Mesomorphic Mixtures of Metal Isocyanide Complexes, Including Smectic C Mesophases at Room Temperature and Liquid Crystalline "Molecular Alloys"

Beatriz Ballesteros, Silverio Coco, and Pablo Espinet*

Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, E-47005 Valladolid, Spain

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The thermotropic behavior and phase diagrams of binary mixtures of copper and gold complexes of the type [MX(CNR)] (X = anionic ligand, R = *p*-alkoxyaryl group) have been studied. The systems examined are mixtures of the pairs of complexes such that new compounds cannot be formed in the mixture by ligand rearrangement. These include pairs differing in just one structural parameter, where rearrangements would not give rise to new complexes: (i) complexes $[AuCl(C{\equiv}NC_6H_4C_6H_4OC_nH_{2n+1})]$ changing the alkoxy length ($n = 4$ and $n = 12$); (ii) complexes $[AuCl(C{\equiv}N(C_6H_4)_mOC_{12}H_{25})]$ with different numbers of aromatic rings ($m = 1$ and $m = 2$); and (iii) complexes differing in the metal, namely the derivative $[CuCl(C{\equiv}NC_6H_4OC_{12}H_{25})]$ (which is not liquid crystal) and the mesomorphic $[AuCl(C{\equiv}NC_6H_4C_6H_4OC_nH_{2n+1})]$; also (iv) complexes $[Au(C_6F_4OC_{10}H_{21})(C{\equiv}NC_6H_4C_6H_4OC_6H_{13})]$ and $[Au(C_6F_4OC_6H_{13})(C{\equiv}NC_6H_4C_6H_4OC_{10}H_{21})]$, in which a study proves that rearrangement does not occur. All the mixtures studied display liquid crystal behavior with improved properties with respect to the pure components. Smectic C mesophases from room temperature to ca. 200 °C have been obtained. Upon cooling and crystallization, segregation occurs and separate nets of the starting complexes are observed, except for mixture (iv), which gives a solid solution.

Introduction

Liquid crystals are a growing area in materials research due to the continuing interest in special materials for displays.[1,2] Applications for liquid crystals are very demanding in temperature range, adequate response to an electric field, stability, viscosity, etc. Generally, the desired properties do not occur in a single liquid crystal, and consequently all the industrial devices use multicomponent liquid crystals.[1] In the younger field of metal-containing liquid crystals (that is, materials based on metal salts and coordination complexes),[3−6] the study of mixtures is limited to binary alkaline salt systems of carboxylic acids,[7] mixtures of copper and rhodium alkanoates,[8] mixtures of *n*-alkanoates and perfluoro-*n*-alkanoates of dimolybdenum,[9] mixtures of lead(II) alkanoates and *n*-alkanoic acids,[10] binary mixtures of copper soaps with hydrocarbons,[11] and mixtures of lanthanide(III) dodecanoates.[12] Perhaps it is the fact that a mixture of several metal-complexes often brings about ligand scrambling in the molten phase, producing complex mixtures hard to study, that has discouraged this type of work.

We have chosen a simple approach to carry out studies of thermotropic behavior and phase diagrams of binary mixtures of copper and gold complexes of type [MX(CNR)] (X = anionic ligand, R = *p*-alkoxyaryl group). The selection of complexes (Figure 1) follows from our previous studies, which established that the coordinatively simple molecules $[MX(C{\equiv}NR)](M = Au^I, Cu^I)$ display, as a group, a rich mesopolymorphism.[13−17] In this work the selection of complexes has been made by mixing, in each case, two complexes that differ only in one structural parameter (X, R, or M), to avoid the problems derived from ligand scrambling. As an excep-

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* To whom correspondence should be addressed. E-mail: espinet@qi.uva.es.

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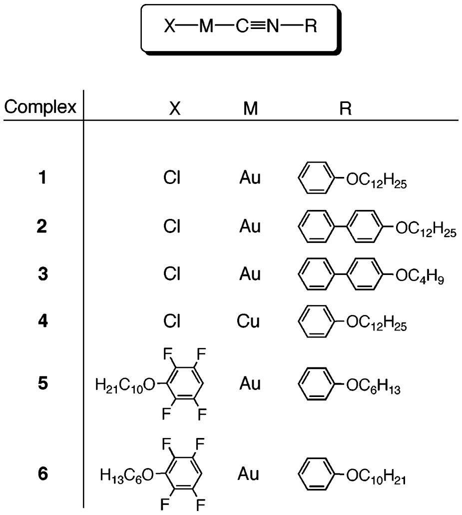

Figure 1. Copper and gold complexes of this study.

tion, in one of the mixtures the two complexes differ in two structural parameters (X and R), but it could be demonstrated that, for that precise case, there was no ligand scrambling. All the mixtures studied display liquid crystal behavior, and improved properties with respect to their pure components.

