0.22 mmol) was heated to reflux with stirring for 1 d. After cooling, the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel (CH_2Cl_2/ethanol (30/1) as eluent). Yield: 128 mg (59 %).

$(Bu_4N)_2$-**2**: Positive-ion FAB-MS: *m*/*z*: 3198 [M^+]; ^{13}C NMR (67.9 MHz, CD_2Cl_2, 20 °C, TMS): $\delta = 133.8$ (m, *ipso*-Ph), 131.8, 130.8 (m, *o*-Ph), 130.1 (m, *p*-Ph), 127.9 (m, *m*-Ph), 59.0 (s, Bu), 37.4 (d, $^1J(P,C) = 30.8$ Hz, ($PCH_2CH_2CH_2)_2$), 17.5 (d, $^2J(P,C) = 20.0$ Hz, ($PCH_2CH_2CH_2)_2$), 24.7 (s, Bu), 21.6 (d, $^3J(P,C) = 3.8$ Hz, ($PCH_2CH_2CH_2)_2$), 20.4 (s, Bu), 14.1 (s, Bu); ^{31}P NMR (109.3 MHz, $CDCl_3$, 20 °C): $\delta = -29.9$ (s). **3a**: Positive-ion FAB-MS: *m*/*z*: 2914 [M^+]; ^{31}P NMR ($CDCl_3$, 20 °C): $\delta = -30.5$ (s).

3b: Elemental analysis calcd for $C_{60}H_{64}I_2P_4Se_8Re_6 \cdot CH_2Cl_2 \cdot 1.5\,H_2O$: C 24.23, H 2.30, I 8.39; found: C 24.45, H 2.35, I 8.94; positive-ion FAB-MS: *m*/*z*: 2914 [M^+]; ^{13}C NMR (CD_2Cl_2, 20 °C): $\delta = 134.8$ (m, *ipso*-Ph), 132.1 (m, *o*-Ph), 130.9 (m, *p*-Ph), 128.3 (m, *m*-Ph), 37.5 (d, $^1J(P,C) = 33.0$ Hz, ($PCH_2CH_2CH_2)_2$), 37.3 (d, $^1J(P,C) = 29.6$ Hz, ($PCH_2CH_2CH_2)_2$), 27.1 (d, $^2J(P,C) = 14.0$ Hz, ($PCH_2CH_2CH_2)_2$), 27.0 (d, $^2J(P,C) = 14.0$ Hz, ($PCH_2CH_2CH_2)_2$), 21.4 (s, ($PCH_2CH_2CH_2)_2$), 21.3 (s, ($PCH_2CH_2CH_2)_2$); ^{31}P NMR ($CDCl_3$, 20 °C): $\delta = -31.0$ (s), -31.3 (s).

4-$(SbF_6)_2$: Elemental analysis calcd for $C_{90}H_{96}F_{12}P_6Sb_2Se_8Re_6$: C 30.16, H 2.70; found C 30.18, H 2.85; positive-ion FAB-MS: *m*/*z*: 3586 [M^+]; ^{13}C NMR (CD_2Cl_2, 20 °C): $\delta = 133.6$ (m, *ipso*-Ph), 133.0 (m, *o*-Ph), 131.8, 131.4 (m, *p*-Ph), 128.7 (m, *m*-Ph), 37.9 (d, $^1J(P,C) = 33.5$ Hz, ($PCH_2CH_2CH_2)_2$), 26.6 (d, $^2J(P,C) = 15.1$ Hz, ($PCH_2CH_2CH_2)_2$), 21.7 (d, $^3J(P,C) = 3.9$ Hz, ($PCH_2CH_2CH_2)_2$); ^{31}P NMR (CD_2Cl_2, 20 °C): $\delta = -29.7$ (s).

