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Chapter 4

[Rh\(^1\)(Br)(2,2':6',2''-Terpyridine)]: Easy Access to the Synthesis of Neutral Octahedral Rh(III)-based Metallomesogens Displaying Lyotropic Mesomorphism with Dichloromethane.

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Abstract

Rh1-terpyridine complexes are rigid (Chapter 2) and reactive towards carbon-halide bonds (Chapter 3). These two properties of complex [Rh-Bin2.2 / 6.2-terpyridine] 1 were used to synthesise lyotropic liquid crystals. For this, complex 1 was reacted with the highly flexible dendrimer wedge [BrCH –Sn(CH2)4SnCH2CH2Br = (G2)]. The oxidative addition reaction of 1 with G2 gave complex [Rh –CH2CH2Sn(CH2)4SnCH2CH2Rh –Br(lpy)2 = Lpy = 2.2 (2’6’2”-terpyridine)]. Complex 2 showed lyotropic liquid crystalline behaviour in the presence of small amounts of CHCl3. Possible stacking interactions between monomers of complex 2 in CDCl3 were studied with 1H NMR techniques.

Within the liquid crystalline phases, the Rh terpyridine moiety of complex 2 is responsible for a degree of orientational order through anisotropic intermolecular interactions, while the dendrimer part of complex 2 is responsible for some flexibility/ordor. The order of the molecules in the lyotropic liquid crystalline phase lies between that of completely ordered solid crystalline phases and fully isotropic liquid phases. The lyotropic liquid crystals of complex 2 were studied with a polarised optical microscope and X-ray (powder) diffraction techniques. The space group and unit-cell volume of complex 2 could be determined (Pnca and ca. 12,100 Å3, respectively), while the orientation of the correlating monomers 2) within the lyotropic liquid crystalline phase is unknown.

Based on the obtained results and semi-empirical calculations, the structure and intermolecular orientation of the lyotropic liquid crystals has been simulated.
Introduction

Since the synthesis of the Ni-based mesomorphic dithiolene complexes was reported by Giroud-Godquin and Mueller-Westerhoff in 1977, many metal-containing liquid crystals have been synthesised by complexing metals with mesomorphic organic ligands. The rapid growth in number of metallomesogens is due to the expected advantages of combining the properties of liquid crystal phases with those of the incorporated metals. Accordingly, specific properties such as colour, paramagnetism, electric conductivity, and chirality can be more easily obtained with metal-organic complexes than with purely organic compounds. Molecular properties such as polarizability or hyperpolarizability can be enhanced by the presence of metals. Furthermore, the inclusion of metals into mesogenic materials enables the formation of new molecular geometries (octahedral, trigonal bipyramidal, etc.), and consequently the formation of new metastable phase types.

Up till now, the standard approach towards new metal-containing liquid crystal systems involved modification of promising ligands to obtain materials displaying mesomorphic behaviour. Frequently used ligands for this purpose are mesomorphic oligopyridines, since they easily form well-defined chelate complexes with many metals. The use of modified 2,2',6,2'-terpyridines for the synthesis of metal-containing liquid crystal phases has not received much attention in literature. The vast majority of mesogenic metal-containing complexes exhibiting liquid crystal behaviour are derived from d-10 transition metals. A few examples of rhodium-based liquid crystals have been described including dicarbonylrhodium(II)-β-diketonates, Rh(II)-4′-alkoxyaniline and 4′-alkoxy-2,2′-bipyridine complexes. Furthermore, Rh(II) dimetallic complexes with Schiff base-salen type ligands have been modified to promote mesomorphism. The use of Rh(III) metallomesogens is mostly restricted to the synthesis of liquid crystals of fatty acids. These bimetallic metal-metal bonded compounds are known as rhodium soaps of the general formula [CH2CH₂CO₂]Rh₃. Organometallic liquid crystals based on octahedral Rh(III) metallomesogens have only been mentioned by Rourke et al.

In general, liquid crystals are materials exhibiting intermediate structures. The characteristic order of liquid crystals lies between the fully ordered solid crystalline phases and the completely isotropic liquid phases. There are many different types of liquid crystalline phases. These phases are
characterised and classified according to molecular ordering that constitutes the phase structure. Two of them are relevant for the present study. The so-called nematic phase is characterised by an absence of positional order and the orientation of the long axis of the molecules along a given direction. The smectic phase exhibits the same type of orientational order, with in addition a positional order in one direction. This means that the molecules form layers. Different types of order inside the layers are possible. The molecules can for instance be perpendicular to the layers, as in smectic A phases, or tilted with respect to the layers as in smectic C phases. In all liquid crystalline phases, the mean orientation of the molecules, also called director, defines the optical axis of the material.

