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Liquid crystalline behaviour in gold(I) and silver(I) ionic isocyanide complexes: smectic and columnar mesophases

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The synthesis, characterization and mesomorphic properties of gold(I) and silver(I) ionic isocyanide complexes $[Au(CNR)_2]Y$ [$R = C_6H_4OC_nH_{2n+1}$, $C_6H_4C_6H_4OC_nH_{2n+1}$, $C_6H_2(3,4,5\text{-}OC_nH_{2n+1})_3$; $Y = PF_6^-$, BF_4^- ($n = 4$, 8, 12), $Y = NO_3^-$ ($n = 8$)] and $[Ag(CNR)_2]Y$ [$R = C_6H_4OC_nH_{2n+1}$ ($n = 8$, 12), $C_6H_4C_6H_4OC_nH_{2n+1}$ ($n = 4$, 8, 12), $C_6H_2(3,4,5\text{-}OC_nH_{2n+1})_3$ ($n = 4$, 8 12); $Y = NO_3^-$, BF_4^-] are described. The free phenyl and 3,4,5-trialkoxyphenyl isocyanides are not liquid crystals but most of the gold and silver derivatives prepared are mesogens. Only the nitrate series of gold, which decompose on melting, and the complexes $[Au(CNR)_2]PF_6$ [$R = C_6H_4OC_4H_9$, $C_6H_2(3,4,5\text{-}OC_4H_9)_3$] do not display mesogenic behaviour. The phenyl and biphenyl gold derivatives show smectic A phases and the analogous silver complexes display SmA and SmC mesophases, while the 3,4,5-trialkoxyphenyl isocyanide complexes of gold and silver show hexagonal columnar mesophases.

The influence of the metal atom, the anion and the isocyanide on mesogenic behaviour for these kinds of complexes is discussed.

Introduction

The study of metallomesogens (liquid crystals containing transition or post-transition metals) constitutes an active branch of liquid crystals research.[1–9] An important aspect of this research area is to undertake systematic investigations of structure/property relationships in order to design new materials, and ultimately predict the properties that will arise.

Although alkali metal soaps were among the first thermotropic liquid crystals to be systematically studied,[10] the majority of metallomesogens reported are based on molecular and macromolecular species, and ionic liquid crystalline derivatives have been reported less frequently.[11–13]

The diversity of metallomesogens is very wide, and a large variety of metals and ligands have been used to prepare mesogenic systems. Some of them are based on isocyanide complexes: some complexes of Au(I),[8,14–22] Pd(II) and Pt(II),[22–26] iron(0)[27] and very recently a few isocyanide complexes of copper(I).[28]

We have worked extensively with the coordinatively simple mesogenic system [MX(CNR)] (X = anionic ligand; M = Au, Cu), and have studied the influence on the mesogenic behaviour of the isocyanide, anionic ligand[16–21,25,27] and metal.[28] That work allowed us to establish certain useful relationships between the molecular features of the complexes and their thermal behaviour.

As a continuation of this study, we look now at the effect of substituting halides for an isocyanide which involves doubling the number of alkyl chains per molecule and the introduction of ionic interactions. Here we report the synthesis and liquid crystalline behaviour of ionic gold(I) isocyanide complexes of type $[Au(CNR)_2]Y$ ($R = C_6H_4OC_nH_{2n+1}$, $C_6H_4C_6H_4OC_nH_{2n+1}$, $C_6H_2(3,4,5\text{-}OC_nH_{2n+1})_3$; $Y = NO_3^-$, PF_6^-, BF_4^-). Moreover, we have prepared the analogous silver complexes $[Ag(CNR)_2]Y$ in order to study the effect of the metal on the mesogenic properties.

Reports on silver isocyanide complexes are very scarce,[29,30] and to the best of our knowledge liquid crystals based on silver(I) isocyanide complexes have not been described before.

Results and discussion

Synthesis and characterization of the complexes

The syntheses of cationic gold(I) and silver(I) compounds were carried out according to Scheme 1.