Experimental Section

Literature methods were used to prepare [AuCl(C≡NC$_6$H$_4$C$_6$H$_4$OC$_n$H$_{2n+1}$)] ($n = 4$, 12),[13] and [AuCl(C≡NC$_6$H$_4$OC$_{12}$H$_{25}$)].[14] [Au(C$_6$F$_4$OC$_{10}$H$_{21}$)(C≡NC$_6$H$_4$C$_6$H$_4$OC$_6$H$_{13}$)] and [Au(C$_6$F$_4$OC$_6$H$_{13}$)(C≡NC$_6$H$_4$C$_6$H$_4$OC$_{10}$H$_{21}$)] were prepared similarly to analogous tetrafluorophenylgold isocyanide derivatives described before.[16] Optical characterization was performed using a Leica DMRB microscope equipped with a Mettler FP82HT hot stage and a Mettler FP90 central processor (temperature resolution 0.1 °C), at a heating rate of 10 °C min^{-1}. For differential scanning calorimetry (DSC), a Perkin-Elmer DSC7 instrument calibrated with water and indium was used; the scanning rate was 10 °C min^{-1}, the samples were sealed in aluminum capsules in the air, and the holder atmosphere was dry nitrogen (calorimetric precision better than ±0.1%; temperature precision ±0.1 °C). Although the precision in the temperature determination is high, the complex manipulation (weighing, mixing, and heating of the samples) and the effect of the heating rate in viscous materials, makes it advisable to give the transition temperatures in this paper an allowance of ±1 °C. X-ray diffraction experiments on polycrystalline samples were carried out on a Phillips PW1710 diffractometer (with Cu Kα radiation, $\lambda = 1.5406$ Å) fitted with a PW1820 goniometer.

Preparation of [CuCl(CNC$_6$H$_4$OC$_{12}$H$_{25}$)]. The procedure to prepare [CuCl(CNC$_6$H$_4$OC$_{12}$H$_{25}$)] is similar to that reported for a copper biphenylisocyanide derivative.[17] To a suspension of CuCl (0.5 mmol) in dichloromethane (40 mL), under nitrogen atmosphere, was added a slight excess of CNC$_6$H$_4$OC$_{10}$H$_{21}$ (0.56 mmol). After 1 h stirring, the resulting solution was filtered in air, and hexane (10 mL) was added. The solution was concentrated and the compound crystallized as a white solid. Yield 83%. mp = 117 °C. IR (KBr) ν(C≡N)/cm^{-1}: 2149. ^{1}H NMR (CDCl$_3$): δA 7.35, δB 6.89 (aromatic proton, AA′BB′ spin system, $J_{A,B} + J_{A,B'} = 8.8$ Ar−H), 3.96 (t, 2H, CH$_2$O), 1.8−0.85 (m, 23 H, alkyl chains). Anal. Calcd. for C$_{17}$H$_{25}$ClCuNO: C, 56.97; H, 7.03; N, 3.91. Found: C, 57.18; H, 6.92; N, 4.01.

Results and Discussion

The binary mixtures of pure compounds were prepared by dissolving the corresponding weights of the two compounds together in CH$_2$Cl$_2$ at ambient temperature and subsequently eliminating solvent in a vacuum. The mesomorphic properties of these systems have been investigated by DSC and by hot-stage polarized optical microscopy, and the phase diagrams have been constructed using these data. The temperatures given for two-phases regions correspond to the beginning and the end of the transition. The textures observed in the mixtures studied are similar to those of the pure isocyanide metal complexes. The SmA mesophases present the typical oil steles and homeotropic textures reorganizing to the fan-shaped texture at temperatures close to the clearing point, and the focal-conic texture on cooling from the isotropic liquid (Figure 2). The SmC mesophases show the schlieren texture on cooling from the SmA mesophase with homeotropic texture (Figure 3).[18,19]

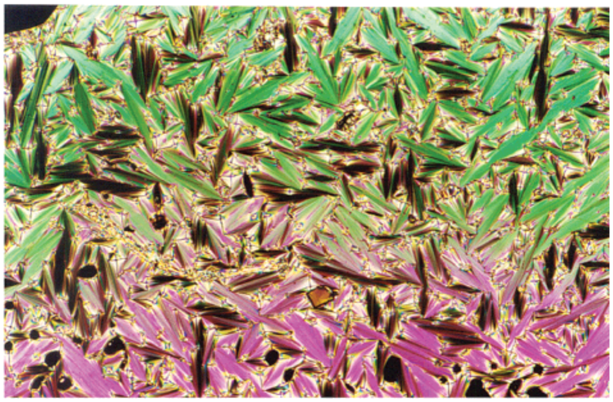

Figure 2. Polarized optical microscopic fan-shaped texture (×100) observed for the mixture 30% [AuCl(CNC$_6$H$_4$OC$_{12}$H$_{25}$)] (**1**) + 70% [CuCl(CNC$_6$H$_4$OC$_{12}$H$_{25}$)] (**4**) obtained on cooling from the isotropic liquid at 123 °C.