One strategy to obtain metallomesogenic liquid crystals is the incorporation of a flexible and a rigid part in the building block. The metal-containing rigid part provides strong enough anisotropic intermolecular interactions to induce orientational order. In contrast, the flexible part provides the material structure with the necessary disorder to have some degree of translational freedom. The observation that Rh-Bi-terpyridine complexes undergo oxidative addition very easily with 1-Bi-alkanes (Chapter 3), prompted us to investigate the simple oxidative addition reaction of the rigid complex \([\text{Rh}^{+}\text{Br}]+\text{tpy}\), 1, Tpy = 2,2'-6,2'-terpyridine and the highly flexible dendrimer wedge \(\text{G}_2\) \(\text{[Br}_{1}\text{CH} = \text{CH}_{1}\text{Si} \text{CH}_{2} \text{CH} = \text{CH}_{1}\text{Si} \text{CH}_{2} \text{CH} = \text{CH}_{1}\text{Si} \text{CH}_{2} \text{CH} = \text{CH}_{1}\text{Si} \text{CH}_{2} \text{CH} = \text{CH}\text{Br}]\). We expected that the product could exhibit liquid crystalline behaviour, since it contains rigid and flexible parts. Surprisingly, the use of oxidative addition reactions with a range of alkyl halides to prepare metallomesogens has not been thoroughly investigated yet, although it is known that the oxidatively added ligands on metals of metallomesogenic liquid crystalline materials can dramatically alter the liquid crystalline properties. In this chapter we report the synthesis and properties of the neutral octahedral RhIII complex 2 \([\text{Br}_{1}\text{CH} = \text{CH}_{1}\text{Si} \text{CH}_{2} \text{CH} = \text{CH}_{1}\text{Si} \text{CH}_{2} \text{CH} = \text{CH}_{1}\text{Si} \text{CH}_{2} \text{CH} = \text{CH}_{1}\text{Si} \text{CH}_{2} \text{CH} = \text{CH} \text{Br}]\text{tpy}\) (Scheme 4.1). We observed that lyotropic liquid crystals of complex 2 were formed, when solutions of 2 in CHCl3 were almost completely dried under air atmosphere i.e., high concentrations of complex 2). To investigate if molecules of 2 interact with each other also at relatively low concentration, possible stacking interactions i.e., indefinite self-association \(\text{i}\) were studied with 1H NMR techniques. During the evaporation of the solvent, these interactions could be partly responsible for the formation of the lyotropic liquid crystals.
Upon prolonged standing at room temperature under air atmosphere, lyotropic liquid crystals changed into pure solid crystals suitable for X-ray powder diffraction studies, from which the crystal symmetry and cell-unit could be determined.

COD = 1,5-cyclooctadiene

Scheme 4.1. The in situ synthesis of complex 2.

In order to gain more insight in the criteria to be met in respect to the relationship between size of dendrimer wedge and successful formation of liquid crystals, two other complexes were synthesised comprising a smaller and larger generation (respectively) of the G family. For this purpose, we have synthesised complexes \([\text{CH}_2\text{CHCH}_2\text{Si(CH}_2)_3\text{Rh(Br)}_2\text{(Tpy)}]\) (3) and \([\text{Br(CH}_2)_3\text{Si(CH}_2\text{CH=CH}_2)_3]\) (G1) and \([\text{Br(CH}_2)_3\text{Si}[\text{CH}_2\text{Si(CH}_2)_3\text{(Si(CH}_3)_3]]]\) (G3), respectively.