The reaction of the corresponding isocyanide with $[Au(NCMe)_2]BF_4$ afforded the complexes $[Au(CNR)_2]BF_4$ [$R = C_6H_4OC_nH_{2n+1}$; $C_6H_4C_6H_4OC_nH_{2n+1}$; $C_6H_2(3,4,5\text{-}OC_nH_{2n+1})_3$ ($n = 4$, 8, 12)]. The nitrate and hexafluorophosphate gold(I) derivatives were prepared in a one-pot synthesis starting from $[Au(tht)_2]ClO_4$ (tht = tetrahydrothiophene) by substitution of tht by the corresponding isocyanide and exchange reaction in acetone with the appropriate potassium salt.

The silver compounds were synthesized by direct reaction between the corresponding silver salt and two equivalents of isocyanide.

All the complexes prepared were isolated as white solids and gave satisfactory C, H, N analyses which, together with relevant IR data, are given in Table 1.

The IR spectra show only one ν_{CN} absorption from the isocyanide group, in each case at higher wavenumbers (*ca.* 100 cm^{-1} for gold and *ca.* 60 cm^{-1} for silver) than for the corresponding free isocyanide. Both the σ donation of the antibonding carbon lone pair of the isocyanide to the metal, and the π back-bonding from the metal d orbitals to the π* ligand orbitals contribute with the result of increasing the C≡N stretching frequency upon coordination.[16,30] In the solid state, the frequency increases slightly on going from NO_3^- to both BF_4^- or PF_6^- derivatives. This is to be expected since the metal atom would be less of an acceptor towards the isocyanide in nitrate derivatives, due to some covalent donor interaction

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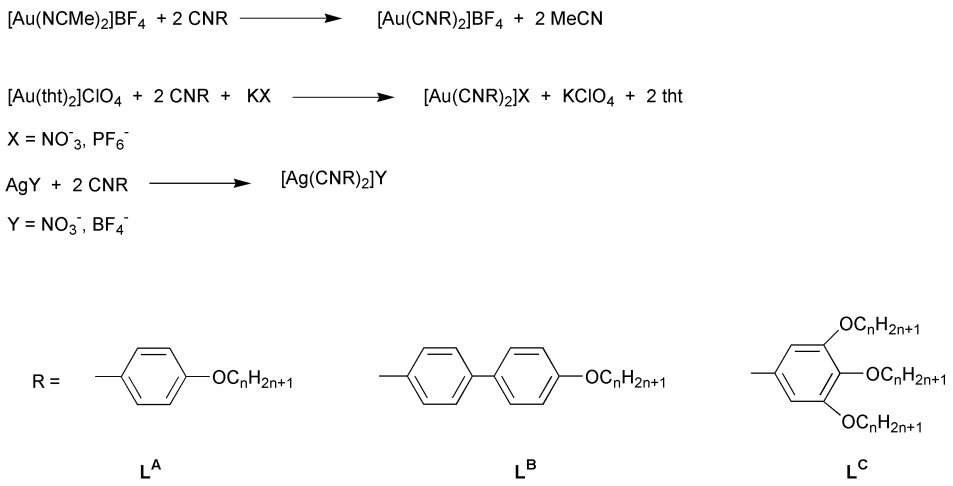

Scheme 1

from the oxygen atoms of the nitrate group to the metal centre, as found in the X-ray structure of $[Au(CNC_6H_3Me_2\text{-}2,6)_2]NO_3$.[31] In the IR spectra there also appears a strong and broad band corresponding to the anions present in the compounds; at 1050 cm^{-1} for BF_4^-,[32] 1350 cm^{-1} for NO_3^-,[33] and 840 cm^{-1} for PF_6^-.[34]

The ^1H NMR spectra of the compounds are all similar for each family. At 300 MHz the aromatic hydrogens from *p*-alkoxyphenyl isocyanide complexes (which strictly are an AA'BB' system) show two somewhat distorted "doublets' in the range 6.9–7.5 ppm, with apparent coupling constants ($N = J_{AB} + J_{AB'}$) of 9.0 Hz. In addition, the first methylene group of the alkoxy chain is observed as a triplet at 3.9–4.1 ppm. The remaining chain hydrogens appear in the range 0.8–1.8 ppm. Analogously, the ^1H NMR spectra of biphenyl isocyanide complexes show four "doublets' from aromatic hydrogens (two AA′BB′ spin systems).