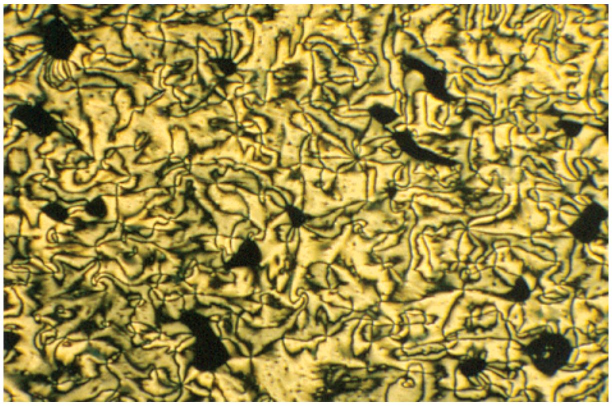

Figure 3. Polarized optical microscopic schlieren texture (×100) observed for the mixture 90% [AuCl(CNC$_6$H$_4$C$_6$H$_4$OC$_{12}$H$_{25}$)] (**2**)/10% [AuCl(CNC$_6$H$_4$C$_6$H$_4$OC$_4$H$_9$)] (**3**) obtained on cooling from a homeotropic SmA at 125 °C.

System [AuCl(C≡NC$_6$H$_4$OC$_{12}$H$_{25}$)] (1) + [AuCl(C≡NC$_6$H$_4$C$_6$H$_4$OC$_{12}$H$_{25}$)] (2). The mixture of the mesogenic compounds [AuCl(C≡NC$_6$H$_4$OC$_{12}$H$_{25}$)] and [AuCl(C≡NC$_6$H$_4$C$_6$H$_4$OC$_{12}$H$_{25}$)], which differ only in the number of phenyl rings, give mesomorphic behavior in all the range composition (Table 1). The corresponding phase diagram is shown in Figure 4.

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Table 1. Optical, Thermal, and Thermodynamic Data of Mixtures $[AuClC{\equiv}NC_6H_4OC_{12}H_{25})]$ (1) + $[AuCl(C{\equiv}NC_6H_4C_6H_4OC_{12}H_{25})]$ (2)

composition mole % **2**	transition[a]	temperature[b] (°C)	ΔH^b (kJ/mol)
0	C→SmA	125.0	32.5
	SmA→I	171 (dec)	8.0
10	C→C+SmA	81.6	25.3
	C+SmA→SmA	121.2	5.4
	SmA→I	173.7 (dec)	
25	C→C+SmA	80.0	26.5[d]
	C+SmA→SmA	115.4	
	SmA→I	220[c] (dec)	
35	C→C+SmA	81.9	24.5[d]
	C+SmA→SmA	111.5	
	SmA→I	225[c] (dec)	
50	C→C′	79.6	−2.6
	C′→C′+SmA	82.7	26.5[d]
	C′+SmA→SmA	101.4	
	SmA→I	230[c] (dec)	
65	C→C+SmA	80.7	25.5[d]
	C+SmA→SmA	101.3	
	SmA→I	250[c] (dec)	
75	C→C+SmA	84.1	17.3[d]
	C+SmA→SmA	121.8	
	SmA→I	255[c] (dec)	
90	C→C′	57.2	1.5
	C′→C′+SmA	88.7	21.0[d]
	C′+SmA→SmA	126.2	
	SmA→I	285[c] (dec)	
100	C→SmC	120.8	25.5
	SmC→SmA	140	
	SmA→I	300[c] (dec)	

[a] C, C′ solid phases (whether mixture of solids, or solid solution; see text and figures for details); Sm, smectic; I, isotropic liquid. [b] Data referred to the second DSC cycle starting from the crystal. [c] Microscopic data. dec, decomposition. [d] Combined enthalpies.

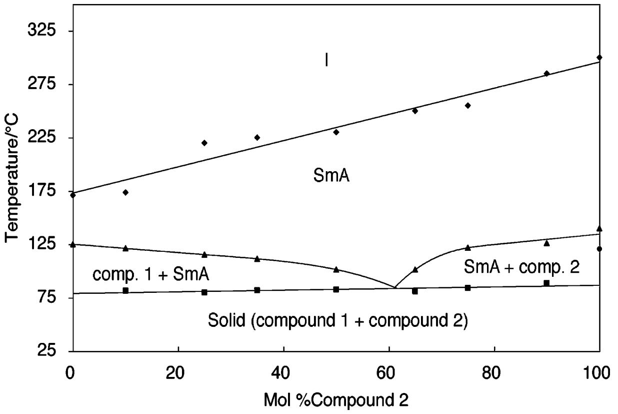

Figure 4. Phase diagram of the system $[AuCl(C{\equiv}NC_6H_4OC_{12}H_{25})]$ (**1**) + $[AuCl(C{\equiv}NC_6H_4C_6H_4OC_{12}H_{25})]$ (**2**).

