Liquid-crystalline Gold–Isonitrile Complexes

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Gold-isonitrile complexes as a new family of metallomesogens are prepared and even non-mesomorphic isonitriles have been found to form liquid crystals when coordinated to an Au^ICI moiety.

Recently liquid crystals incorporating transition metals, socalled metallomesogens, have been receiving much attention in expectation of potential properties due to metals in addition to the intrinsic liquid-crystalline properties of the organic compounds. A large number of metallomesogens containing a variety of metals have already been prepared¹ and some interesting findings in their electronic and magnetic properties have been reported.²

Most metallomesogens consist of a mesomorphic organic part and a metal moiety, however the latter seems simply to act as a substituent in the organic mesogen, although in one case³ non-mesomorphic organic compounds form liquid crystals on coordination to a metal.

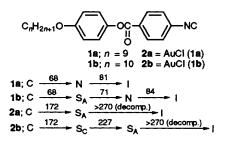
Previously we reported⁴ the first liquid-crystalline isonitrile complexes of Group 10 metals such as platinum and palladium. Isonitriles are well-known to act as good ligands for stabilizing both low- and high-oxidation states of various transition metals. Now, we have extended our work to Group 11 metal isonitrile complexes and found that even nonmesomorphic isonitriles form stable mesophases upon coordination to univalent gold.

Several stable organometallic complexes of Au¹ and Au¹¹¹ are known and we have chosen the former which adopts twocoordinate linear geometry. Initially we prepared gold(i) complexes of the type AuCl(CNR) 2 using mesomorphic isonitriles CNR 1 by ligand exchange with AuCl(SMe₂),⁵ which smoothly proceeded under usual reaction conditions to give complexes 2 in 80–90% yield⁶ [eqn (1)].

A

$$\operatorname{AuCl}(SMe_2) + CNR \to \operatorname{AuCl}(CNR) \tag{1}$$

The complexes thus obtained have been demonstrated to show mesomorphic properties and form smectic A (S_A) and C (S_{C}) phases in a wide temperature range. However, the transition temperatures are very high despite the fact that the molecules have only two aromatic nuclei, and some decomposition of the complexes was observed at or just above the clearing point. In the literature there have already appeared two examples of liquid-crystalline gold complexes, Au^{III}Cl₂. (dithiobenzoates)⁶ and Au^ICl(stilbazole),⁷ which also show very high phase-transition temperatures with decomposition at their clearing points. The behaviour of these gold plexes in phase transitions may be understood on the basis of strong intermolecular interactions as seen in general for gold complexes. The formation of smectic phases but not nematic ones by complexes 2, despite the fact that free isonitriles form N phases, may also suggest somewhat strong interactions among the molecules. We then tried to weaken such interactions by introducing a bulky substituent at a lateral position of the phenyl ring in the isonitrile ligand. Isonitriles 3 which bear an alkoxy group on the phenyl ring were prepared



from the corresponding nitro compounds and their thermal properties have been investigated. None of the isonitriles 3 prepared in this work exhibited any liquid-crystalline proper ties in the free state, e.g. 3a (n = 10, m = 1), mp 102 °C; 3b (n = 10, m = 2), mp 117 °C, whereas their coordination complexes 4 with univalent gold clearly showed mesomorphic properties (Table 1). They form stable N and/or SA phases at a lower temperature than do complexes 2 and no decomposition was observed at the clearing points. Thermal analysis indicated complexes 4 to be stable up to 260 °C. When the terminal alkyl in 4 was decyl (n = 10), the complexes with a lateral alkoxy group (m = 1 or 2) showed enantiotropic S_A phases, while those with a longer lateral group $(m \ge 3)$ showed monotropic N and/or S_A phases. Longer lateral chains seem to suppress S properties resulting in the formation of N phases.8 It should be noted, however, that 4f(m = 6) bearing a very long lateral group still retains liquid-crystalline properties. The preliminary X-ray structural analysis9 of 4a has revealed that the nearest intramolecular Au...Au distance in the crystal is 3.4 Å which suggests the existence of only weak interactions between molecules.¹⁰ This weak intermolecular interaction may be reflected in the rather high melting points of 4 and seems to play an important role for forming mesophases even after melting.

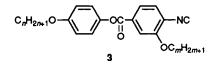
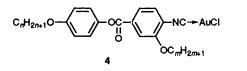


Table 1 Phase transition temperatures (°C) and entropies $[kJ mol^{-1}]^a$ for complexes 4



	n	m	С		SA		N		I
4a	10	1	•	157		190	_		
4b	10	2		[38] 120	•	[5.3] 135	_		
4c	10	3	·	[45] 120	(•	[2.9] 94		99) ^b	
4d	10	4		[36] 120	_	[1.4]	(•	87) ^ø	
4 e	10	5	•	[44] 110	_		(•	[0.7] 81) ^ø	
4f	10	6		[37] 87			(•		
4g	12	2	•	[31] 124		145		[0.8]	
4h	11	2		[49] 117		[4.0] 140			
4i	9	2		[32] 117		[2.6] 119		129 ⁶	
4j	8	2		[32] 119	(•	<u> </u>		[2.1] 127	
.,	0	-		[47]	`	110)		[1.1]	

^{*a*} Measured on the second heating cycle at a rate of 10 °C. ^{*b*} Monotropic transition.

In conclusion, non-mesomorphic isonitriles, on complexation to an Au¹Cl moiety, lead to liquid-crystalline materials in which the Au-Cl group affords an effective contribution to the intermolecular interaction suitable for forming liquid crystals.

Received, 17th February 1994; Com. 4/00980K

Footnote

† All new gold complexes were identified by elemental analyses and IR and ¹H NMR spectra.

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