Scheme 4.2. The syntheses of complexes 3 and 4.
Experimental Section

General. The *in situ* syntheses of complexes 2-4 were performed in an inert atmosphere (purified argon), by using standard Schlenk techniques. Solvents were dried and purified by standard procedures. Attempts have been made to purify complex 4 by size-exclusion chromatography (SEC) over BioBeads-SX-1, using CH₂Cl₂ as an eluent. ¹H NMR spectra of complex 2-4 were recorded at 294K, with a Varian Mercury 300 spectrometer operating at 300 MHz for ¹H. Attempted stacking interaction (self-association) of complex 2 was studied with a Varian Inova 500 spectrometer operating at 500 MHz for ¹H. ¹³C NMR spectrum of complex 2 was recorded at 294 K, with a Varian Inova 500 spectrometer operating at 125.6 MHz for ¹³C. The assignment of ¹H NMR signals of complex 2-4 is partly based on 2D NMR techniques. Fast Atom Bombardment (FAB⁺) mass spectrometry was carried out using a JEOL JMS SX/SX102A four-sector mass spectrometer, coupled to a JEOL MS-7000 data system. The samples were loaded in a matrix phase (glycerol) on a stainless steel probe and bombarded with xenon atoms with an energy of 3 KeV. During the high resolution FABMS measurements a resolving power of 5000 (10% valley definition) was used. CsI and glycerol were used to calibrate the mass spectrometer. Elemental analyses were carried out by H. Kolbe Mikroanalytisches Laboratorium (Mülheim an der Ruhr, Germany).

Syntheses.

[![Chemical structure of complex 2](image)]

At room temperature, a solution of 0.130 g of [Rh(Br)(COD)]₂ (0.22 mmol) and 0.163 g of Tpy (0.45 mmol) in EtOH was refluxed for 10 minutes. After cooling to room temperature, 3.5 g of G2 (4.8 mmol) was added to the dark blue suspension of complex 1. After stirring overnight at room temperature, a yellow suspension was formed. The solids were precipitated by centrifugation. After decanting of the supernatant liquid, the solids were washed with pentane (3×10 ml). The remaining solids were purified from uncharacterised brown side-products by dissolving selectively (based on difference in
Synthesis of lyotropic liquid crystals with Rh(I)-Tpy complex and dendrimer-wedge solubility in mixtures of CH₂Cl₂ and pentane) the yellow products. After filtering the side products, the product was dried by removing the solvent under reduced pressure (10⁻⁵ bar) for 16 hours. 0.46 g of complex 2 (90% yield) was collected as a yellow powder.

**¹H NMR** (300 MHz Mercury, CD₂Cl₂, δ): 9.52 (d, 5.7 Hz, 2H(6,6″)), 8.18-8.10 (m, 5H(3″,3′,5″,5′′,4″′)), 8.02 (t, 8.4 Hz, 2H(4,4″)), 7.62 (t, 6.6 Hz, 2H(5,5″)), 5.78 (m, 9H(16)), 4.86 (m, 18H(17)), 2.06 (dt, 8.7 Hz, 2J(Rh,H) = 2.7 Hz, 2H(7)), 1.59 (m, 2H(8)), 1.55 (d, 8.1 Hz, 18H(15)), 1.14 (m, 6H(12)), 0.63 (m, 2H(9)), 0.52 (t, 8.4 Hz, 6H(11)), 0.27 (t, 8.4 Hz, 6H(13)).

**¹³C {¹H} NMR** (500 MHz Inova, CD₂Cl₂, δ): 156.62 (C2′,C6′), 155.41 (C2,C2″), 155.01 (C6,C6″), 138.21 (C4,C4″), 137.26 (C′), 134.82 (C16), 127.98 (C5,C5″), 123.40 (C3,C3″), 122.64 (C3′,C5′), 113.45 (C17), 34.63 (C7), 26.45 (C8), 19.87 (C13), 18.26 (C12), 17.47 (C11), 16.63 (C15), 14.28 (C9).

FAB' MS: m/z 1064.36 [M⁺-Br].

Calculated for C₆₃H₆₆N₃Si,RhBr₂: C 56.58%, H 7.03%, N 3.67%, Si 9.80%, Br 13.94%; found C 56.51%, H 7.11%, N 3.63%, Si 9.75%, Br 13.85%.

**[CH₂=CHCH₂]₂Si(CH₂)₃Rh(Br)₂(Tpy), 3**

At room temperature, a solution of 0.006 g of [Rh(Br)(COD)]₂ (0.01 mmol) and 0.005 g of Tpy (0.02 mmol) in EtOH was refluxed for 10 minutes. After cooling to room temperature, 0.2 g of G1 (0.73 mmol) was added to the dark blue suspension of complex 1. After stirring overnight at room temperature, a yellow suspension was formed. The solids were precipitated by centrifugation. After decanting of the supernatant liquid, the solids were washed with pentane (3×10 ml). After drying the product by removing the solvent under reduced pressure, 0.012 g of complex 2 (0.017 mmol = 87% yield) was collected as a yellow powder.