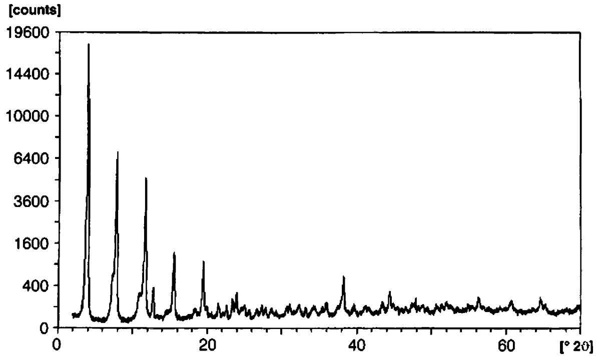

Figure 5. Diffraction pattern of polycrystalline $[AuCl(C{\equiv}NC_6H_4OC_{12}H_{25})]$ (**1**).

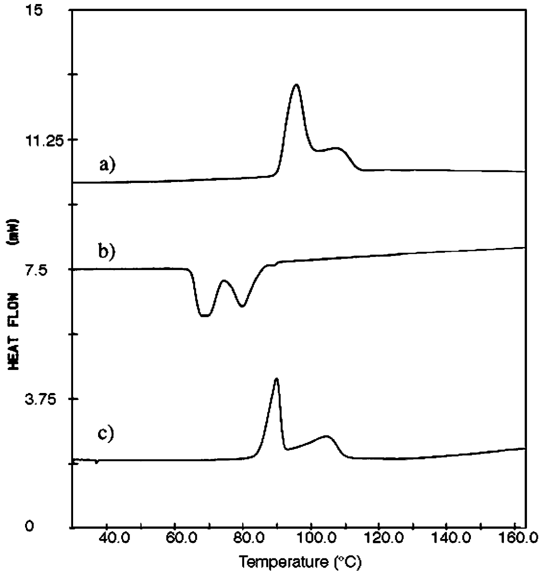

Figure 6. DSC scans of 75%(**1**)/35%(**2**): (a) first heating, (b) first cooling, and (c) second heating.

The pure compound with one aryl ring, **1**, shows a smectic A (SmA) mesophase, whereas the biphenyl derivative displays a smectic C (SmC) and SmA mesophase.[13] The single crystal X-ray diffraction molecular structures of [AuCl(CNAryl)] complexes, and their supramolecular arrangement, have been systematically studied. The molecular structures are all linear and are connected by Au···Au aurophilic interactions in an antiparallel arrangement of contiguous molecules. This gives rise to pairs (in the case of aryl = mesityl) and to zigzag chain arrangements of gold atoms, with the chains producing a kind of bilayer arrangement.[20] The X-ray powder diffraction pattern of the pure solid **1** shows a series of intense reflections, which are successive orders of diffraction from a layer structure, and can be indexed as (00*l*) reflections with $l \leq 7$ (Figure 5).

The interlayer spacing measured from the diffraction pattern (22.5 Å) agrees well with the molecular length calculated with molecular models (24.7 Å). The pure biaryl component **2** shows a somewhat more complex powder diffraction pattern with three series of intense reflections at spacings 32.8, 24.6, and 9.9 Å, again suggesting some layered structure for a molecule which has a calculated length of 31.5 Å. The solid obtained from cooling a molten mixture with 50% concentration of **1** and **2** shows clearly the sum of the two patterns just described, proving that, whatever its origin, the solid is a mixture of both pure components. When the mixed solid is heated, a partial melting takes place and a mixture of crystals and a fluid phase is observed. Subsequent heating produces only a SmA mesophase, and finally the sample becomes an isotropic liquid. In agreement with the optical observation, the melting point appears in the DSC scans as two endothermic peaks revealing a simple eutectic system, the one at lower temperature corresponding to the partial melting (eutectic temperature), and the second one corresponding to the transition from the two-phases region to the SmA phase (Figure 6). In this system the transition to the isotropic liquid occurs with decomposition. For this

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Table 2. Optical, Thermal, and Thermodynamic Data of Mixtures [AuCl($C_6H_4C_6H_4OC_{12}H_{25}$)] (2) + [AuCl($CNC_6H_4C_6H_4OC_4H_9$)] (3)