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[10] Red crystals of **3b** were obtained by slow diffusion of diethyl ether into a solution of **3b** in CH_2Cl_2. Crystal data for **3b** $\cdot CH_2Cl_2 \cdot 1.5\,H_2O$ ($C_{61}H_{69}Cl_2I_2O_{1.5}P_4Re_6Se_8$): $M_r = 3023.75$, monoclinic, space group $P2_1/c$ (no. 14), $a = 19.712(1)$, $b = 16.587(1)$, $c = 22.437(1)$ Å, $\beta = 100.321(3)°$, $V = 7217.6(7)$ Å^3, $Z = 4$; $\rho_{calcd} = 2.782$ g cm^{-3}; crystal dimensions $0.30 \times 0.20 \times 0.20$ mm^3; $\mu(Mo_{K\alpha}) = 151.20$ cm^{-1}; $T = 173$ K. Data were collected on a Rigaku R-AXIS RAPID diffractometer equipped with an image plate detector with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å). Total reflections collected 16258. Full-matrix least-squares refinement, final $R = 0.049$, $R_w = 0.064$, GOF = 1.30 for 8526 observed reflections ($I > 3\sigma(I)$) and 735 variable parameters. The maximum and minimum peaks around the rhenium atoms on the final difference Fourier map were +3.66 and −2.95 e Å^{-3}. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-145486. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Coordinatively Unsaturated Metal Centers as Building Blocks for High Coordination Number Metallomesogens**

Koen Binnemans* and Katleen Lodewyckx

Most literature on metal-containing liquid crystals (metallomesogens) is devoted to compounds with Rh^I, Ir^I, Ni^{II}, Pd^{II}, Pt^{II}, Cu^{II}, and Ag^I as the central metal ion, because these complexes have a linear or planar geometry and mimic therefore conventional organic calamitic (rodlike) liquid crystals.[1] Obtaining high coordination number calamitic metallomesogens is a challenge.[2] One approach is to make the ligand as anisometric as possible by increasing the number of aromatic rings.[3, 4]

The design of lanthanide-containing liquid crystals is difficult[5] because the trivalent lanthanide ions have even

[*] Dr. K. Binnemans, K. Lodewyckx
Katholieke Universiteit Leuven
Department of Chemistry
Celestijnenlaan 200F, 3001 Leuven (Belgium)
Fax: (+32) 16-32-79-92
E-mail: Koen.Binnemans@chem.kuleuven.ac.be

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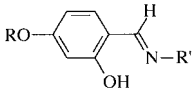
higher coordination numbers (CNs) than d-group transition metal ions. In general, lanthanide complexes have coordination numbers 8 or 9. Octahedral lanthanide complexes (CN = 6) do exist and the best known examples are tris(β-diketonato)lanthanide(III) complexes.[6] Lanthanide complexes with coordination number 6 are coordinatively unsaturated and can expand their coordination sphere by adduct formation with neutral molecules. Because the trivalent lanthanide ions are hard Lewis acids, hard Lewis bases are preferred for adduct formation. Most of the molecules which add to lanthanide ions are oxygen donors and, to a lesser extent, nitrogen donors. Water is a very common ligand for adduct formation. When tris(β-diketonato)lanthanide(III) complexes are prepared in an aqueous solution, they are most often obtained as dihydrates. This leads to a coordination number of eight, not six for the lanthanide ion.

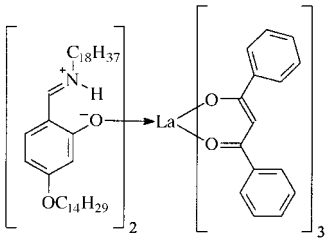
We serendipitously discovered that adducts of tris(β-diketonato)lanthanide(III) complexes with a salicylaldimine Schiff base as Lewis base have mesomorphic properties.



Scheme 1. *N*-Alkyl-4-alkyloxy-2-hydroxybenzaldimine Schiff base ligands. For ligand L discussed in the text, $R = C_{14}H_{29}$, $R' = C_{18}H_{37}$.

We used 1,3-diphenyl-1,3-propanedione (dibenzoylmethane, Hdbm) as the β-diketone ligand and 2-hydroxy-*N*-octadecyl-4-tetradecyloxybenzaldimine (L, Scheme 1) as the Schiff base. This result was totally unexpected, because work by Giroud-Godquin and Rassat has shown that six alkyl chains are insufficient for octahedral tris(β-diketonato)iron(III) complexes to form a real mesophase.[7] Swager and Zheng found that tris(β-diketonato) complexes of Fe^{III}, Mn^{III}, and Cr^{III} complexes should have 12 or more alkyl chains (attached to the β-diketone ligand) in order to exhibit stable mesomorphism.[8, 9] In our complexes, only four long alkyl chains are present.