**¹H NMR** (300 MHz Mercury, CD₂Cl₂, δ): 9.51 (d, 2H(6,6″)), 8.15 (m, 5H(3″,3′,5″,5′′,4″′)), 8.10 (t, 8.4 Hz, 2H(4,4″)), 7.63 (t, 6.6 Hz, 2H(5,5″)), 5.51 (m, 3H(12)), 4.65 (m, 6H(13)), 2.09 (dt, 8.7 Hz, 2J(Rh,H) = 2.8 Hz, 2H(7)), 1.29 (d, 8.1 Hz, 6H(11)), 0.63 (m, 2H(8)), 0.32 (m, 2H(9)).

FAB' MS: m/z 608.06 [M⁺-Br].

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[[(CH₃)₃Si(CH₂)₃Si(CH₂)₃Si(CH₂)₃Rh(Br)₂(Tpy)], 4

At room temperature, a solution of 0.016 g of [Rh(Br)(COD)]₂ (0.03 mmol) and 0.013 g of Tpy (0.06 mmol) in EtOH was refluxed for 10 minutes. After cooling to room temperature, 0.4 g of G₃ (0.30 mmol) was added to the dark blue suspension of complex 1. After stirring for several days, a yellow suspension was formed. After centrifuging the mixture, the wet phase was separated from the brownish solids (side products). After removing the solvent under reduced pressure, the remaining yellow oil was purified by SEC (cf. experimental section). After removing the eluent (CH₂Cl₂) under reduced pressure, 0.01 g of a mixture of complex 4 and another uncharacterised product (A) was collected as a yellow oil. ¹H NMR measurement of this mixture reveal a product distribution of 4:A = 70:30 (9.4% yield).

¹H NMR (300 MHz Mercury, CD₂Cl₂, δ): 9.51 (d, 5.4 Hz, 2H(6.6")), 8.14-7.85 (m, 7H(3.3";3.5";4.4";4")), 7.60 (m, 2H(5.5")), 2.05 (m, 2H(7)), 1.70 (m, 2H(8)), 1.32 (m, 18H(16)), 1.06 (m, 6H(12)), 0.54 (m, 38H(17,15,9)), 0.39 (m, 6H(13 or 11)), 0.21 (m, 6H(13 or 11)), -0.04 (s, 81H(19)).

FAB+MS: m/z 1734 [M⁺-Br]. Due to complications (e.g. impurity), no absolute mass could be found for complex 4.

**Determination mesogenic textures of complex 2.**

The textures of metallomesogenic phases were observed under a Leica DM IRB polarising optical microscope at room temperature. Solutions with different concentrations of complex 2 dissolved in CH₂Cl₂ (0.08-0.2 M) were prepared. Drops of these solutions were placed on glass slides. The drying processes were monitored under the optical polarising microscope between crossed polarisers. Isotropic materials appear then dark while anisotropic materials transmit some light with an intensity depending on the degree of anisotropy and the orientation of the optical axis with respect to the polarisers of the microscope. The different structures of liquid crystalline phases lead to characteristic optical textures that can be used to identify these phases.[42]

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Possible stacking interaction (self-association) of complex 2.

The formation of lyotropic liquid crystals of complex 2 in the presence of CHCl₃ occurs at relatively high concentrations of complex 2 (weight ratio complex 2:solvent > 1:2.5). To investigate intermolecular interactions of complex 2 molecules in solvent at lower concentrations, the assumed self-association through stacking interactions was monitored by ¹H NMR techniques. The latter interactions should influence certain ¹H chemical shifts of complex 2, compared to those of the non-self-associated molecules of 2. The stacking interactions could be partly responsible for the formation of the observed lyotropic liquid crystals when solvent evaporated.

X-ray powder diffraction measurement of complex 2.

In order to measure the powder diffractogram of complex 2, three different instruments have been used.

*Günnier-Johansson camera*

This instrument was used because of its excellent resolution, combined with easy sample preparation. The Günnier-Johansson camera makes use of an incident Johannson monochromator, which is a large single crystal, cut and oriented to diffract the Kα₁ component of the incident radiation. This monochromator is also bent and its curvature is designed to use the whole surface of the crystal to diffract simultaneously, thus yielding a large diffracted intensity. As a consequence of this curvature and the orientation of the crystal, the monochromator not only separates Kα₁ from Kα₂ easily, but converts the divergent incident beam to an intense convergent diffracted beam focussed onto a sharp line. The monochromator is placed in such a way that this line coincides with the photographic film. In the Günnier camera the convergent Kα₁ beam irradiates the sample that is located on the same circle where the film is placed. As a consequence of the focussing of the primary beam, also all diffracted beams will be focussed on the film, resulting in a high-resolution diffraction diagram (full width at half maximum = ca. 0.06° 2θ).