composition mole % **2**	transition[a]	temperature[b] (°C)	Δ*H*[b] (kJ/mol)
0	C→SmA	169.2	21.2
	SmA→N	266.9	0.4
	N→I	269 (dec)[c]	
5	C→C′+SmA	94.3	1.3
	C′+SmA→SmA	164.4	13.6
	SmA→I	270 (dec)[c]	
10	C→C′+SmA	94.5	2.4
	C′+SmA→SmA	162.5	10.5
	SmA→I	270 (dec)[c]	
30	C→ C′+SmA	94.5	11.9[d]
	C′+SmA→SmA	127.8	
	SmA→I	270 (dec)[c]	
35	C→C′+SmA	95.9	12.2[d]
	C′+SmA→SmA	120.7	
	SmA→I	270 (dec)[c]	
40	C→C′+SmA	87.6	12.4[d]
	C′+SmA→SmA	111.0	
	SmA→I	280 (dec)[c]	
50	C→C′+SmA	91.5	13.7[d]
	C′+SmA→SmA	97.0	
	SmA→I	280 (dec)[c]	
60	C→C′+SmA	89.0	13.0[d]
	C′+SmA→SmA	102	
	SmA→I	270 (dec)[c]	
70	C→C′+SmC	85.5	13.9[d]
	C′+SmC→SmC	113.0	
	SmC→SmA	116[c]	
	SmA→I	275 (dec)[c]	
80	C→C′+SmC	91.1	15.0
	C′+SmC→SmC	119.7	2.8
	SmC→SmA	123.0[c]	
	SmA→I	270 (dec)[c]	
90	C→C′	67.0	0.9
	C′→C″+SmC	94.3	19.8[d]
	C″+SmC→SmC	122.1	
	SmC→SmA	140.0[c]	
	SmA→I	280 (dec)[c]	
100	C→SmC	120.8	25.5
	SmC→SmA	140.0[c]	
	SmA→I	300 (dec)[c]	

[a] C, C′, C″ solid phases (whether mixture of solids or solid solution; see text and figures for details); N, nematic; Sm, smectic; I, isotropic liquid. [b] Data referred to the second DSC cycle starting from the crystal. [c] Microscopic data. dec, decomposition. [d] Combined enthalpies.

reason, the significance and accuracy of the clearing temperatures are low (a straight line has been interpolated from the wavy distribution of experimental points in Figure 4). In summary, the mixture of the phenyl and biphenylisocyanide gold(I) complexes, with respect to the pure components, produce an enhancement of the range of the SmA mesophase mainly at the eutectic composition.

System [AuCl($C{\equiv}NC_6H_4C_6H_4OC_{12}H_{25}$)] (2) + [AuCl($C{\equiv}NC_6H_4C_6H_4OC_4H_9$)] (3). The mixtures of the mesogenic compounds [AuCl($C{\equiv}NC_6H_4C_6H_4OC_4H_9$)] and [AuCl($C{\equiv}NC_6H_4C_6H_4OC_{12}H_{25}$)], which differ only in the length of their alkoxy chains, give mesomorphic behavior for all of the mole ratio range of the components (Table 2), and their phase diagram is shown in Figure 7.

Both pure components display liquid crystal behavior. The butyloxy derivative shows a SmA and a nematic (N) mesophase, and the dodecyloxy compound shows a SmC and a SmA mesophase. Irrespective of the composition, the mixtures display SmA mesophases, and, for concentrations greater than 70% in [AuCl($C{\equiv}NC_6H_4C_6H_4OC_{12}H_{25}$)], the system shows also SmC mesophases. Some of the binary mixtures show crystal-to-crystal transitions before melting. Generally, mesogenic binary mixtures show clearing temperatures slightly lower than those of their main component. In this system, however, the clearing temperatures for the mixtures are similar to or even somewhat higher than those of the pure components and show only small variations with changes in concentration. The melting points for the mixtures are lower than those of the pure components, expanding the range of mesogenic behavior of the mixtures compared to those of the parent compounds. When the samples are heated to the melting temperature, the coexistence of both solid phase and mesophase is observed. Consistently, their DCS scans show a peak corresponding to the eutectic temperature, and a broad transition related to the incongruent melting behavior of the system.

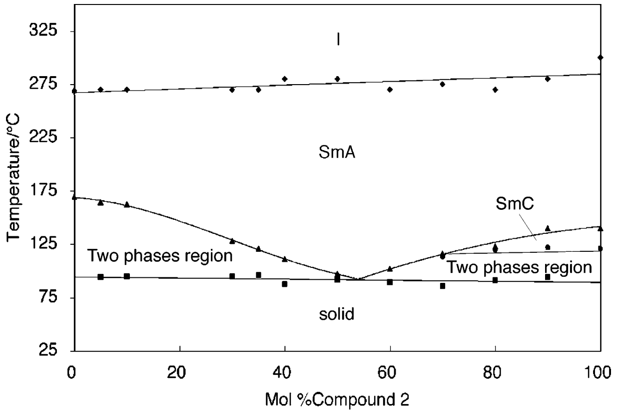

Figure 7. Phase diagram of the system [AuCl($C{\equiv}NC_6H_4C_6H_4OC_{12}H_{25}$)] (**2**) + [AuCl($C{\equiv}NC_6H_4C_6H_4OC_4H_9$)] (**3**).