The ^1H NMR spectra of the 3,4,5-trialkoxyphenyl isocyanide complexes show a singlet corresponding to two equivalent aromatic protons at *ca.* δ 7, plus signals for the aliphatic chains.

Mesogenic behaviour

It is now well established that the coordination of a non-mesogenic ligand to a metal can give rise to a liquid crystal. This effect has been exploited many times and is remarkable in the case of the phenyl isocyanides coordinated to gold(I) because the resulting complexes are liquid crystalline although they have only one aryl ring.[17] When the halide of the [AuX(CNR)] complexes is substituted by another isocyanide to obtain the ionic complexes $[Au(CNR)_2]Y$, a range of mesogenic behaviour is observed (Table 2). Although that substitution doubles the number of the alkyl chains in the molecule and introduces an additional ionic interaction, both kind of complexes (neutral and ionic) display the same type of mesophase (SmA) and have similar mesogenic ranges (the ionic complexes with $Y = NO_3^-$ cannot be compared because they decompose on melting). As can be seen in Fig. 1 (where the thermal properties for the complexes with X = Cl and $Y = PF_6^-$ are represented) the mesogenic range is greater for neutral complexes when the chains are short. However, the increase in the length of the chains affects more the ionic complexes (that have double the number of alkoxy chains), and for the longest chain derivative the greater mesogenic range corresponds to the ionic complex. The smectic A (SmA) mesophase has been identified in optical microscopy by the typical myelinic and homeotropic textures which reorganize to the fan-shaped texture at temperatures close to the clearing point.

The incorporation of a second phenyl ring in the system (biphenyl isocyanide complexes) produces a small increase in the liquid crystal range, possibly linked to the greater polarizability anisotropy of the resulting compounds. These complexes show only a smectic A phase, except for the nitrate derivatives which decompose without melting, and the dodecyloxy tetrafluoroborate derivative which shows smectic C (SmC) and SmA mesophases. The smectic C phase has been optically identified by the typical schlieren texture, and by the fact that under mechanical stress it is not possible to obtain either homeotropic regions or brownian flashes. The free biphenyl isocyanides are mesomorphic, showing nematic and SmA phases in the range 40–85 °C, and their coordination to gold(I) leads to compounds with a higher tendency to show smectic mesophases (in this case the nematic phase is only found in the shortest chain derivative) at higher temperatures.[16,24] The coordination of two biphenyl isocyanides to a gold(I) atom to obtain an ionic complex gives rise to the same behaviour with smectic mesophases and higher melting temperatures. The mesogenic ranges cannot be compared with those of the neutral halogold(I) complexes in this case because the clearing temperatures of the ionic biphenyl isocyanide complexes are, in fact, decomposition temperatures.

The introduction of two additional alkoxy chains in the phenyl group (3,4,5-trialkoxyphenyl complexes) causes a dramatic change in the structure of the molecule, which cannot be considered rod-like any longer. Consistently, the complexes show hexagonal columnar mesophases for some of them at room temperature, in spite of the free trialkoxyphenyl isocyanide not being liquid crystalline.[20] Their crystallization is not observed due to supercooling of the mesophases, as a consequence of their high viscosity. The optical textures, when viewed with a polarizing microscope, are characteristic of hexagonal columnar mesophases and display linear birefringent defects, large areas of uniform extinction and fan domains. The hexagonal nature of the mesophase was confirmed by X-ray studies and is discussed below.

The $[Au\{CNC_6H_2(3,4,5\text{-}OC_nH_{2n+1})_3\}_2]PF_6$ complexes show higher clearing temperatures than the corresponding chloro complexes.[20]

It is interesting to note the influence of the counteranion on the thermal behaviour. Irrespective of the isocyanide used, all the gold nitrate derivatives prepared show a low thermal stability and undergo extensive decomposition at relatively low temperatures (only the low-melting trialkoxyphenyl derivative shows liquid crystal behaviour). In contrast, the corresponding silver complexes are more thermally stable and produce mesophases. This thermal instability of the gold(I) compared to silver(I) nitrate derivatives is associated with the easy decomposition of the anion in the presence of many heavy metal cations,[35] and can be traced back to the simple nitrates: whereas $Ag(NO_3)$ is a commercial product, $Au(NO_3)$ is not