Complex $[La(dbm)_3L_2]$ (Scheme 2) was obtained from anhydrous $[La(dbm)_3]$ and L. It can be assumed that the coordination number of La^{III} in $[La(dbm)_3L_2]$ is eight, with the two Schiff base ligands binding in a monodentate fashion. It was found for complexes of the type $[LnL_3(NO_3)_3]$ that the Schiff base is in a zwitterionic form and binds to the lanthanide ion through the phenolic oxygen only.[5d,e]



Scheme 2. Schematic structure of $[La(dbm)_3L_2]$ complex.

It should be noted that neither L nor $[La(dbm)_3]$ are mesomorphic: the melting point of L is 73 °C, and $[La(dbm)_3]$ decomposes when heated in air. $[La(dbm)_3L_2]$ melts at 95 °C to an isotropic liquid, without forming a mesophase. On cooling, a monotropic mesophase was formed at 80 °C. This phase was according to the texture observed under the polarizing microscope a smectic A phase (Sm A). When cooling the isotropic liquid, bâtonnets formed at the clearing point and they coalesced to the typical focal-conic texture (fan texture). It was also possible to observe regions with homeotropic alignment. When the Sm A phase was heated, clearing occurred at 81 °C. The rather low viscosity of the mesophase indicates that a real mesophase and not a plastic crystal phase is present. The mesophase ordering could be frozen into a glassy state. By cooling the mesophase, the viscosity gradually increased and finally a solid was obtained. The glassy mesophase had the same optical texture as the (liquid) mesophase. With high cooling rates (we used cooling rates up to $100\,K\,min^{-1}$) it was possible to obtain a glass that did not contain any crystallites. Upon heating the glass, the mesophase was reobtained above 75 °C and the compound cleared at 81 °C. However, when the compound was kept in the mesophase at a constant temperature or when the compound was slowly cooled, the clearing process was not complete at 81 °C. Some birefringent regions appeared which only cleared at 95 °C (i.e. at the melting point of the crystalline compound). These birefringent regions were thus crystallites. The melting enthalpy of $[La(dbm)_3L_2]$ is $104\,kJ\,mol^{-1}$ (DSC, first heating run), and the clearing enthalpy is $-13.8\,kJ\,mol^{-1}$ (DSC, first cooling run). The clearing enthalpy is comparable to those found for lanthanide-containing Schiff base complexes exhibiting enantiotropic mesomorphism.[5b,e]

Liquid crystallinity was also observed for other $[Ln(dbm)_3L_2]$ compounds (Table 1). To obtain mesomorphic adducts, it is possible to follow a route which is used for the synthesis of hydrogen-bonded liquid crystals: dissolving accurately weighed amounts of $[Ln(dbm)_3]$ and L in a 1:2 molar ratio in dichloromethane and subsequently evaporating the solvent.[10] This method is fast, yields are quantitative, and the transition temperatures are the same as those of the separately synthesized $[Ln(dbm)_3L_2]$ compounds.

Table 1. Mesomorphic behavior of $[Ln(dbm)_3L_2]$ complexes.

Ln	R[a]	R′[a]	Transition temperatures [°C][b, c]
La	$C_{14}H_{29}$	$C_{18}H_{37}$	Cr 95 (Sm A 81) I
	$C_{16}H_{33}$	$C_{18}H_{37}$	Cr 93 (Sm A 77) I
	$C_{12}H_{25}$	$C_{16}H_{33}$	Cr 100 (Sm A 81) I
Nd	$C_{16}H_{33}$	$C_{18}H_{37}$	Cr 89 (Sm A 63) I
Eu	$C_{14}H_{29}$	$C_{18}H_{37}$	Cr 90 (Sm A 60) I

[a] R = 4-alkoxy chain; R′ = *N*-alkyl chain (see Scheme 1). [b] Cr = crystalline solid; Sm A = smectic A phase; I = isotropic liquid. [c] Clearing points were determined by heating the monotropic mesophase. In general, clearing points determined by cooling the isotropic liquid are 1 K lower than the values reported here.

Because $[Ln(dbm)_3]$ has molecular dimensions similar to those of [60]fullerene, it is interesting to compare [60]fullerene-containing liquid crystals with our mesomorphic complexes. Chuard and Deschenaux functionalized the C_{60} core with a twin cholesterol malonate derivative and observed a monotropic smectic A phase.[11] Although the cholesteryl group is known to be strongly mesophase-promoting, two cholesteryl groups were necessary to induce monotropic mesomorphism in the [60]fullerene derivative. By another

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approach, Deschenaux et al. were able to obtain an enantiotropic smectic A mesophase by functionalizing [60]fullerene with 12 alkyl chains each terminated by a cyanobiphenyl group.[12] It is therefore amazing to observe liquid crystallinity in [Ln(dbm)$_3$] complexes functionalized by only four alkyl chains.

