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Liquid crystals based on palladium orthometallated complexes with amido or dialkyldithiocarbamato ligands†

Laura Díez, Pablo Espinet* and Jesús A. Miguel

Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, 47005 Valladolid, Spain. E-mail: espinet@qi.uva.es

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The dinuclear cyclopalladated compounds $[Pd_2(\mu\text{-}OAc)_2(L^n)_2]$ **2** derived from imines $HL^n = p\text{-}C_nH_{2n+1}OC_6H_4CH{=}NC_6H_4OC_nH_{2n+1}\text{-}p$ **1** (n = 2, 6 or 10) react with NaOH to give dinuclear derivatives $[Pd_2(\mu\text{-}OH)_2(L^n)_2]$ **3**. The reaction of **3** with amines (1 : 1 molar ratio) yields the corresponding hydroxo–amido complexes $[Pd_2(\mu\text{-}NHR)(\mu\text{-}OH)(L^n)_2]$ ($R = C_mH_{2m+1}$ (m = 1, 6, 10, 14 or 18) **4** or $C_6H_4C_{14}H_{29}\text{-}p$ **5**). With excess of amine $[Pd_2(\mu\text{-}NHR)_2(L^n)_2]$ **6** ($R = C_mH_{2m+1}$) are formed. Complexes **4** react with thiols or decanoic acid in 1 : 1 mole ratio to give the corresponding amido–thiolato or amido–carboxylato complexes $[Pd_2(\mu\text{-}SC_jH_{2j+1})(\mu\text{-}NHR)(L^n)_2]$ **7** (j = 4, 10 or 18) or $[Pd_2(\mu\text{-}O_2CC_9H_{19})(\mu\text{-}NHR)(L^n)_2]$ **8**. The mononuclear complexes $[Pd(S_2CNR'_2)(L^n)]$ ($R' = C_2H_5$ **9a** or C_8H_{17} **9b**) are prepared when complexes **3** are treated with dialkylamines in the presence of carbon disulfide. Most of the complexes show liquid crystal behaviour and nematic, smectic A and smectic C phases are found.

Introduction

Many metal-containing liquid crystals (metallomesogens) have been reported in the last years. Recent reviews show that the field is dominated by coordination compounds and there are fewer liquid crystals of the organometallic type.[1] Among the latter, a large family is constituted by dinuclear and mononuclear orthometallated complexes. It was using variations of this versatile family of molecules that our group reported: (i) the first examples of ferroelectric metallomesogens,[2] and the improvement of their properties;[3] (ii) ways to reach an important decrease in melting points and viscosity of these materials;[4] and (iii) the first cholesteric metal-containing liquid crystal.[5] Within this family of complexes, the dinuclear $[Pd(\mu\text{-}X)L^n]_2$ permit one to induce thermotropic changes not only by modifying terminal alkyl or alkoxy chains in L^n (which we have studied for X = halide),[3,6,7] but also by modifying the bridging system (X = others). In this respect we have reported mesomorphic materials containing one or two bridging thiolates.[5,8]

The reactivity of dinuclear compounds $[Pd(\mu\text{-}OH)L^n]_2$ towards protic substrates like amines, thiols, and carboxylic acids bearing alkyl chains can provide a fairly general entry to other dinuclear complexes with double and mixed bridges. We report here the synthesis, structural characterization and thermotropic properties of uncommonly air stable amido–hydroxo, anilido–hydroxo, bis-amido, amido–thiolato, and amido–carboxylato complexes that extend the number of amido complexes and mixed bridges, which are the first examples of metallomesogens with these ligands. Specially remarkable is the thermal stability of those with amido ligands containing β-hydrogens: the number of known dinuclear amido-bridged palladium complexes is limited[9–21] and even fewer possess β-hydrogens,[18,19] because there is a strong tendency for the late transition metal amido complexes to undergo β-hydrogen elimination, usually followed by decomposition.[22]

In addition, based on the reaction of the $[Pd(\mu\text{-}OH)L^n]_2$ with an amine in the presence of carbon disulfide, we describe a way to new mesomorphic mononuclear orthometallated palladium complexes containing *N*,*N*-dialkyldithiocarbamate.

Results and discussion

1 Syntheses and structures

The imines **1** and the acetato-bridged dimeric palladium precursors **2** were prepared and characterized according to the literature procedures.[23,24] Reaction of **2** with NaOH in acetone–water solution led to exchange of the bridging acetato ligands by hydroxo groups, giving **3** in very good yield (*ca.* 95%) (Scheme 1). Their analytical data are consistent with the proposed formulae, and the presence of the μ-OH ligands is supported by a weak IR band at 3606 cm^{-1}. The ^1H NMR spectra reveal that the complexes exist in solution as a 4 : 1 mixture of *trans* and *cis* isomers, depending on the arrangement of the two imine moieties. Similar mixtures of isomers have been found for the complexes $[Pd_2R_2(PR'_3)_2(\mu\text{-}OH)_2]$ (R = Ph or Me; R′ = Ph, Cy or ^iPr).[25–27] The *trans* isomers show only one singlet at δ −2.07 for the bridging hydroxo groups, while those of the *cis* isomers have different chemical environments and, consequently, appear as two singlets at δ −0.99 and −2.80.