Table 1 Relevant IR data, yields and microanalytical data for the complexes [M(CNR)$_2$]Y

M	R	Y	*n*	ν(C≡N)/cm^{-1}		Microanalysis^a		
				CH$_2$Cl$_2$	Nujol	% C	% H	% N
Au	L^A	BF_4^-	4	2233	2234	41.39 (41.66)	4.25 (4.13)	4.27 (4.42)
Au	L^A	BF_4^-	8	2233	2234	47.95 (48.27)	5.61 (5.67)	3.66 (3.75)
Au	L^A	BF_4^-	12	2233	2238	52.94 (53.16)	6.68 (6.81)	3.07 (3.26)
Au	L^B	BF_4^-	4	2235	2223	52.23 (51.93)	4.61 (4.36)	3.51 (3.56)
Au	L^B	BF_4^-	8	2235	2231	55.92 (56.14)	5.78 (5.61)	3.06 (3.12)
Au	L^B	BF_4^-	12	2235	2232	59.76 (59.41)	6.87 (6.58)	2.95 (2.77)
Au	L^C	BF_4^-	4	2234	2238	49.29 (49.47)	6.05 (6.34)	3.24 (3.04)
Au	L^C	BF_4^-	8	2225	2237	59.39 (59.14)	8.30 (8.48)	2.32 (2.23)
Au	L^C	BF_4^-	12	2232	2234	64.59 (64.72)	9.59 (9.73)	1.66 (1.76)
Au	L^A	PF_6^-	4	2234	2233	38.12 (38.16)	3.75 (3.79)	4.38 (4.05)
Au	L^A	PF_6^-	8	2233	2239	44.51 (44.87)	4.92 (5.22)	3.62 (3.48)
Au	L^A	PF_6^-	12	2233	2240	49.65 (49.78)	6.17 (6.38)	3.25 (3.06)
Au	L^B	PF_6^-	4	2234	2235	48.01 (48.35)	3.92 (4.06)	3.21 (3.32)
Au	L^B	PF_6^-	8	2234	2237	54.46 (54.55)	5.61 (5.77)	2.90 (2.77)
Au	L^B	PF_6^-	12	2234	2236	56.12 (56.18)	6.16 (6.22)	2.59 (2.62)
Au	L^C	PF_6^-	4	2226	2236	46.59 (46.54)	5.84 (5.96)	2.55 (2.86)
Au	L^C	PF_6^-	8	2232	2235	56.90 (56.52)	7.97 (8.11)	1.84 (2.13)
Au	L^C	PF_6^-	12	2234	2237	62.61 (62.45)	9.40 (9.38)	1.82 (1.69)
Au	L^A	NO_3^-	8	2227	2227	49.83 (49.93)	6.23 (5.87)	5.64 (5.82)
Au	L^B	NO_3^-	8	2223	2237	57.47 (57.73)	5.59 (5.77)	4.90 (4.81)
Au	L^C	NO_3^-	8	2228	2226	60.27 (60.32)	8.52 (8.65)	3.18 (3.40)
Ag	L^A	BF_4^-	8	2283^b	2201	54.60 (54.82)	6.53 (6.44)	4.31 (4.26)
Ag	L^A	BF_4^-	12	2194^b	2204	58.98 (59.31)	7.44 (7.60)	3.49 (3.64)
Ag	L^B	BF_4^-	4	2195^b	2196	58.26 (58.56)	4.99 (4.91)	3.86 (4.02)
Ag	L^B	BF_4^-	8	2195^b	2208	62.04 (62.32)	6.13 (6.23)	3.46 (3.46)
Ag	L^B	BF_4^-	12	2191^b	2194	64.89 (65.15)	7.06 (7.22)	2.89 (3.04)
Ag	L^C	BF_4^-	4	2196^b	2204	54.50 (54.76)	6.94 (7.01)	3.23 (3.36)
Ag	L^C	BF_4^-	8	2191^b	2202	63.60 (63.64)	9.06 (9.13)	2.45 (2.39)
Ag	L^C	BF_4^-	12	2185^b	2189	68.05 (68.55)	10.15 (10.30)	2.01 (1.86)
Ag	L^A	NO_3^-	8	2182^b	2192	56.58 (56.97)	6.82 (6.69)	6.62 (6.64)
Ag	L^A	NO_3^-	12	2183^b	2299	61.10 (61.28)	7.83 (7.85)	5.74 (5.64)
Ag	L^B	NO_3^-	4	2181^b	2190	60.41 (60.72)	5.11 (5.10)	6.11 (6.25)
Ag	L^B	NO_3^-	8	2181^b	2188	64.69 (64.28)	6.40 (6.42)	5.25 (5.36)
Ag	L^B	NO_3^-	12	2181^b	2193	66.62 (66.95)	7.27 (7.42)	4.49 (4.69)
Ag	L^C	NO_3^-	4	2185^b	2194	56.50 (56.43)	7.26 (7.23)	5.00 (5.20)
Ag	L^C	NO_3^-	8	2185^b	2197	64.99 (65.02)	9.49 (9.33)	3.71 (3.67)
Ag	L^C	NO_3^-	12	2185^b	2199	69.45 (69.70)	10.26 (10.47)	2.98 (2.84)