For concentrations of **2** above 70%, a SmC mesophase appears between the two-phases region and the SmA phase. The X-ray powder diffraction pattern of the pure butoxy component **3** does not show a layer-type structure (Figure 8b). Comparing the X-ray pattern observed for a solid obtained from a melt of an 8:2 mixture of **2**/**3** with those of the individual components, it is clear that, in the diffractogram of the mixture can be recognized the pattern of the [AuCl($C{\equiv}NC_6H_4C_6H_4OC_{12}H_{25}$)] component, but several new broad signals, which are not shown by the pure components, are also observed (Figure 8). The width of the peaks indicates the presence of a crystalline but rather disordered solid. These observations are consistent with a mixture of crystalline [AuCl($C{\equiv}NC_6H_4C_6H_4OC_{12}H_{25}$)] and a random solid solution of the two original species.

Thus, the behavior of this system in the solid state is complex, showing partial immiscibility, but the mixture of two compounds shows a phase diagram for a eutectic system. Moreover, compared to the parent pure components, the mixture gives rise to a wider range of SmA mesophases with lower melting points, and to SmC mesophases for mixtures richer in the dodecyloxy component **2**.

System [AuCl($C{\equiv}NC_6H_4OC_{12}H_{25}$)] (1) + [CuCl($C{\equiv}NC_6H_4OC_{12}H_{25}$)] (4). Mixtures of the nonmesogenic compound [CuCl($C{\equiv}NC_6H_4OC_{12}H_{25}$)] with the mesogenic derivative [AuCl($C{\equiv}NC_6H_4OC_{12}H_{25}$)] show SmA phases above 30% mol of the gold component (Table 3).

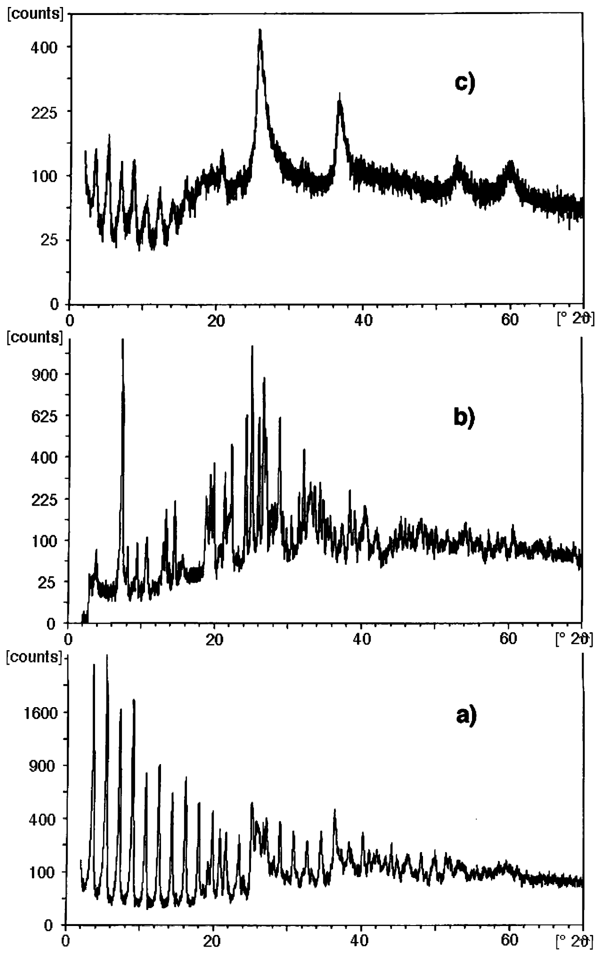

Figure 8. Diffraction patterns of: (a) polycrystalline [AuCl-(C≡$NC_6H_4C_6H_4OC_{12}H_{25}$)] (**2**), (b) polycrystalline [AuCl(C≡N-$C_6H_4C_6H_4OC_4H_9$)] (**3**), and (c) solid 80% (**2**)/20% (**3**).

Their phase diagram is shown in Figure 9. When samples with concentrations lower than 30% mol gold component are heated to the melting temperature, the coexistence of solid phase and liquid is observed. Accordingly, their DCS scans show one peak corresponding to the eutectic temperature and a broad peak for the transition from the two-phases region to the isotropic liquid. These mixtures do not display mesomorphic behavior. For concentration above 30% mol of the gold component, a similar behavior is observed initially, displaying incongruent melting points, but subsequent heating produces a SmA mesophase, and finally the sample becomes an isotropic liquid. The X-ray diffraction pattern of the pure copper component **D** shows a series of intense reflections for a layer structure, indexed as (00*l*) reflections with $k \leq 6$. The interlayer spacing corresponding to the layer measured from the diffraction pattern (27.2 Å) is slightly larger than the molecular length calculated with molecular models (24.9 Å). Comparing the solid X-ray pattern observed for a 7:3 mixture of **1**/**4** with those obtained from the individual components, the diffractogram of the binary system shows the mixture of both pure products.