The amount of material needed is small; usually ca. 5 mg, if needed even less.
**Synthesis of complexes 2-4.**

Complex 2 was synthesised at room temperature in situ using freshly distilled H2O as solvent, sodium as drying agent as solvent (Scheme 4.1). The synthesis of 2 is most successful when using also freshly prepared dendrimer wedge G2, since G2 is prone to polymerisation. Complex 2 dissolves very easily in various organic solvents other than alkane and prone polar solvents.
CHCl₃, CH₂Cl₂, benzene, toluene, Et-O, THF). At high concentrations (>0.2 M in CH₂Cl₂),
complex 2 forms nematic lyotropic liquid crystal phases as observed using an optical polarised
microscope.

The synthesis of complex 3 is almost instantaneously. Like complex 2, complex 3 is also a
yellow solid. However, in contrast to complex 2, complex 3 is poorly soluble in organic solvents,
and showed no liquid crystalline behaviour.

The complete conversion of starting material to complex 4, under the applied reaction
conditions, takes several days. To separate complex 4 (yellow oil) from G3 (colourless oil), the
SFC technique was used. Unfortunately, the purification of complex 4 was not possible, since the
unknown compound A co-eluted with complex 4. Based on very similar 1H NMR signals and the
coe-lution of A with 4, both products must be fairly similar in structure and size. Complex 4
dissolves in many organic solvents, and the mixture complex 4 and compound A showed no liquid
crystalline behaviour.

Complexes 2-4 are air and thermally stable.

Observation of metallomesogenic textures of complex 2 with CH₂Cl₂.

When drops of solution of complex 2 in CH₂Cl₂ were drying, the isotropic liquid phase was
found, under polarised optical microscope, to change into a liquid crystal phase (Figure 4.1). This
was best observed starting with highly concentrated solutions of 2 (>0.2 M in CH₂Cl₂). The
solution in the isotropic phase is black and the dried liquid crystalline phase left behind by the
evaporation of CH₂Cl₂ is brightly coloured (blue). When the solvent evaporates (weight ratio
material:solvent > 1:2.5), the front line between the solution and the dried area migrates in the
direction of the white arrow (Figure 4.1). Close to the dried phase, in the solvent-rich phase small
areas of liquid crystalline phases are already observable as light regions (e.g. the region at the start
of the white arrow in Figure 4.1). A flow could be observed in the solvent poor phase close to the
front line between the solution and dried phase. This indicates that these anisotropic regions are
liquid.
Figure 4.1. Formation of a liquid crystalline phase, based on complex 2, upon evaporation of CH₂Cl₂.
The white arrow indicates the direction of motion of the front between the isotropic liquid (dark) and the dried liquid crystalline phase (light). The white bar is 100 μm long.

When the solvent is fully evaporated, the texture of the liquid crystalline phase is immobilised by the glass substrate. This substrate-induced memory effect is a known phenomenon for both thermotropic and lyotropic liquid crystals. The resulting texture depends on the concentration of the solution deposited on the glass. When a drop of dilute solution of complex 2 (<0.05 M in CH₂Cl₂) is dried at room temperature in air (Figure 4.2a), a texture appears at the edge of the initial droplet, while the rest remains dark. This texture is reminiscent of the one observed in very thin films of thermotropic nematic liquid crystals. When drops of a more concentrated solution of 2 (0.05-0.1 M in CH₂Cl₂) are dried, similar patterns can be observed at the edge of the droplet (left upper corner Figure 4.2b). However, moving towards the centre of the droplet, another type of texture can be observed. The latter can be characterised as Schlieren texture, and appears in the optical microscopy of bulk nematic and smectic C liquid crystalline phases under crossed polarisers when the director field exhibits defects. The dark streaks or brushes, which are typical for Schlieren textures, appear around disclinations, i.e. line defects arising from singularities in director field. At even higher concentrations of the initial solutions, the whole dried drop presents a
Synthesis of lyotropic liquid crystals with Rh(I)-Tpy complex and dendrimer-wedge

Schlieren texture (Figure 4.2c). The latter shows under the microscope a different pattern than in Figure 4.2b, because of a larger thickness of material left behind after the drying process.