Aminolysis reactions of late transition metal hydroxo complexes have been reported for Rh and Ir[28] and Pt,[29] as well as for Pd. As reported for the latter,[11–15,18,19] the basic character of our hydroxo bridged palladium complexes allows for the preparation of new dinuclear amido complexes. Thus, the reaction of **3** with RNH_2 (R = alkyl or *p*-substituted aryl) in dichloromethane (molar ratio 1 : 1 when R = alkyl and 1 : 2 when R = aryl) gave the corresponding μ-hydroxo–μ-amido complexes **4** and **5**, resulting in a facile and fast method for the synthesis of monoamido-bridged derivatives. The observation of only one set of ^1H NMR resonances of the orthopalladated imine ligands suggests the isomeric purity of **4** and **5** as far as *cis* (*syn*) or *trans* (*anti*) arrangement of the orthometallated imines is concerned, and supports *cis* (or *syn*) for them. The main different feature between **4** and **5** is the appearance of the iminic OCH_2 protons, which appear as diastereotopic for **5** and as equivalent for **4**. Since the amido group defines two different situations at each side of the square planes of the Pd atoms,

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† Electronic supplementary information (ESI) avaiable: analytical data for complexes 3–9. See http://www.rsc.org/suppdata/dt/b1/b101650o/

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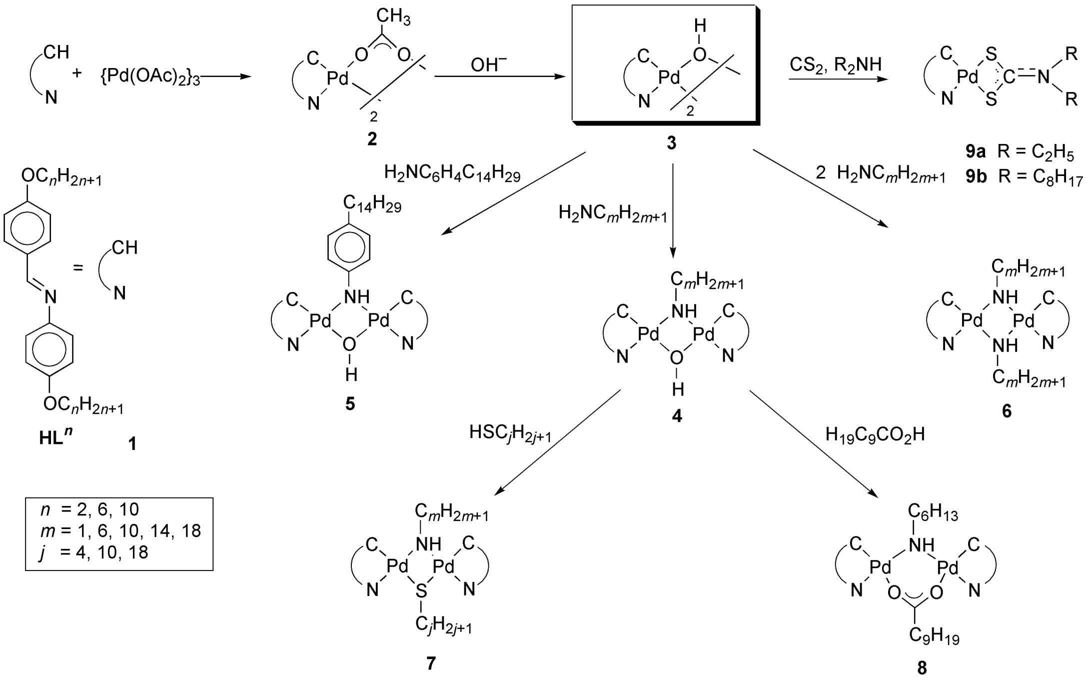


Scheme 1

diastereotopic iminic OCH_2 protons should be expected both for **4** and **5**.