Table 3. Optical, Thermal, and Thermodynamic Data of Mixture [AuCl($CNC_6H_4OC_{12}H_{25}$)] (1) + [CuCl($CNC_6H_4OC_{12}H_{25}$)] (4)

composition mole % **1**	transition[a]	temperature[b] (°C)	Δ*H*[b] (kJ/mol)
0	C→I	117.0[c]	
10	C→C+I	101.2	22.1[d]
	C+I→I	111.0	
15	C→I	101.5	22.26
20	C→C+I	99.7	18.7[d]
	C+I→I	109.9	
30	C→C+I	102.1	16.4[d]
	C+I→SmA	121.8	0.3
	SmA→I	130.6	
50	C→C+I	94.5	20.2[d]
	C+I→SmA	125.2	0.3
	SmA→I	150.0[c]	
60	C→C+I	90.0	19.9[d]
	C′+I→SmA	124.9	1.7
	SmA→I	160[c]	
70	C→C′	87.8	2.4
	C′→C′+I	104.0	22.3[d]
	C+I→SmA	126.2	2.8
	SmA→I	157.6	
90	C→C+I	108.0	24.5[d]
	C+I→SmA	126.9	3.6
	SmA→I	156.5	
100	C→SmA	125.0	25.5
	SmA→I	171.0	8.0

[a] C, C′ solid phases (whether mixture of solids or solid solution; see text and figures for details); Sm, smectic; I, isotropic liquid. [b] Data referred to the second DSC cycle starting from the crystal. [c] Microscopic data. [d] Combined enthalpies.

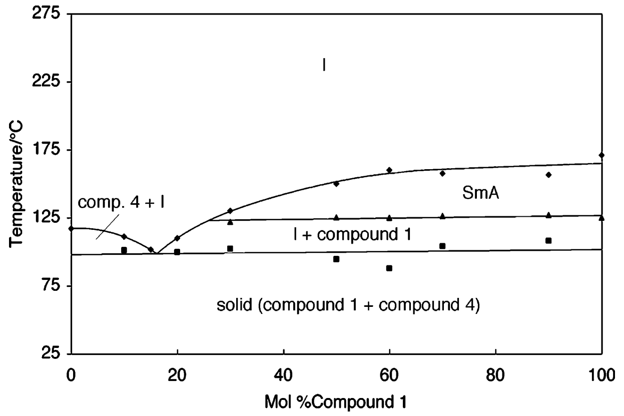

Figure 9. Phase diagram of the system [AuCl(C≡NC_6H_4-$OC_{12}H_{25}$)] (**1**) + [CuCl(C≡$NC_6H_4OC_{12}H_{25}$)] (**4**).

Thus, the mixture of these two compounds, one of which is not liquid crystal, shows mesogenic behavior for a large range of concentrations, and affords a single fluid material with an ordered homogeneous distribution of the two metal complexes. This procedure for producing homogeneous ordered mobile phases of different metal-containing molecules (in this case gold and copper) could be of interest for electronics and for metal deposition. We suggest for this kind of materials the name "liquid crystalline molecular alloys" to distinguish them from heterometallic mesophases based on mesogenic heterometallic molecules, i.e., where there is only one kind of molecule which contains two or more metals in its structure (the latter have been named "mixed M−M′ metallomesogens").[21,22]

System [Au($C_6F_4OC_{10}H_{21}$)(C≡$NC_6H_4C_6H_4OC_6H_{13}$)] (5) + [Au($C_6F_4OC_6H_{13}$) (C≡$NC_6H_4C_6H_4OC_{10}H_{21}$)] (6). In this pair the components differ in the anionic ligand

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(21) Binnemans, K.; Lodewyckx, K.; Donnio, B.; Guillon, D. *Chem. Eur. J.* **2002**, *8*, 1101.

(22) During the revision of this manuscript the denomination "*n*-Alkane Binary Molecular Alloys" has appeared in reference to binary alkane systems with no liquid crystals behavior. Mondieig, D.; Rajabalee, F.; Mativaud, V.; Oonk, H. A. J.; Cuevas-Diarte, M. A. *Chem. Mater.* **2004**, *16*, 786.

Table 4. Optical, Thermal, and Thermodynamic Data of Mixtures $[Au(C_6F_4OC_6H_{13})(CNC_6H_4C_6H_4OC_{10}H_{21})]$ (5) + $[Au(C_6F_4OC_{10}H_{21})(CNC_6H_4C_6H_4OC_6H_{13})]$ (6)

composition mole % **5**	transition[a]	temperature[b] (° C)	ΔH^b (kJ/mol)
0	C→SmC	55.4	5.6
	SmC→SmA	114.0[c]	
	SmA→I	205.3	1.3
10	C→C′	9.9	−9.9
	C′→SmC	39.6	21.5
	SmC→SmA	75.0[c]	
	SmA→I	187.7	5.2
50	C→C′	−8.9	−5.9
	C′→SmC	13.8	4.6
	SmC→SmA	50.0[c]	
	SmA→I	189.1	4.6
90	C→C′	−8.6	−4.9
	C′→C″	12.4	−9.2
	C″→SmC	37.2	20.9
	SmC→SmA	70.0[c]	
	SmA→I	197.1	5.7
100	C→SmC	49.9	5.5
	SmC→SmA	104.0[c]	
	SmA→I	209.3	1.4

