Mesogenic binuclear oxamide derivatives with discotic and calamitic properties

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Synthesis

The synthetic procedure giving the complexes \( \text{a} \) is sketched in Scheme S1.

\[
\begin{align*}
\text{b} & \quad + \quad \text{e} \quad \xrightarrow{\text{CH}_2\text{Cl}_2, \text{Et}_3\text{N}} \quad \text{d} \\
\text{d} & \quad + \quad \text{Cl} \quad \xrightarrow{\text{M(OAc)}_2, \text{MeOH}} \quad \text{f} \\
\text{f} & \quad + \quad \text{MeOH} \quad \xrightarrow{\text{M(OAc)}_2, \text{MeOH}} \quad \text{a}
\end{align*}
\]

\[R_1 = \text{C}_9\text{H}_{19}, \text{2,3,4-(H}_1\text{,C}_8\text{O})_3\text{Ph}, \]
\[4\text{-H}_1\text{,C}_8\text{Ph} \]
\[R_2 = \text{H}, \text{OC}_8\text{H}_{17} \]
\[R_3 = \text{H}, \text{C}_7\text{H}_{15}, \text{C}_8\text{H}_{17} \]
\[\text{M} = \text{Ni(II), Cu(II)} \]

Scheme S1. Synthetic route to di-metallic complexes.
All the compounds were prepared in similar manner as described previously. The synthesis of the starting material b is shown below and the substance c was obtained from Claisen reaction between ethyl formate and appropriate ketone. 4-octyloxy or 4,5-dioctyloxy-1,2-phenylenediamine (b) (1 mmol) and formyl ketone sodium salt (c) (1 mmol) obtained by Claisen reaction were dissolved in methanol (100 ml) and neutralised with acetic acid (to pH about 6) in room temperature. For non-symmetric diamine with one octyloxy chain the reaction runs regioselectively. Precipitated intermediate d 1-3 was separated and purified by recrystallisation from hexane or octane. (yield 80 %) The substance d (1 mmol) was dissolved in a mixture of triethylamine (1.2 mmol) and methylene chloride (30 ml) then solution of oxalyl chloride (e) (0.5 mmol) in methylene chloride (10 ml) was added. After evaporation of the solvent to dryness, the solid remnants containing ligand f were dissolved in boiling isopropanol (30 ml).

To the hot solution nickel or copper acetate (1.2 mmol) dissolved in methanol (20 ml) was added in droplets. The reaction mixture was boiled (5 min) and cooled. The solid complex 1 was recrystallised from toluene or isooctane (yield ~ 40 – 50 %).

1-Ni

$^1$H NMR (toluene d8): $\delta = 0.85-1.65$ (m, 64H), 2.16 (t, J = 7.5 Hz, 4H), 3.76 (t, J = 6.5 Hz, 4H), 5.06 (d, J = 6.2 Hz, 2H), 6.43 (dd, J1 = 2.7 Hz, J2 = 9.0 Hz, 2H), 6.45 (d, J = 6.2 Hz, 2H), 6.65 (d, J = 9.0 Hz, 2H), 7.53 (d, J = 2.7 Hz, 2H). Elemental analysis for C54H82O6N4Ni2: calculated: C 64.80%; H 8.28%; N 5.60. Found: C 64.77%; H 8.30%; N 5.60%. ($^{13}$C NMR has not been recorded because of too low solubility in toluene.)

1-Cu

Elemental analysis for C54H82O6N4Cu2: calculated: C 64.18%; H 8.20%; N 5.55. Found: C 64.20%; H 8.25%; N 5.51%.

2-Ni

$^1$H NMR (toluene d8): $\delta = 0.88-1.85$ (m, 94H), 2.21 (t, J = 7.5 Hz, 4H), 3.82 (m, 8H), 5.10 (d, J = 6.1 Hz, 2H), 6.49 (d, J = 6.1 Hz, 2H), 6.57 (s, 2H), 6.73 (s, 2H), 7.59 (s, 2H); $^{13}$C NMR (toluene d8): $\delta = 14.2, 23.1, 23.2, 26.7, 27.2, 29.8, 29.9, 30.0, 30.1, 30.2, 30.4, 32.4, 32.5, 39.0, 70.2, 71.1, 97.7, 101.1, 108.3, 131.5, 140.8, 145.6, 148.4, 148.5, 167.9, 184.0. Elemental analysis for C70H114O8N4Ni2: calculated: C 66.87%; H 9.15%; N 4.46. Found: C 66.82%; H 9.13%; N 4.48%.