![Figure 4.2a](image1.png) Texture formed after drying drop (<0.05 M).
The white bar is 100 µm long.

![Figure 4.2b](image2.png) Texture formed after drying drop (0.05-0.1 M).
The white bar is 100 µm long.

![Figure 4.2c](image3.png) Texture formed after drying drop (0.1-0.2 M).
The white bar is 100 µm long.

Drying a highly concentrated drop of sample 2 (0.2 M in CH₂Cl₂) renders the formation of various different types of textures along the radius of the drop (Figure 4.3a-d). This is possibly caused by the thickness gradient along the radius, and also the different drying history at different positions in the drop. At the edge of the dried drop (Figure 4.3b-c), similar textures are observed as seen in Figure 4.2a-c. In the middle of the radius of the dried drop, large areas with the same director orientation can be observed. This is evidenced by the appearance of rather large areas with a relatively uniform intensity (Figure 4.3d). In the centre of the dried drop, most probably, very small single crystals are grown (Figure 4.3a, inner part of the white circle).

All observed characteristics of the various studied textures of dried solutions of 2 in CH₂Cl₂ under the optical polarising microscope clearly indicate the formation of nematic or smectic lyotropic liquid crystalline phases of 2 in the presence of small amounts of CH₂Cl₂.

Attempts to observe thermally induced phase transitions of nearly dry liquid crystalline phases of complex 2 using DSC (Differential Scanning Calorimetry) (T = 20-200 °C) failed. No degradation
or melting of complex 2 was observed, indicating a high thermal stability and a melting point higher than 200 °C for complex 2. During DSC experiments, it is almost certain that all CH₂Cl₂ solvent molecules have evaporated out of the liquid crystalline phases at elevated temperatures.

As mentioned earlier, after drying, the studied lyotropic liquid crystal phase of complex 2 changed eventually into a dry solid phase containing very small single crystals, which were used for
powder diffraction studies (*vide infra*). Finally, after several months of standing at room temperature in air, larger crystals could be observed under the polarised microscope (Figure 4.4). Unfortunately, these single crystal plates were too thin for X-ray measurements.

![Figure 4.4. A representative single crystal plate of complex 2, formed after more than 30 days. The white bar is 100 μm long.](image)

**Monitoring self-association of complex 2.**

At different concentrations of complex 2, the chemical shifts of the aromatic protons H(5,5") and H(6,6") of complex 2 were measured (Table 4.1). The NMR signals of H(5,5") and H(6,6") shift slightly downfield with lowering in concentration of complex 2. The chemical shifts of H(5,5") and H(6,6") do not shift significantly at concentrations below 0.0025 M for complex 2. At different concentrations of complex 2, only aromatic ¹H NMR signals shifted slightly, while the ¹H NMR signals of the dendrimer moiety did not shift at all.

**Table 4.1.** Chemical shifts (ppm) of H(5,5") and H(6,6") in CDCl₃ at different concentrations of complex 2 (M).

<table>
<thead>
<tr>
<th>Concentration</th>
<th>0.075</th>
<th>0.015</th>
<th>0.0075</th>
<th>0.005</th>
<th>0.0025</th>
<th>0.0015</th>
<th>0.00015</th>
</tr>
</thead>
<tbody>
<tr>
<td>δH(5,5&quot;)</td>
<td>7.622</td>
<td>7.645</td>
<td>7.650</td>
<td>7.652</td>
<td>7.656</td>
<td>7.656</td>
<td>7.658</td>
</tr>
</tbody>
</table>
Complex 2 seems to undergo self-association with the involvement of the Tpy ligands in the studied concentration domain. The self-association process is possibly facilitated by π-π stacking interactions between the aromatic ring systems of monomers of complex 2.

The possible unstacked and stacked units (built from monomers) in solvent are in rapid equilibrium; the designations unstacked and stacked describe an average over many unspecific conformations. The average association constant for molecules of complex 2 in solvent has been calculated with curve-fitting software: k = 4.2 \times 10^9 \text{ mol}^{-1}. The relative amounts of bound species varies from 50% at the lower concentration studied (0.00015 M) to 86% at the higher concentration (0.075 M). The calculated chemical shifts for H6.5' and H6.6' obtained from the fitting procedure are 7.66 and 9.56 ppm for the free monomers and 7.57 and 9.45 ppm for the bound species.

X-ray powder diffraction study of crystalline complex 2.