However any dynamic process producing fast inversion of the amido group can bring about chemical equivalence of these methylenic protons, as observed for **4**. Inversions of bridging amido groups have been reported for related complexes,[9,16,18,30] and possible mechanisms have been proposed.[9] The NMR pattern observed for the aromatic proton signals of the anilido group indicates that rotation about the C–N bond in **5** is rapid on the ^1H NMR timescale. An arrangement of the amido group *cis* to the metallated carbon atoms is supported by NOE experiments for the complexes $[Pd_2(\mu\text{-}NHCH_3)(\mu\text{-}OH)(L^2)_2]$ and $[Pd_2(\mu\text{-}NHC_6H_4C_{14}H_{29}\text{-}p)(\mu\text{-}OH)(L^6)_2]$, and is in accord with the structure observed by X-ray diffraction in the related mixed amido–hydroxo bridged complex $[Pd_2Ph_2(PPh_3)_2\text{-}(\mu\text{-}OH)(\mu\text{-}NH^tBu)]$.[18] The IR spectra of **4** and **5** show two weak bands near 3615 and 3280 cm^{-1}, assigned to ν-OH and ν-NH respectively. The presence of the hydroxo ligand is also established by the observation of a high-field resonance at *ca.* δ −3.0, whereas the amido NH resonance is detected in the proton NMR spectra at *ca.* δ 1.1 and 2.9 for complexes **4** and **5** respectively. Attempts to prepare analogous complexes with other primary amines, such as the *p*-substituted benzylamines $H_2NCH_2C_6H_4OC_{10}H_{21}\text{-}p$, or with dialkylamines ($HNEt_2$, $HN(C_8H_{17})_2$) resulted in the decomposition of **3**. This result is in agreement with observations reported recently about reactivity for other dimeric palladium hydroxides with dialkylamines.[18]

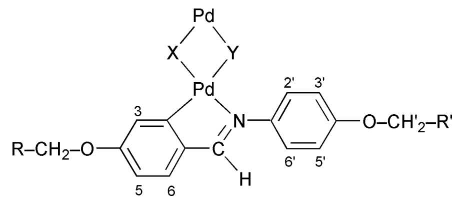
A large excess of alkylamine was needed to achieve dinuclear species **6** involving bis(μ-amido) bridges (otherwise there is a persistent problem of impurities in the corresponding μ-hydroxo, μ-amido complexes). The complexes **6** turned out to be highly soluble, even in non-polar hydrocarbon solvents such as hexane, and we were unable to isolate significant amounts of pure **6**. The NMR spectrum of $[Pd_2(\mu\text{-}NHC_{18}H_{37})_2(L^{10})_2]$ showed the presence of one single isomer with diastereotopic OCH_2 protons. On the other hand the NCH_2 protons were diastereotopic but did not show cross peaks in a COSY experiment. These data suggest a non-planar *cis* (or *syn*) complex. On the other hand, with *p*-substituted anilines and despite their higher acidity, the bis(μ-anilido) complexes were not even detected. A similar behaviour has been reported for other neutral palladium complexes, where kinetic inhibition, presumably as a result of steric crowding, was postulated.[11,14,18,19]

Treatment of **4** with HSC_jH_{2j+1} ($j = 4$, 10 or 18, molar ratio 1 : 1) led to displacement of the bridging hydroxo ligand by thiolato, giving the corresponding dinuclear complexes **7**, with mixed amido–thiolato bridges. The ^1H NMR resonances of the orthopalladated imine ligand indicate a planar structure, isomeric purity of the complexes, and a *cis* arrangement of the two imine moieties in these complexes. An arrangement with the thiolato group *cis* to the iminic nitrogen atoms is proposed consistent with the upfield shift of the methylene groups of the SR chain, because in this position they lie in the region of anisotropic shielding by the close phenyl group, in accordance with the values found for SR chains in similar environments.[31] The assignments of resonances for **7** given in Table 1 were made with the help of COSY. The arrangement proposed is in discrepancy with the usual antisymbiotic behaviour of the soft palladium atom.[32] Attempts at introducing first the thiol and then the amine in order to get the isomer with the thiolato group *trans* to the iminic nitrogen were unsuccessful, because the reaction of **3** with 1 equivalent of alkanethiol converted half of **3** to $[Pd(\mu\text{-}SR)L^n]_2$. Unfortunately, despite repeated attempts under different conditions, we have been unable to obtain crystals of **7** suitable for an X-ray analysis.

n-Decanoic acid was also deprotonated by complexes **4** to give **8**, containing mixed μ-amido–μ-carboxylato bridges. The ^1H NMR resonances of the orthopalladated imine ligand indicate a non-planar structure and an isomerically pure *cis* arrangement of the two imine moieties in these complexes. A similar arrangement has been reported in the cyclometallated complex *cis*-$[\{Pd(CH_2C_9H_6N)\}_2(\mu\text{-}O_2CCH_3)(\mu\text{-}NHR)]$ (R = aryl) obtained by reaction of *cis*-$[\{Pd(CH_2C_9H_6N)\}_2(\mu\text{-}O_2CCH_3)(\mu\text{-}OH)]$ with H_2NR.[12]

The hydroxo complexes allow also for the preparation of new mononuclear *N*,*N*-dialkyldithiocarbamate complexes **9**, by reaction with the corresponding dialkylamines in the presence of carbon disulfide, a well known reactivity of hydroxo complexes.[33] As reported in other cases,[33,34] the rotation around the C–N bond of the dithiocarbamate group is hindered, and the alkyl groups on the dithiocarbamate are inequivalent and give two separate sets of resonances for NR_2 protons. The most relevant absorption bands expected in the IR spectra for $R_2NCS_2^-$ ligands bonded in a bidentate coordination mode[35] are overlapped with the imine ligand absorptions.