^{a}Calculated values in parentheses. ^{b}THF.

Table 2 Optical, thermal and thermodynamic data for $[Au(CNR)_2]Y$

R	Y	*n*	Transition[a]	Temperature[b] (T/°C)	ΔH^b/kJ mol^{-1}
L^A	PF_6^-	4	C– – –I	121.4	20.3
L^A	PF_6^-	8	C– – –SmA	108.0	14.4
			SmA– – –I	164.3	5.7
L^A	PF_6^-	12	C– – –SmA	117.3	22.3
			SmA– – –I	186.5	4.7
L^A	BF_4^-	4	C– – –C′	47.5	2.0
			C′– – –SmA	80.5	8.0
			SmA– – –I	108.2	3.1
L^A	BF_4^-	8	C– – –SmA	77.0	8.5
			SmA– – –I	186.7	3.7
L^A	BF_4^-	12	C– – –SmA	39.8	14.3
			SmA– – –I (dec)	198.0[c]	
L^A	NO_3^-	8	C– – –dec	45.6	6.5
L^B	PF_6^-	4	C– – –SmA	220.9	37.3
			SmA– – –I (dec)	226.8	2.0
L^B	PF_6^-	8	C– – –SmA	140.6	13.7
			SmA– – –I (dec)	225[c]	
L^B	PF_6^-	12	C– – –SmA	103.0	8.7
			SmA– – –I (dec)	215[c]	
L^B	BF_4^-	4	C– – –SmA	64.4	1.4
			SmA– – –I (dec)	245.0[c]	
L^B	BF_4^-	8	C– – –SmA	92.7	2.5
			SmA– – –I (dec)	250.0[c]	
L^B	BF_4^-	12	C– – –SmC	60.9	5.1
			SmC– – –SmA	165.0[c]	
			SmA– – –I (dec)	248.0[c]	
L^B	NO_3^-	8	C– – –dec	88.4	12.6
L^C	PF_6^-	4	C– – –I (dec)	140.0 [c]	
L^C	PF_6^-	8	Col_h– – –I	103.4	13.0
L^C	PF_6^-	12	Col_h– – –I	104.9	12.1
L^C	BF_4^-	4	C– – –Col_h	71.0	7.3
			Col_h– – –I (dec)	200.0[c]	
L^C	BF_4^-	8	C– – –Col_h	66.5	0.8
			Col_h– – –I (dec)	187.0[c]	
L^C	BF_4^-	12	C– – –Col_h	10.4	19.3
			Col_h– – –I	154.5	1.6
L^C	NO_3^-	8	C– – –Col_h (dec)	51.2	2.2

[a] C, crystal; Sm, smectic; Col_h, hexagonal columnar; I, isotropic liquid. [b] Data refer to the second DSC cycle starting from the crystal. Temperature data as peak onset. [c] Microscopic data.