The determination of crystal structures from single-crystal data has become routine, provided it is possible to grow suitable crystals (0.1-0.5 mm). If only polycrystalline powder is available then structure determination becomes complicated. In the last decade a number of groups have tried to tackle this problem and a couple of program packages that enable the calculation of the structure from the X-ray powder diffraction diagrams exist nowadays, for instance POWSIM[2][3] and SIRPOW.[7] The main problem in structure determination is the number of “single” reflections that can be extracted from a powder diffractogram. Especially for lower symmetries up to orthorhombic and larger structures the overlap of reflections prevents the extraction of reliable intensities especially at higher Q values.

Ideally, the polycrystalline material consists of many randomly oriented crystals with dimensions of ca. 0.1-10 μm. To measure a powder diffractogram, suitable for a structure determination, the crystals should not be smaller than 0.1 μm, because this would cause broadening of the reflection profiles leading to a decrease in resolution. Also crystals larger than 10 μm result loss in resolution. A decreasing number of crystallites will affect the crystal statistics.
and thus the reliability of the reflection intensities. Furthermore, the crystallites should have a random orientation in the specimen. Presence of texture will again affect the reliability of the intensities. Finally, the diagram should represent one single phase, although traces of contamination with a second phase does not present major problems.

X-ray powder diffraction studies of dried crystals of complex 2 have been done with three different techniques (Guinier-Johannson camera, Xpert powder diffractometer and Parallel beamline diffractometer at ESRF Grenoble). The samples used for each technique contain crystals formed after a different drying history. For the Guinier-Johannson camera, the crystals were grown on a thin polymer film. After ca. 3 days of drying, the crystalline phase was completely yellow and suitable for measurement. In the case of the Xpert powder diffractometer, the crystals were grown on a polymer disc. The yellow crystalline phase was already obtained after ca. 6 hours of drying. Finally, for the Parallel beamline diffractometer at ESRF, the sample was dried in a capillary. After 1-2 weeks of drying, the crystalline phase was yellow of colour.

Guinier-Johannson camera

After several trials (ca. 5 attempts) a diffraction diagram was recorded with good resolution (Figure 4.5). However, the occurrence of reflections of different profile widths indicates that the material possibly consists of a mixture of several phases. Attempts were made to eliminate a possible contamination by evacuation of the camera under reduced pressure, and by heating the specimen to moderate temperatures (up to 60 °C). After each attempt, a diffraction diagram was recorded. Since the diagrams remained essentially unchanged, it is likely that the diffraction diagram as shown in Figure 4.5 represents one single phase.
'Xpert powder diffractometer

As mentioned earlier, using this technique, two different specimens were prepared as described above. From the first specimen, a diffraction diagram was recorded with very low intensities (Figure 4.6). It could be possible that only a small part of the material was in the solid crystalline state, while the larger part was in liquid crystalline state. After drying, another measurement of the very same sample gave a diffractogram very similar to the second specimen (Figure 4.7).
With respect to the line positions, the diagram of the second specimen (Figure 4.7) is similar to the Guinier-Johannson diagram (Figure 4.5). However, since their diffraction intensities are very much different, it can be assumed that either or both the Guinier-Johannson specimen and the 'Xpert specimen are textured.
Figure 4.7. X-ray powder diffraction diagram of second specimen of complex 2, recorded with an 'Xpert powder diffractometer.

Parallel beamline diffractometer at ESRF

It is likely that the specimen for the ESRF diffractometer was less textured than the Guinier-Johannson and the 'Xpert diffractometer specimens, since the latter two specimens consist of a flat thin layer, while the ESRF specimen is a glass capillary (diameter 1.0 mm) filled with material. During the measurement the capillary is rotated (spinned) along its axis. With respect to the reflection positions, the resulting diagram (Figure 4.8) was found to be very similar to the Guinier-Johannson and the 'Xpert diagrams. In contrast, their intensities are completely different, which indicates that texture states are different for the three cases. The resolution of the ESRF measurement is better than for the other two measurements, while texture might be smaller.
Synthesis of lyotropic liquid crystals with Rh(I)-Tpy complex and dendrimer-wedge

Determination of the unit cell and the spacegroup of complex 2.