Table 1 Parameters of ^{1}H NMR for compounds **3**–**9**[a]



Compound	X	Y	H	H^3	H^5	H^6	H$^{2'6'}$,H$^{3'5'}$ [b]	OCH$_2$/OCH'$_2$	Others [c]
3-*trans*	OH	OH	7.78 s	6.44 d (2.3)	6.53 dd (8.3, 2.3)	7.23 d (8.3)	7.35, 6.89 (8.9)	3.90 m	−2.08 s OH
3-*cis* [d]	OH	OH	7.84 s	—	—	—	7.17, 6.75 (8.9)	3.90 m	−1.08 s, −2.90 s OH
4	NHR″	OH	7.91 s	6.76 d (2.3)	6.53 dd (8.3, 2.3)	7.28 d (8.3)	7.07, 6.71 (8.9)	4.02 t, 3.90 t (6.6)	3.18 m $\mathrm{NC}H_2$; −2.90 s OH; 1.10 m NH
5	$\mathrm{NHC_6H_4C_{14}H_{29}}$	OH	7.84 s	6.64 d (1.8)	6.49 dd (8.3, 1.9)	7.21 d (8.3)	7.08, 6.74 (8.9)	3.98 m	7.64, 6.96[b] (7.9) $\mathrm{C_6}H_4$; 2.88 s NH; 2.46 m $\mathrm{NC_6H_4C}H_2$; −3.07 s OH
6	NHR″	NHR″	7.92 s	6.85 d (2.0)	6.54 dd (8.3, 2.0)	7.27 d (8.3)	7.25, 6.83 (8.8)	4.04 t, 3.89 t (6.6)	3.10 m $\mathrm{NC}H_2$; 2.24 m $\mathrm{NCH_2C}H_2$; 1.18 m NH; 0.58 m; 1.09 m; 0.36 m
7	NHR″	$\mathrm{SC_4H_9}$	7.86 s	6.78 d (2.3)	6.57 dd (8.3, 2.3)	7.32 d (8.3)	7.28, 6.78 (8.9)	4.04 t, 3.89 t (6.6)	3.10 m $\mathrm{NC}H_2$; 2.24 m $\mathrm{NCH_2C}H_2$; 1.18 m NH; 0.58 m $\mathrm{SC}H_2$; 1.09 m $\mathrm{SCH_2C}H_2$; 0.36 m $\mathrm{SCH_2CH_2C}H_2$
8	NHR″	$\mathrm{O_2CC_9H_{19}}$	7.90 s	6.85 d (2.0)	6.53 dd (8.3, 2.0)	7.26 d (8.3)	7.22, 6.82 (8.8)	3.90 m	2.46 m $\mathrm{NC}H_2$
9a	$\mathrm{S_2CN(C_2H_5)_2}$		8.09 s	6.67 d (2.3)	6.58 dd (8.3, 2.3)	7.40 d (8.3)	7.29, 6.89 (8.9)	4.09 t, 4.03 t (6.9)	3.82 q, 3.78 q (7.2) $\mathrm{NC}H_2$, 1.33 t, 1.25 t (7.2) $\mathrm{NCH_2C}H_3$

[a] In CDCl$_3$ at 300.13 MHz; the numbers in parentheses correspond to J(^{1}H–^{1}H) in Hz; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. [b] AA′BB′ spin system. [c] Aliphatic protons ($R = R' = C_5H_{11}$ and $R'' = C_6H_{13}$) appear in the range δ 0.8–1.9. [d] *cis* or *trans* signals overlapped by *trans* or *cis* signals.