[a] C, C′, C″ solid phases (whether mixture of solids or solid solution; see text and figures for details); Sm, smectic; I, isotropic liquid. [b] Data referred to the second DSC cycle starting from the crystal. [c] Microscopic data.

and in the neutral ligand. Differently from the previous pairs, if ligand scrambling occurred it should give rise to a four-component mixture containing $[Au(C_6F_4OC_{10}H_{21})(C{\equiv}NC_6H_4C_6H_4OC_{10}H_{21})]$ and $[Au(C_6F_4OC_6H_{13})(C{\equiv}NC_6H_4C_6H_4OC_6H_{13})]$, in addition to the initial pair. As **5** and **6** are hardly distinguishable by ^1H or ^{19}F NMR spectroscopy, the possible ligand scrambling was checked on the model complexes $[Au(C_6F_4Br\text{-}o)(C{\equiv}NBu^t)]$ and $[Au(C_6F_4Br\text{-}p)(C{\equiv}NC_6H_4C_6H_4OC_{10}H_{21})]$,[15] which are easy to distinguish. No exchange was observed in a solution of a mixture of these complexes in $CDCl_3$ solution heated at 55 °C for 1 h and then kept at 30 °C for 1 month. This example shows that these compounds seem to have no tendency to ligand rearrangement.

The mixtures of **5** and **6**, which differ only in the position of the alkoxy chains, show an interesting behavior (Table 4). Their phase diagram is presented in Figure 10. In contrast to the other systems studied here, the melting point curve of these mixtures displays a minimum at 14 °C for 50% mol composition. The theoretically expected coexistence of solid phase and fluidic phases is not observed under the scanning conditions, and the DCS scans show fairly sharp peaks. These observations are consistent with a solid solution of the original species. The two pure compounds display SmC and SmA mesophases, and these appear in very analogous ranges of temperature. Their mixtures show the same type of mesophases. The clearing temperatures are just slightly lower for the mixtures than for the pure compounds and show only small variations with composition change. In contrast, the melting temperatures are clearly lower than those of pure complexes, leading to room-temperature SmC mesophases, and to a range of mesomorphic behavior noticeably higher than for any of the pure components. In fact, by tuning the mixture, liquid crystal behavior can be obtained from room temperature to ca. 200 °C. The behavior observed fits well with the model that considers that the crystal-to-mesophase transition is associated with disordering of the chains ("melting" of the alkyl chains), whereas the clearing involves disordering the cores. The two components are constituted by the same rigid core ($-C_6F_4-Au-C{\equiv}NC_6H_4C_6H_4-$) and the same pair of alkoxy chains, but the positions of the latter on asymmetric core are interchanged. Although the core-to-core intermolecular interactions, which are responsible for holding the molecules ordered in the mesophase, will not be identical in the mixture and in the pure compounds, they must be very similar, leading to little variation in the clearing temperatures, as observed. On the other hand, the melting points of the mixtures, sensitive to the chains, will show a continuous increase in entropy as a second component is added to a pure compound, reaching a maximum for the 50/50 mixture. Consistently, a descent in the melting temperatures is observed with a minimum for the 50/50 mixture.

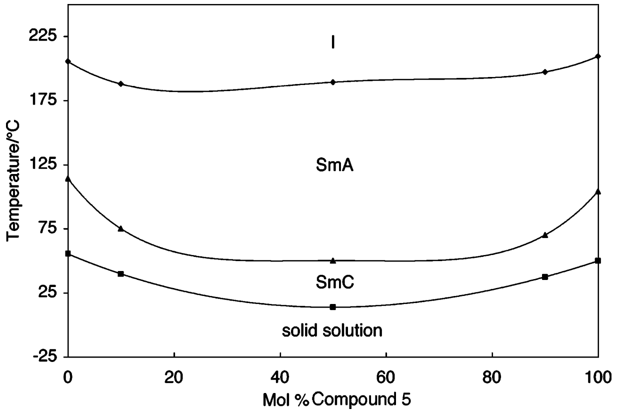

Figure 10. Phase diagram of the system $[Au(C_6F_4OC_{10}H_{21})(C{\equiv}NC_6H_4C_6H_4OC_6H_{13})]$ (**5**) + $[Au(C_6F_4OC_6H_{13})(C{\equiv}NC_6H_4C_6H_4OC_{10}H_{21})]$ (**6**).

In summary, all the binary mixtures of metal isocyanide complexes of the type [MX(CNR)] (X = anionic ligand, R = *p*-alkoxyaryl group) studied display thermotropic liquid crystal behavior, including the mixture of a mesogenic gold and a nonmesogenic copper complex, which provides the first example of mesomorphism in heterometallic mixtures of organometallic complexes. The mixtures show improved mesomorphic properties with respect to the pure components, and SmC mesophases lasting from room temperature to ca. 200 °C have been obtained.

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