known.[36] It is also well established that $[Au(CNR)(NO_3)]$ complexes are thermally unstable.[37] TLC (thin-layer chromatography) of heated samples of the complexes described here reveals free isocyanide ligand, suggesting that the decomposition of these nitrate gold derivatives might occur on intermediates where at least one isocyanide ligand is released. This decoordination of isocyanide should be facilitated by coordination of the nitrate anion. The probable easy formation of $[Au(CNR)(NO_3)]$ neutral complexes as intermediates for the decomposition of our cationic nitrate complexes is also suggested by the observation of a covalent interaction between gold and the O atoms of the nitrate in the X-ray structure of $[Au(CNC_6H_3Me_2\text{-}2,6)_2]NO_3$[31] and by the lower ν_{CN} value for these NO_3^- complexes, compared to the corresponding BF_4^- or PF_6^- complexes. The lower coordinating ability of the later counteranions is supported by the absence of sub-van-der-Waals contacts between the cations and the tetrafluoroborate anions in $[Au(CNC_6H_3Me_2\text{-}2,6)_2]BF_4$.[38]

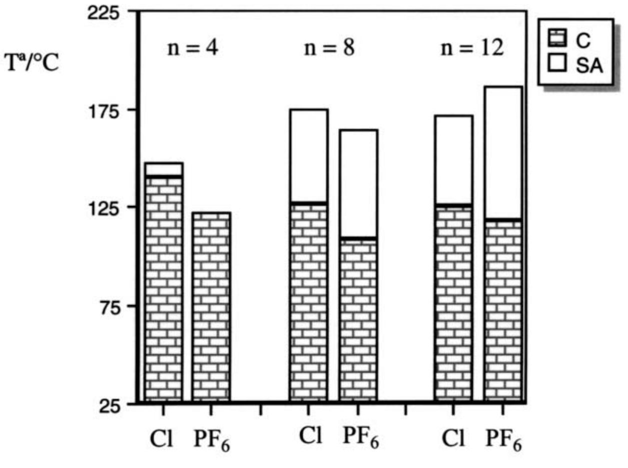

Fig. 1 Comparison of the thermal properties of complexes $[AuCl(CNC_6H_4OC_nH_{2n+1}\text{-}p)]$ reported in ref. 17 and $[Au(CNC_6H_4OC_nH_{2n+1}\text{-}p)_2][PF_6]$.

The influence of the "spherical' counteranions BF_4^- and PF_6^- on the thermal behaviour of these gold(I) derivatives is quite regular. For the three kinds of isocyanide used, the general trend of melting temperatures is $PF_6^- > BF_4^-$, but the variation in clearing temperatures is the inverse, $BF_4^- > PF_6^-$. Both counteranions have different geometrical structures and volumes in the order $BF_4^- < PF_6^-$.[39] This should allow for different cation–cation approximations, which determine mesogenic behaviour. Thus, the molecular arrangement in the solid phase of the PF_6^- derivatives must be more effective than that of BF_4^- compounds, and as a consequence the melting point of PF_6^- complexes would be greater than that of the BF_4^- derivatives, as observed. The same trend has been found in hexafluorophosphate and tetrafluoroborate pyridine silver derivatives.[40] In contrast, the clearing transition is mainly due to the melting of the anion–cation arrangement in the mesophase.[12] Thus, it is not unexpected that the clearing points would be lower for bulkier anions, as experimentally found.

The analogous silver complexes $[Ag(CNR)_2]Y$ [$R = C_6H_4OC_nH_{2n+1}$, $C_6H_4C_6H_4OC_nH_{2n+1}$, $C_6H_2(3,4,5\text{-}OC_nH_{2n+1})_3$; $Y = BF_4^-$, PF_6^-, NO_3^-] display liquid crystal behaviour and their thermal properties are summarized in Table 3. Again,