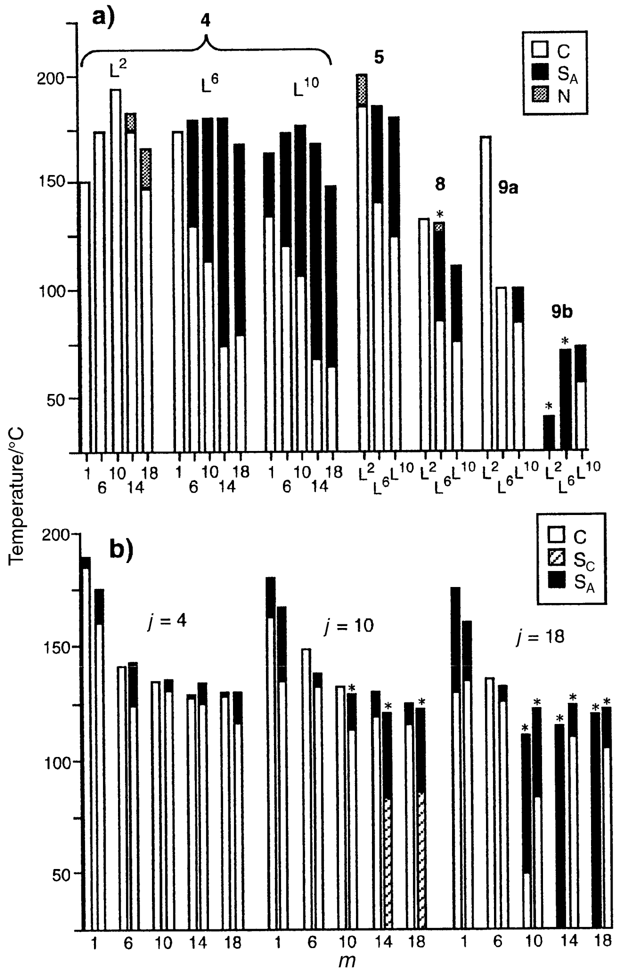


Fig. 1 Thermal behaviour of compounds (a) **4**, **5**, **8**, **9a** and **9b**, (b) **7**. For **4**, m represents the number of carbon atoms in the amide. For **7**, m and j represent the number of carbon atoms in the amide and thiolate respectively; in each pair, the left bar corresponds to the L^6 derivative and the right bar to the L^{10} derivative. C = Crystal; S$_C$ = smectic C; S$_A$ = smectic A; N = nematic; * = monotropic transition.

2 Mesogenic behaviour

The mesogenic behaviour of complexes **3**–**9** is summarized in Table 2 and in Fig. 1. The hydroxo complexes **3** are not liquid crystals in contrast with the long ranges of mesogenic behaviour displayed by analogous complexes containing (μ-Cl)$_2$ or (μ-Br)$_2$ bridges and medium or long chains. This difference can be attributed to the probable non-planar structure of **3**, which hinders good molecular packing; in fact the crystal structure of [Pd$_2$Ph$_2$(PPh$_3$)$_2$(μ-OH)$_2$] reveals a butterfly structure with an O–Pd–O–Pd torsion angle of *ca.* 36°.[27] Thus **3** should be structurally quite similar to the acetato-bridged complexes, also with butterfly structures,[36] which are non-mesomorphic as well.[24]

Many of the complexes **4** are mesomorphic. We have studied the influence of the alkoxy chain in the imines (n = 2, 6 or 10) and the effect of changing the alkyl length of the bridging alkylamido ligand (m = 1, 6, 10, 14 or 18). These μ-hydroxo–μ-amido complexes decompose upon clearing, around 175 °C. With the shortest chain in the imine, L^2, only the compounds with longer chains in the amido group (m = 14 or 18) are liquid crystals, exhibiting short ranges of nematic mesophase. With longer imines, L^6 and L^{10}, the materials are enantiotropic showing wide ranges of S$_A$ mesophase. On increasing the chain length of the imine from six to ten, the melting and clearing points decrease, and for the shortest chain in the amido group (m = 1) a mesophase is induced for L^{10}.

The μ-hydroxo–μ-anilido complexes **5** are liquid crystals showing a nematic phase with the shortest chain length of the imine (L^2) and a smectic A phase for the rest, a similar behaviour to the complexes with the alkylamido longest chains (m = 14 or 18), although with higher transition temperatures and narrower ranges of mesophase.

The replacement of the hydroxo bridge in complexes **4** by thiolates bearing alkyl chains (SC$_j$H$_{2j+1}$, j = 4, 10 or 18) to give complexes **7** could provide a better filling of the space between the two imine moieties and have an important influence on the thermal properties of the materials. However, the compounds turned out not to have good thermal stability. Most (except those with long chains in the amine, thiolate, and amido groups) decomposed at clearing (Table 2), even in cases when this was at reasonably low temperatures (about 130 °C). Overall, the results are disappointing since only for quite long chains the compounds display mesophases, usually S$_A$. The melting points are always above 100 °C leading to mesophase ranges lower than for the parent compounds **4**. Even so, for the combinations of highest chains in the amido and thiolato groups (m = 10, 14 or 18, k = 10 or 18), the compounds clear without decomposition and give rise to monotropic S$_A$ or S$_C$ phases upon cooling, which eventually solidify in a glassy state. This is not uncommon in compounds with low crystallization temperatures, high molecular weight and high viscosity, and is interesting in view of the possible use of the materials for optical storage.[31,37] It is remarkable and surprising that the compounds **7** with the imine L^6 show liquid crystal behaviour only when the amido group is very short (m = 1) or very large (m = 10).

The replacement of μ-OH in **4** by μ-carboxylato to give **8** produces better results. Comparing the properties of compounds **7** and **8**, both bearing an alkyl chain in the amido group of six carbons, there is a noticeable lowering of both the melting and clearing temperatures. Moreover, the compounds can be taken into the isotropic state without showing signs of decomposition.

Finally, the change from dinuclear complexes to the mononuclear complexes **9** involves a dramatic change in the molecular shape. The complexes with diethyldithiocarbamate show liquid crystalline properties only when the imine bears the longest chain, L^{10}. The effect of increasing the chain length of the dithiocarbamato (to R = C$_8$H$_{17}$) is to decrease the transition temperatures noticeably, and the complexes are liquid crystals, monotropic for the imines L^2 and L^6, and enantiotropic for L^{10}. All of them retain mesophase ordering on cooling to give glassy solids.

