activated in the mesophase. The solid phase spectrum is recovered on cooling the sample to room temperature.

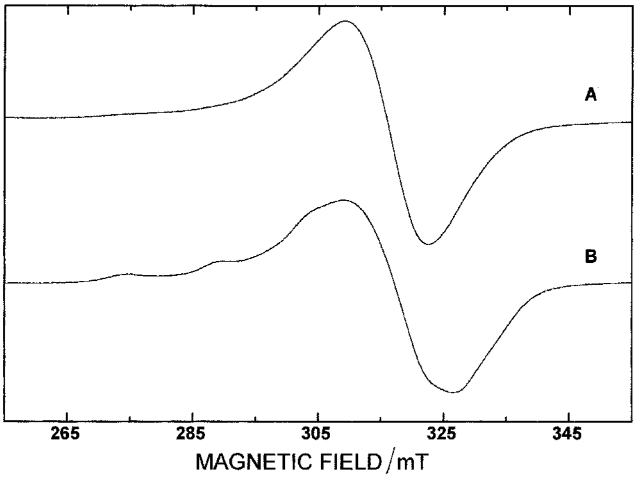


Figure 3. X-band ($\nu = 9.29$ GHz) EPR spectra of samples dissolved in toluene and frozen at LNT. (A) DAB-dendr-$(L18)_4Cu_2$; (B) DAB-dendr-$(L18)_8Cu_4$.

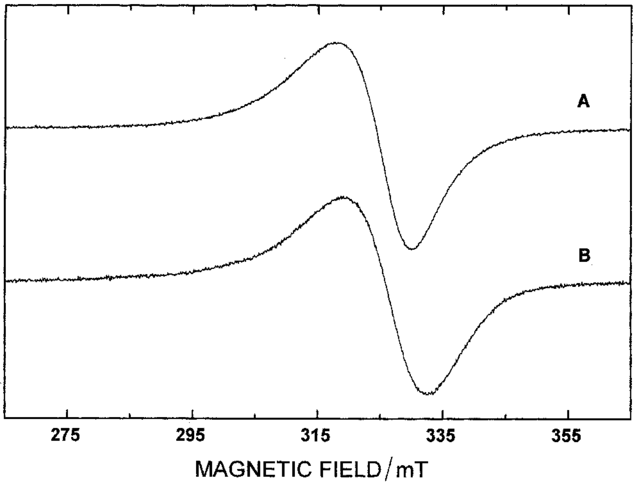


Figure 4. X-band ($\nu = 9.60$ GHz) EPR spectra of DAB-dendr-$(L18)_4Cu_2$. (A) RT (solid phase); (B) smectic phase.

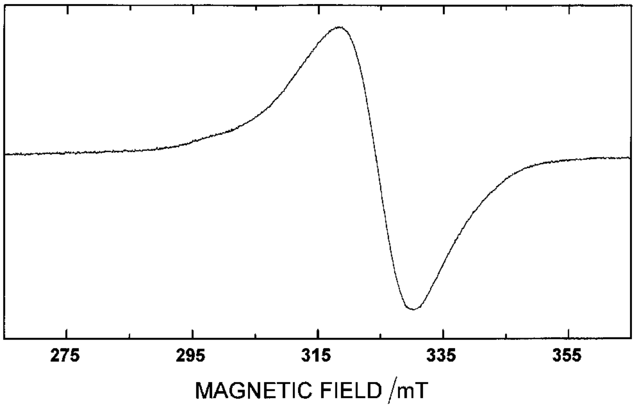


Figure 5. X-band ($\nu = 9.60\,\mathrm{GHz}$) EPR spectrum of DAB-dendr-(L18)$_8$Cu$_4$.

An additional anisotropic broadening is observed in the EPR spectrum (figure 5) of DAB-dendr-(L18)$_8$Cu$_4$ due to intermolecular dipolar interaction. Nevertheless, the spin Hamiltonian parameters are not modified. The spectra show no differences when the smectic or even the isotropic liquid phases are reached.

4. Conclusions

Six copper-containing dendromesogens belonging to the first and second generations of poly(propylenimine)-derived dendrimers have been prepared and characterized. The free organic dendrimeric ligands show liquid crystalline behaviour, namely nematic and smectic, which can be explained assuming a parallel arrangement of the mesogenic units extending up and down from the centre of the molecule. The introduction of a complexing metal, such as copper, breaks the parallel arrangement giving rise to an 'opening' of the mesogenic branches of every molecule. This fact allows the interdigitation of the mesogenic branches of the molecules located in neighbouring layers. As a consequence, the formation of a mesophase structure is prevented in some cases, whereas in others, the smectic mesophases exhibited by three of the copper-containing dendromesogens are organized in layers with a smaller thickness than those of their corresponding organic ligands.

The EPR signals of two of the copper-containing dendromesogens have been characterized. The corresponding spectra have been interpreted on the basis of a standard spin Hamiltonian of Cu(II) in a square planar environment. The effect of a weak intramolecular exchange and dipolar interactions on the EPR spectra has also been discussed.

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