Table 3 Optical, thermal and thermodynamic data for $[Ag(CNR)_2]Y$

R	Y	n	Transition[a]	Temperature[b] (T/°C)	ΔH[b]/ kJ mol^{-1}
L^A	BF_4^-	8	C– – –SmC	58.8	22.2
			SmC– – –SmA	86.0[c]	
			SmA– – –I	152.1	5.1
L^A	BF_4^-	12	C– – –SmC	40.9	38.3[d]
			SmC– – –SmA	46.7	
			SmA– – –I(dec)	160.0[c]	
L^A	NO_3^-	8	C– – –SmC	42.1	15.5[d]
			SmC– – –SmA	55.0	
			SmA– – –I(dec)	110.0[c]	
L^A	NO_3^-	12	C– – –SmC	42.8	40.2[d]
			SmC– – –SmA	47.5	
			SmA– – –I(dec)	110.0[c]	
L^B	BF_4^-	4	C– – –SmA	71.9	9.6
			SmA– – –I (dec)	240.0[c]	
L^B	BF_4^-	8	C– – –C′	64.7	0.9
			C– – –SmC	80.6	11.8
			SmC– – –SmA	190.0[c]	
			SmA– – –I (dec)	230.0[c]	
L^B	BF_4^-	12	C– – –SmC	58.3	24.9
			SmC– – –SmA	200.0[c]	
			SmA– – –I (dec)	245.0[c]	
L^B	NO_3^-	4	C– – –C′	57.6	3.8
			C′– – –SmA	74.8	19.4
			SmA– – –I (dec)	150.0[c]	
L^B	NO_3^-	8	C– – –SmC	62.5	17.8
			SmC– – –SmA	125.0[c]	
			SmA– – –I (dec)	165.0[c]	
L^B	NO_3^-	12	C– – –SmC	56.5	40.1
			SmC– – –SmA	138.0[c]	
			SmA– – –I (dec)	168.0[c]	
L^C	BF_4^-	4	C– – –Col_h	38.1	13.0
			Col_h– – –I (dec)	196.0[c]	
L^C	BF_4^-	8	C– – –Col_h	34.8	12.3
			Col_h– – –I (dec)	170.0[c]	
L^C	BF_4^-	12	C– – –C′	31.1	31.7
			C– – –Col_h	44.2	61.0
			Col_h– – –I (dec)	144.0[c]	
L^C	NO_3^-	4	C– – –Col_h	87.5	29.7
			Col_h– – –I (dec)	124.0[c]	
L^C	NO_3^-	8	C– – –Col_h	30.9	9.9
			Col_h– – –I (dec)	120.0[c]	
L^C	NO_3^-	12	C– – –C′	20.7	13.8
			C– – –Col_h	40.9	42.5
			Col_h– – –I(dec)	113.0[c]	

[a] C, crystal; Sm, smectic; Col_h, hexagonal columnar; I, isotropic liquid. [b] Data refer to the second DSC cycle starting from the crystal. Temperature data as peak onset. [c] Microscopic data. [d] Combined enthalpies.

although the free phenyl and 3,4,5-trialkoxyphenyl isocyanides are not liquid crystals, all their silver derivatives prepared are mesomorphic. Only the butoxybiphenyl complexes do not show liquid crystal behaviour.

It is interesting to compare the thermal properties of the gold and silver complexes in order to try to understand the influence of the metal atom on the liquid crystal behaviour in these kinds of systems. In addition to the different stabilities of the nitrates, already discussed, the main difference observed is that the silver complexes show an enhancement of smectic C phases in respect to the corresponding gold complexes. Rationalizing this difference is not a simple matter. However, in the silver derivatives, like for the gold complexes discussed above, some covalent donor interaction from the O or F atoms of the anions to the silver centre should be expected. Silver(I) is a harder acid than gold(I), and coordination numbers higher than 2 are more frequent for silver(I) than for gold(I), due to the relativistic stabilization of the 6s and $6p_{1/2}$ orbitals in gold.[41] This might result in a partially covalent interaction with the corresponding counteranions, not involving ligand displacement, which is stronger for silver(I) than for gold(I). This covalent interaction might be more effective in the molecular ordering than a purely ionic interaction, thus leading to the formation of more ordered mesophases, as observed.