Conclusion

We have established a new route for the preparation of organometallic liquid crystals using the highly reactive dinuclear hydroxo-bridged species [Pd$_2$(μ-OH)$_2$(L^n)$_2$] **3**. This seems to be a versatile entry into other dinuclear complexes with double or mixed bridges: amido–hydroxo, anilido–hydroxo, bis-amido, amido–thiolato, and amido–carboxylato. The strategy could be applied to other protic bridging ligands, and to related complexes.

Each moiety in the system can be varied easily and influences the thermal properties of the materials. Although the complex shape of the molecules does not permit one to establish simple relationships to the properties observed, it is clear that mesophases can be obtained from varied molecules, showing the great potential of the basic unit in the structure, the orthometallated moiety, to induce mesomorphism.

Experimental

Literature methods were used to prepare the imines HL^n **1**,[23] [Pd$_2$(μ-OAc)$_2$(L^n)$_2$] **2**.[24] H$_2$NC$_6$H$_4$C$_{14}$H$_{29}$-p, aliphatic amines H$_2$NC$_m$H$_{2m+1}$, aliphatic thiols HSC$_j$H$_{2j+1}$, and dialkylamines HN(R)$_2$ were obtained from commercial sources and used without further purification. C, H, N analyses were carried out

Table 2 Phase transition temperatures (°C) and enthalpies (kJ mol^{-1}) (in parentheses) for the compounds **3**–**9**[a]