2-Cu

Elemental analysis for C70H114O8N4Cu2: calculated: C 66.36%; H 9.09%; N 4.42. Found: C 66.40%; H 9.05%; N 4.44%.

3-Ni

$^1$H NMR (toluene d8): $\delta = 0.88-1.88$ (m, 116H), 2.35 (t, J = 7.5 Hz, 4H), 2.35 (t, J = 7.4 Hz, 4H), 3.82 (m, 8H), 6.46 (dd, J1 = 2.5 Hz, J2 = 8.9 Hz, 2H), 6.73 (s, 2H), 6.81 (d, J = 8.9 Hz, 2H), 7.57 (d, J = 2.5 Hz, 2H); $^{13}$C NMR (toluene d8): $\delta = 14.2, 23.1, 23.2, 26.7, 27.2, 29.8, 29.9, 30.0, 30.1, 30.2, 30.3, 31.7, 32.4, 32.5, 33.2, 35.5, 69.1, 108.0, 109.0, 112.7, 113.3, 138.1, 141.3, 147.9, 157.6, 169.0, 181.7. Elemental analysis for C70H114O6N4Ni2: calculated: C 68.61%; H 9.40%; N 4.57. Found: C 68.57%; H 9.43%; N 4.56%.

3-Cu

Elemental analysis for C70H114O6N4Cu2: calculated: C 68.08%; H 9.32%; N 4.50. Found: C 68.11%; H 9.33%; N 4.50%.

4-Ni

$^1$H NMR (toluene d8): $\delta = 0.88-1.80$ (m, 124H), 2.24 (t, J = 7.6 Hz, 4H), 2.24 (t, J = 7.3 Hz, 4H), 3.88 (t, J = 6.4 Hz, 4H), 3.91 (t, J = 6.4 Hz, 4H), 6.76 (s, 2H), 6.81 (s, 2H), 7.63 (s, 2H); $^{13}$C NMR (toluene d8): $\delta = 14.2, 23.1, 23.2, 26.8, 26.9, 27.193, 29.8, 30.0, 30.1, 30.3, 30.4, 31.8, 32.4, 32.5, 33.2, 35.6, 70.2, 71.3, 103.1, 109.0, 113.6, 141.2, 147.7, 148.2, 148.5, 168.0, 182.0. Elemental analysis for C86H146O8N4Ni2: calculated: C 69.71%; H 9.95%; N 3.78. Found: C 69.66%; H 9.97%; N 3.75%.

4-Cu

Elemental analysis for C86H146O8N4Cu2: calculated: C 69.25%; H 9.85%; N 3.76. Found: C 69.27%; H 9.80%; N 3.80%.

5-Ni

$^1$H NMR (toluene d8): $\delta = 0.82-1.88$ (m, 116H), 2.33 (t, J = 7.8 Hz, 4H), 2.57 (t, J = 7.8 Hz, 4H), 3.64 (t, J = 6.4 Hz, 4H), 3.81 (t, J = 6.5 Hz, 4H), 6.78 (s, 2H), 7.07 and 7.38 (AA’BB’, J = 8.0 Hz, 8H), 7.07 (s, 2H), 7.56 (s, 2H); $^{13}$C NMR (toluene d8): $\delta = 14.2, 14.3, 23.1, 23.2, 26.6, 26.7, 29.5, 29.6, 29.9, 29.8, 30.0, 30.1, 30.3, 31.8, 31.9, 32.3, 32.4, 32.5, 33.5, 36.5, 69.7 71.0, 101.0, 107.8, 109.9, 125.5, 129.3, 131.7, 137.8, 140.5, 143.6, 148.3, 148.7, 149.0, 168.0, 177.0. Elemental analysis for C86H146O6N4Ni2: calculated: C 71.55%; H 9.35%; N 3.55. Found: C 71.57%; H 9.39%; N 3.52%.