X-Ray studies

The X-ray patterns of the mesophases of compounds $\{Ag[CNC_6H_2(3,4,5\text{-}OC_{12}H_{25})_3]_2\}BF_4$ and $\{Au[CNC_6H_2(3,4,5\text{-}OC_{12}H_{25})_3]_2\}BF_4$ are similar, as expected from compounds with very analogous molecular structures, the only difference being the nature of the metal. The silver complex yields numerous reflections with a reciprocal spacing ratio of $1:\sqrt{3}:\sqrt{4}:\sqrt{v7}:\sqrt{13}:\sqrt{16}$, consistent with a well-developed two-dimensional hexagonal lattice. The high number of maxima observed must be due to the presence of the heavy metal centre, which is known to increase the structure factor at large angles and reinforce the scattered intensity over the whole angular range.[42] For the gold derivative, the X-ray measurements indicate that this compound is mesomorphic at room temperature. The reciprocal spacing ratio of the small-angle reflections is $1:\sqrt{3}:\sqrt{4}:\sqrt{7}$. The hexagonal lattice constant is 36.2 Å for the silver compound at 50 °C, and 35.3 Å for the gold species at room temperature. In the diffraction patterns of both compounds, the presence of only a diffuse halo at 4.5 Å in the large-angle regions indicates that, as in the rest of the compounds, there is no periodicity along the columnar axis. For these two compounds the data are consistent with two molecules occupying a column slice of 4–4.5 Å, which does not necessarily imply that there are discrete discs formed by two molecules. However, because of the linear coordination of the Ag(I) and Au(I) atoms, in this case it is probable that neighbouring molecules tend to stack rotated by an angle of 90°, so that the hydrocarbon chains fill efficiently the peripheral space around the columnar core.

Experimental section

Materials and techniques. $[AuCl(tht)]$,[43] $[Au(tht)_2]ClO_4$,[43] and isocyanides CNR ($R = C_6H_4OC_nH_{2n+1}$,[17] $C_6H_4C_6H_4OC_nH_{2n+1}$,[16] $C_6H_2(3,4,5\text{-}OC_nH_{2n+1})_3$,[20] were prepared by literature methods. Techniques were as in a previous paper.[27]

Preparation of the compounds. Only representative examples are described as the syntheses were similar for the rest of the complexes.

Preparation of $[Au(CNR)_2]BF_4$ ($R = C_6H_4OC_nH_{2n+1}$, $C_6H_4C_6H_4OC_nH_{2n+1}$, $C_6H_2(3,4,5\text{-}OC_nH_{2n+1})_3$). To a solution of $[Au(NCCH_3)_2]BF_4$, prepared by reaction of [AuCl(tht)] (0.31 mmol) with $AgBF_4$ (0.31 mmol) in 20 mL of acetonitrile for 15 min and subsequent filtration of the AgCl generated, was added the corresponding isocyanide in 10 mL of acetonitrile. After the solution had been stirred for 30 min the solvent was removed under reduced pressure and the residue was extracted with dichloromethane (20 mL). The solvent was removed to obtain a white solid which was washed with diethyl ether (61–70% yield).

Preparation of $[Au(CNR)_2]PF_6$ [$R = C_6H_4OC_nH_{2n+1}$, $C_6H_4C_6H_4OC_nH_{2n+1}$, $C_6H_2(3,4,5\text{-}OC_nH_{2n+1})_3$]. To a solution of $[Au(tht)_2]ClO_4$, (0.21 mmol) in 30 mL of acetone, was added 2 equivalents of the corresponding isocyanide in acetone (10 mL) and solid KPF_6 (2.12 mmol). After the solution had been stirred for 30 min the solvent was removed under reduced pressure and the residue was extracted with dichloromethane (20 mL). The solvent was removed to obtain a white solid which was recrystallised from tetrahydrofuran/acetonitrile (42–85% yield).

Preparation of $[Au(CNR)_2]NO_3$ ($R = C_6H_4OC_8H_{17}$, C_6H_4-$C_6H_4OC_8H_{17}$, $C_6H_2(3,4,5\text{-}OC_8H_{17})_3$). The method followed was the same as above but using KNO_3 instead of KPF_6 (45–56% yield).

Preparation of $[Ag(CNR)_2]Y$ ($Y = BF_4^-$, NO_3^-; $R = C_6H_4$-OC_nH_{2n+1}, $C_6H_4C_6H_4OC_nH_{2n+1}$, $C_6H_2(3,4,5\text{-}OC_nH_{2n+1})_3$). To a suspension of AgY ($Y = BF_4^-$, NO_3^-) (0.29 mmol) in 30 mL of tetrahydrofuran, was added the corresponding isocyanide (0.62 mmol) in tetrahydrofuran (10 mL). After the mixture had been stirred for 4 h, the resulting solution was filtered. The volume was reduced to 10 mL and diethyl ether was added to obtain the product as a white solid (51–80% yield).

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