Compound	*n*	*m*	*j*	Heating scan
3	2			Cr 191 I^{b,c}
3	6			Cr 202 I^{b,c}
3	10			Cr 167 I^{b,c}
4	2	1		Cr 150 I^{b,c}
4	2	6		Cr 180 I^{b,c}
4	2	10		Cr 193.5 (68.1) I^{b}
4	2	14		Cr 173.7 (37.7) N 181.6 (0.6) I^{b}
4	2	18		Cr 147.6 (28.4) N 165.1 (0.3) I^{b}
4	6	1		Cr 174.7 (16.7) I^{b}
4	6	6		Cr 128.6 (31.5) S_A 179.2 (4.2) I^{b}
4	6	10		Cr 104.6 (35.0) S_A 180 I^{b,c}
4	6	14		Cr 74.2 (46.5) S_A 180.5 (5.5) I^{b}
4	6	18		Cr 79.1 (39.8) S_A 168.7 (2.3) I^{b}
4	10	1		Cr 135.6 (21.1) S_A 163 I^{b,c}
4	10	6		Cr 120.8 (29.5) S_A 176.5 (7.6) I^{b}
4	10	10		Cr 106.7 (26.7) S_A 175.3 (5.9) I^{b}
4	10	14		Cr 76.5 (22.5) S_A 167.8 (5.8) I^{b}
4	10	18		Cr 57.4 (18.2) S_A 164 I^{b,c}
5	2			Cr 185.7 (24.8) N 198.0 (1.5) I^{b}
5	6			Cr 139.3 (17.6) S_A 184.8 (3.2) I^{b}
5	10			Cr 82.1 (19.7) Cr′ 123.9 (14.9) S_A 180.2 (5.4) I^{b}
7	2	1	4	Cr 192.8 (30.4) I^{b}
7	2	6	4	Cr 179.8 (33.2) I^{b}
7	2	10	4	Cr 135.9 (3.5) Cr′ 148.6 (32.3) I^{b}
7	2	14	4	Cr 102.4 (1.5) Cr′ 135.8 (35.2) I^{b}
7	2	18	4	Cr 85.2 (3.4) Cr′ 101.9 (12.2) Cr″ 139.1 (31.2) I^{b}
7	2	10	10	Cr 97.9 (1.5) Cr′ 104.5 (12.9) Cr″ 143 I^{b,c}
7	2	18	10	Cr 64.7 (9.6) Cr′ 86.7 (8.7) Cr″ 138.1 (43.0) I^{b}
7	2	10	18	Cr 76.4 (3.1) Cr′ 82.6 (3.9) Cr″ 126.8 (29.0) I
7	2	18	18	Cr 66.3 (14.0) Cr′ 109.5 (29.8) I
7	6	1	4	Cr 113.7 (4.4) Cr′ 185.3 S_A 189.1 (51.4)^{d} I^{b}
7	6	6	4	Cr 141.4 (59.0) I^{b}
7	6	10	4	Cr 135 I^{b,c}
7	6	14	4	Cr 65.3 (2.7) Cr′ 107.7 (20.9) Cr″ 127.2 (39.7) S_A^{b}
7	6	18	4	Cr 102.2 (12.9) Cr′ 128.9 (43.2) S_A^{b}
7	6	1	10	Cr 114.5 (7.9) Cr′ 158.3 Cr″ 163.4 (49.2)^{d} S_A 180 I^{b,c}
7	6	6	10	Cr 149.3 (62.2) I^{b}
7	6	10	10	Cr 101.0 (25.4) Cr′ 132.3 (45.6) I^{b}
7	6	14	10	Cr 106.5 (25.4) Cr′ 119.9 (33.9) S_A 130.1 (7.8) I^{b}
7	6	18	10	Cr 95.4 (35.7) Cr′ 116.7 (34.4) S_A 125.3 (5.9) I^{b}
7	6	1	18	Cr 144.8 Cr′ 150.0 (59.2)^{d} S_A 169.6 (12.6) I^{b}
7	6	6	18	Cr 89.9 (37.1) Cr′ 135.5 (44.9) I^{b}
7	6	10	18	Cr 75.5 (25.1) Cr′ 122.4 (44.7) I I 111.0 (−4.9) S_A^{e,f}
7	6	14	18	Cr 90.3 (36.9) Cr′ 129.1 (51.3) I I 115.5 (−6.2) S_A^{e,f}
7	6	18	18	Cr 132.5 (49.3) I I 119.7 (−5.9) S_A^{e,f}
7	10	1	4	Cr 126.5 (2.8) Cr′ 160.0 (23.3) S_A 174.4 (8.2) I^{b}
7	10	6	4	Cr 103.0 (15.8) Cr′ 124.7 (24.7) S_A 143.5 (8.4) I^{b}
7	10	10	4	Cr 90.0 (4.5) Cr′ 115.7 (17.2) Cr″ 131.1 (34.0) S_A 135.7 (6.6) I^{b}
7	10	14	4	Cr 106.4 (11.6) Cr′ 125.8 (41.5) S_A 134.0 (8.4) I^{b}
7	10	18	4	Cr 86.7 (3.6) Cr′ 99.5 (20.2) Cr″ 117.3 (34.5) S_A 130.7 (8.2) I^{b}
7	10	1	10	Cr 135.5 (25.5) S_A 167.3 (6.7) I^{b}
7	10	6	10	Cr 94.6 (9.7) Cr′ 134.6 Cr″ 135.9 (44.1)^{d} S_A 138.2 (7.1) I
7	10	10	10	Cr 89.4 (23.6) Cr′ 116.5 (2.4) Cr″ 133.8 (55.1) I I 128.9 (−8.1) S_A 113.3 (−24.3) Cr^{e}
7	10	14	10	Cr 86.4 (18.0) Cr′ 127.4 (58.5) I I 122.9 (−7.4) S_A 84.8 (−0.5) S_C^{e,f}
7	10	18	10	Cr 102.3 (2.4) Cr′ 127.1 (60.2) I I 122.4 (−8.2) S_A 86.5 (−1.0) S_C^{e,f}
7	10	1	18	Cr 119.8 (12.5) Cr′ 134.8 (14.2) S_A 160.2 (6.3) I^{b}
7	10	6	18	Cr 54.6 (−4.8) Cr′ 101.5 (13.6) S_A 122.7 (6.8) I^{b}
7	10	10	18	Cr 83.6 (38.6) Cr′ 130.3 (74.2) I I 122.6 (−7.9) S_A 84.7 (−20.3) Cr^{e}
7	10	14	18	Cr 67.0 (30.1) Cr′ 127.2 (70.8) I I 124.3 (−8.2) S_A 110.5 (−36.4) Cr^{e}
7	10	18	18	Cr 68.1 (30.1) Cr′ 124.4 (63.6) I I 122.3 (−8.1) S_A 105.0 (−33.1) Cr^{e}
8	2			Cr 149.3 (31.7) I
8	6			Cr 133.9 (38.1) I I 130.0 (−1.0) N 124.2 (−0.4) S_A 85.8 (0.9) g^{e}
8	10			Cr 75.8 (13.7) S_A 107.5 (1.9) I
9a	2			Cr 170.8 (41.1) I
9a	6			Cr 97.1 (17.3) I
9a	10			Cr 83.8 (11.5) S_A 99.5 (6.4) I

Table 2 (*Contd.*)

Compound	*n*	*m*	*j*	Heating scan
9b	2			Cr 43.0 (4.1) I I 41.1 (−2.8) S_A [e,f]
9b	6			Cr 79.7 (25.8) I I 71.3 (−4.4) S_A [e,f]
9b	10			Cr 56.1 (19.1) S_A 73.4 (4.3) I

[a] Cr, Cr′ = Crystal; S_A = smectic A; S_C = smectic C; I = isotropic liquid; N = nematic; g = glass transition. [b] Decomposition. [c] Observed by means of polarized light microscopy only. [d] Combined enthalpies. [e] Monotropic transition (data for the cooling cycle). [f] A glassy mesophase is obtained on cooling.

on a Perkin-Elmer 2400 microanalyser. All the new compounds gave satisfactory elemental analyses (Table S1, ESI Supplementary Materials†). IR spectra were recorded on a Perkin-Elmer FT-1720X spectrometer using Nujol mulls between polyethylene plates, ^{1}H NMR spectra on a Bruker AC-300 or ARX-300 MHz spectrophotometer. The textures of the mesophases were studied with a Leitz microscope equipped with a Mettler FP82HT hot stage and a Mettler FP90 central processor and polarizers at a heating rate of approximately 10 °C min^{-1}. Transition temperatures and enthalpies were measured by differential scanning calorimetry, with a Perkin-Elmer DSC-7 instrument operated at a scanning rate of 10 °C min^{-1} on heating. The apparatus was calibrated with indium (156.6 °C, 28.5 J g^{-1}) as standard, the samples were sealed in aluminium capsules in air, and the holder atmosphere was dry nitrogen.