5-Cu

Elemental analysis for C86H146O6N4Cu2: calculated: C 71.11%; H 9.29%; N 3.53. Found: C 71.06%; H 9.32%; N 3.53%.
6-Ni
$^1$H NMR (CDCl$_3$): $\delta$ = 0.84-1.86 (m, 150H), 3.83-3.97 (m, 20H), 6.19 (d, $J = 6.6$ Hz, 2H), 6.53 (d, $J = 8.9$ Hz, 2H), 6.70 (s, 2H), 6.96 (d, $J = 6.6$ Hz, 2H), 7.31 (d, $J = 8.9$ Hz, 2H), 7.35 (s, 2H); $^{13}$C NMR (toluene d$_8$): $\delta$ = 14.1, 14.1, 14.1, 22.7, 22.7, 22.7, 25.9, 26.0, 26.2, 29.2, 29.3, 29.4, 29.5, 29.6, 30.4, 30.5, 31.8, 31.9, 68.6, 69.3, 69.7, 73.7, 74.5, 98.5, 99.1, 106.6, 107.7, 124.59, 125.1, 129.8, 139.8, 141.8, 145.4, 146.6, 147.4, 151.7, 154.9, 166.7, 171.8. Elemental analysis for C$_{112}$H$_{182}$O$_{14}$N$_4$Ni$_2$: calculated: C 69.83%; H 9.54%; N 2.91. Found: C 69.81%; H 9.58%; N 2.87%.

6-Cu
Elemental analysis for C$_{112}$H$_{182}$O$_{14}$N$_4$Cu$_2$ calculated: C 69.48%; H 9.49%; N 2.87. Found: C 69.51%; H 9.50%; N 2.83%.

The synthetic procedure of the starting material b (4-octyloxy-1,2-diaminobenzene) when $R_2 = H$ is presented in Scheme S2.

Scheme S2 Synthetic route to b with $R_2 = H$

This compound (b) was obtained according to modified procedure for synthesis of 2-nitro-4-butoxyacetanilide.$^4$ 13g (0.05 mol) of octyloxyacetanilide was dissolved in 50 ml AcOH and the solution of 25 ml HNO$_3$ (d=1.4 g cm$^{-3}$) in 20 ml of AcOH was added; the mixture was stirred for 1h at temperature below 5 °C. Then 300 ml of water was added. The precipitate was filtered off and washed with water. The crude product was crystallized from hexane to obtain yellow crystals of 2-nitro-4-octyloxyacetanilide. (yield 85 %, m.p.74 °C)

$^1$H NMR (CDCl$_3$, 200 MHz, $\delta$): 0.89 (t, $J=6.8$ Hz, 3H), 1.24-1.84 (m, 12H), 2.27 (s, 1H), 3.98 (t, $J=6.6$, 2H), 7.22 (dd, $J=2.9$, 9.3 Hz, 1H), 7.65 (d, $J=2.9$ Hz, 1H), 8.62 (d, $J=9.3$ Hz, 1H), 10.06 (s, 1H).

2-nitro-4-octyloxyacetanilide was hydrolysed in HCl. The product 2-nitro-4-octyloxyaniline was precipitated from reaction mixture after dilution with water, then dried and crystallized from hexane (yield 90 %, m.p.58 °C)

$^1$H NMR (CDCl$_3$, 200 MHz, $\delta$): 0.89 (t, $J=6.8$ Hz, 3H), 1.23-1.80 (m, 12H), 3.92 (t, $J=6.6$, 2H), 5.88 (s, 2H), 6.75 (d, $J=9.3$ Hz, 1H), 7.07 (dd, $J=2.9$, 9.3 Hz, 1H), 7.54 (d, $J=2.9$ Hz, 1H).

2-nitro-4-octyloxyaniline was reduced with SnCl$_2$ in concentrated HCl according to method proposed for 2-nitro-4-butoxyaniline.$^5$ The isopropanol was added to reaction mixture in the same volume as HCl solution. After the reaction, liquid-like ingredients were evaporated to dryness under the vacuum. The residue was dissolved in water and alkalized with
concentrated NaOH. The product \textit{4-octyloxy-1,2-diaminobenzene}, (b) was extracted with Et\textsubscript{2}O, dried with anhydrous K\textsubscript{2}CO\textsubscript{3} and crystallized with hexane. (yield 60\%, m.p. 55 °C). \textit{1H} NMR (CDCl\textsubscript{3}, 200 MHz, \textit{δ}): 0.88 (t, \textit{J}=6.8 Hz, 3H), 1.22-1.76 (m, 12H), 3.24 (wide signal, 4H), 3.85 (t, \textit{J}=6.5 Hz, 2H), 6.25 (dd, \textit{J}=2.9, 8.3 Hz, 1H), 6.31 (d, \textit{J}=2.9 Hz, 1H), 6.61 (d, \textit{J}=8.3 Hz, 1H).

mass spectroscopy: m/z = 237.3 [M + H]+

The synthesis of the starting material \textit{b (4, 5-dioctyloxy-1,2-diaminobenzene)} when R\textsubscript{2} = OC\textsubscript{8}H\textsubscript{17} was described in\textsuperscript{6}