In conclusion, we obtained lanthanide-containing liquid crystals by forming a bisadduct between tris(β-diketonato)-lanthanide(III) complexes and a salicylaldimine Schiff base. Our method is a new approach to the design of lanthanide-containing metallomesogens. This approach is versatile, because the β-diketone ligand, the addend ligand, and the lanthanide ion can be varied.

Experimental Section

^{1}H NMR spectra were obtained on a Bruker WM-250 spectrometer (250 MHz) using $CDCl_3$ as solvent. IR spectra were recorded on a Bruker FTIR spectrometer IFS66 (KBr pellet technique). Elemental analyses (CHN) were obtained on a CE-Instrument EA-1110 elemental analyzer. Optical textures of the mesophases were observed with an Olympus BX60 polarizing microscope equipped with a LINKAM THMS600 hot stage and a LINKAM TMS93 programmable temperature controller. DSC traces were recorded with a Mettler–Toledo DSC821e module.

Synthesis of [Ln(dbm)$_3$L$_2$]: [La(dbm)$_3$] was obtained by careful dehydration of the corresponding mono- and dihydrates in vacuo (10^{-3} mbar).[13] A solution of [La(dbm)$_3$] (3 mmol, 2.42 g) in absolute ethanol was added dropwise to a solution of 2-hydroxy-*N*-octadecyl-4-tetradecyloxybenzaldimine (L) (3 mmol, 1.76 g) in absolute ethanol at 50 °C. The adduct precipitated immediately. After the mixture had been stirred overnight at room temperature, the precipitate was filtered off, washed with ethanol and dried in vacuo. The compound is obtained as a pale yellow powder. Yield: 2.72 g (91 %). IR (KBr): $\tilde{\nu} = 1654$ (C=N, s), 1552 (C=O, s) cm^{-1}. Elemental analysis calcd (%) for $C_{123}H_{175}LaN_2O_{10}$ (1980.6): C 74.57, H 8.91, N 1.42; found: C 74.74, H 8.97, N 1.30.

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Singly and Doubly Oxidized Phthalocyanine (pc) Rings: [Cu(pc)(ReO$_4$)] and [Cu(pc)(ReO$_4$)$_2$]**

Anna S. Gardberg, Peter E. Doan, Brian M. Hoffman,* and James A. Ibers*

Numerous molecular conductors and semiconductors are known that are based on partially oxidized macrocycles,[1–4] and several singly oxidized metal phthalocyanine complexes have been isolated.[5, 6] Doubly oxidized complexes are more intriguing, with the most widely known example being "Compound I", which results from the double oxidation of ferrihemes.[7] This oxidation occurs by the loss of one electron from the metal ion (giving formally iron(IV)) and one from the ring. There are examples of crystalline doubly oxidized metal phthalocyanine complexes[8–11] where both oxidations are metal centered, but there are only a few reports of doubly ring-oxidized metallophthalocyanine complexes, and these only for solutions.[12–14] As far as we know there have been no reports of isolated compounds in which the phthalocyanine (pc) ring is doubly oxidized.

We describe here the syntheses of the singly and doubly oxidized compounds [Cu(pc)(ReO$_4$)] (**1**) and [Cu(pc)-(ReO$_4$)$_2$] (**2**), together with their characterization by means of single-crystal X-ray diffraction (Figure 1) and electron paramagnetic resonance (EPR) methods. The structures of these compounds differ from those of porphyrinic conductors[15] and other singly oxidized derivatives[16] in that they contain isolated, rather than stacked, macrocycles. We show that these both are compounds of Cu^{II}, essentially unperturbed by the oxidation. In **1** the pc ring is singly oxidized to pc$^{\bullet-}$;

[*] Prof. B. M. Hoffman, Prof. J. A. Ibers, A. S. Gardberg, Dr. P. E. Doan
Department of Chemistry and Materials Research Center
Northwestern University, 2145 Sheridan Road
Evanston, IL, USA 60208-3113 (USA)
Fax: (+1) 847-491-2976
E-mail: bmh@northwestern.edu
ibers@chem.northwestern.edu

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