Synthesis of the complexes

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

$[Pd_2(\mu\text{-}OH)_2(L^6)_2]$ 3. To a suspension of **2** (0.500 g, 0.47 mmol) in acetone (40 mL) was added a solution of NaOH (0.11 g, 2.75 mmol) in water (30 mL). The mixture was stirred for 24 h at room temperature. The yellow precipitate was filtered off, washed with water (3 × 5 mL) and acetone (2 × 5 mL), and air dried. Yield: 98%. IR (Nujol, cm^{-1}): $\nu_{(C=N)}$ 1608; $\nu_{(O-H)}$ 3607.

$[Pd_2(\mu\text{-}HNC_6H_{13})(\mu\text{-}OH)(L^6)_2]$ 4. A mixture of **3** (0.200 g, 0.198 mmol) and $H_2NC_6H_{13}$ (26 µL, 0.20 mmol) was stirred in dichloromethane (30 mL) for 12 h. The yellow solution was evaporated to *ca.* 3 mL under reduced pressure. Addition of methanol afforded **4** as a yellow solid, which was filtered off, washed with 2 × 3 mL of cold acetone and vacuum dried. Yield: 65%. IR (Nujol, cm^{-1}): $\nu_{(C=N)}$ 1608; $\nu_{(O-H)}$ 3617; $\nu_{(N-H)}$ 3293.

$[Pd_2(\mu\text{-}HNC_6H_4C_{14}H_{29}\text{-}p)(\mu\text{-}OH)(L^6)_2]$ 5. A mixture of **3** (0.100 g, 0.099 mmol) and $H_2NC_6H_4C_{14}H_{29}$-*p* (42 mg µL, 0.198 mmol) was stirred in dichloromethane (30 mL) for 12 h. The yellow solution was evaporated to *ca.* 3 mL under reduced pressure. Addition of methanol afforded **4** as a yellow solid, which was filtered off, washed with 2 × 3 mL of cold acetone and vacuum dried. Yield: 65%. IR (Nujol, cm^{-1}): $\nu_{(C=N)}$ 1608; $\nu_{(O-H)}$ 3616; $\nu_{(N-H)}$ 3281.

$[Pd_2(\mu\text{-}SC_6H_{13})(\mu\text{-}HNC_6H_{13})(L^6)_2]$ 7. To a solution of **4** (0.100 g, 0.092 mmol) in dichloromethane (20 mL) was added 1-hexanethiol (20 µL, 0.10 mmol). After stirring for 30 min the solvent was evaporated and cold acetone (10 mL) added to obtain a yellow solid, which was filtered off, washed with 2 × 3 mL of cold acetone and air dried. Yield: 63%. IR (Nujol, cm^{-1}): $\nu_{(C=N)}$ 1608. Sometimes it was necessary to purify the precipitate by redissolving it in dichloromethane, treatment with a few mg of charcoal, filtration and crystallization.

$[Pd_2(\mu\text{-}O_2CC_9H_{19})(\mu\text{-}HNC_6H_{13})(L^6)_2]$ 8. n-Decanoic acid (14 mg, 0.08 mmol) was added to a solution of **4** (0.075 g, 0.069 mmol) in dichloromethane (20 mL) and stirred for 30 min. The orange solution was evaporated to a small volume. Addition of methanol afforded **8** as a yellow solid, which was filtered off, washed with 2 × 3 mL of methanol and vacuum dried. Yield: 65%. IR (Nujol, cm^{-1}): $\nu_{(C=N)}$ 1609; $\nu_{(C=O)}$ 1554.

$[Pd_2(S_2CNEt_2)(L^6)_2]$ 9. To a suspension of $[Pd_2(\mu\text{-}OH)_2(L^6)_2]$ **3** (0.100 g, 0.098 mmol) in dichloromethane (20 mL) was added $HNEt_2$ (21 µL, 0.198 mmol) and CS_2 (18 µL, 0.30 mmol) and the mixture stirred for 4 h at room temperature. Acetonitrile (10 mL) was added and the resulting solution concentrated to a small volume. A yellow solid appeared which was filtered off, washed with acetonitrile (2 × 3 mL) and vacuum dried. Yield: 65%. IR (Nujol, cm^{-1}): $\nu_{(C=N)}$ 1605.

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