The first attempts to derive the unit cell and the spacegroup from the powder diagram were carried out before the measurement on the ESRF diffractometer was available. For these attempts the Guinier-Johannson diagram was used. To assess the correctness of a possible unit cell De Wolff\(^{58}\) proposed the use of a figure of merit \(M_{20}(1)\). This figure of merit should be applied to those unit cells, which will index practically all observed reflections. Moreover, the accuracy of reflection positions derived from the diagram is essential. After many attempts, using the indexing program ITO,\(^{59}\) the following orthorhombic unit cell could be derived from the Guinier-Johannson powder diagram using 49 reflections:

\[
\begin{align*}
    a &= 50.90 \, \text{Å} \quad \alpha = 90. \\
    b &= 16.64 \, \text{Å} \quad \beta = 90. \\
    c &= 14.37 \, \text{Å} \quad \gamma = 90. \\
\end{align*}
\]

unit cell volume = 12,171 Å\(^3\)
The spacegroup is most likely Pbcn, indicating an inversion of symmetry within the system unlike the complexes [Rh(CHO)ppy] and [RuCl(Carboxylate)ppy], described in Chapter 2, and the M1 value for this solution is 12. A complication is the large volume of this unit cell. The accuracy of the reflection positions derived from the Guinier-Johannson diagram allows unit cells to be derived which are not larger than c = 10,000 Å. This means that, although all remaining conditions for correct indexing have been fulfilled, there still remains some doubt with respect to the correctness of the unit cell.

After the measurement at ESRF, a powder diagram was available with an improved resolution, from which more accurate line positions could be derived with the program PROFIL. Using these reflection positions the orthorhombic unit cell could be refined to give the following values:

\[ a = 50.78 \text{ Å, } \alpha = 90, \text{ unit cell volume } = 12,000 \text{ Å}^3 \]
\[ b = 16.599 \text{ Å, } \beta = 90, \]
\[ c = 14.355 \text{ Å, } \gamma = 90. \]

The value of M1 increased to 35. The spacegroup is Pbcn. From the chemical formula [Cu2HBr4N3RhSi5], it follows that this unit cell contains 8 molecules, which is also the multiplicity of the general position of this spacegroup.

**Positioning of the molecule in the unit cell using simulation data.** With the knowledge of the unit cell and spacegroup of complex 2, several attempts have been made to elucidate its crystal structure. For this, two possible models were built with Cerius² from C-H-Br-Cu-N, which were taken from the CSD; recode CAIVOY. After changing Cu into Rh the rest of the molecule was added and energy minimization was performed, the resulting model was used for a grid-search procedure. For positioning the models in the asymmetric unit, 250 extracted intensities from the EPD were used in a grid-search technique (Chernyshev and Schenk, 1998). Unfortunately, all attempts to reach a satisfactory solution have failed. This is most likely due to the flexibility of the dendrimer moiety of the molecule.
Simulated structure of complex 2 by semi empirical calculations. To get some insight on the structural organisation of complex 2 within the lyotropic liquid crystalline phases, its structure is simulated with the Spartan program using the PM3 calculations (Figure 4.9a and 4.9b). It must be noted that PM3 is a very approximate method.

Since the rigid terpyridine ligand around the Rh atom is prone to π-stacking (Chapter 2), it is likely that complex 2 can form dimers as shown in Figure 4.9b. This dimer is depicted with an inversion symmetry, which is in accordance with the found space group Pbca of the measured crystals of complex 2. This dimer has one axis (whose projection in the plane of the terpyridine ligands is parallel to the Rh-Br bond in this plane) that is likely to present nematic or smectic-like orientational order.

Figure 4.9a. Simulated structure of complex 2.  

Figure 4.9b. Simulated dimer presentation of complex 2 with inversion of symmetry according to the determined spacegroup Pbca. The (large) arrow, crossing the two monomers, shows approximately the axis of the dimer that most probably exhibits the orientational order responsible for the occurrence of the liquid crystalline state. The projection of this axis (small arrow) is shown in the RhBr-Tpy plane of the top monomer.
Discussion

Like the RhIII-terpyridine complexes described in Chapter 3, the syntheses of complexes 2-4 are very facile. Although G1 and G2 are prone to polymerisation, complexes 2 and 3 showed no polymerisation during the various measurements for their characterisation.

After purification (work up) of complex 2, the complex displayed lyotropic liquid crystalline behaviour in the presence of small amounts of CHCl₃, as observed under a polarised microscope. The observed mesomorphic textures are typical for nematic and smectic C phases, which is further evidenced by the presence of Schlieren textures (Figures 4.2-3).

Another strong indication for the formation of a liquid crystalline phase has been observed while measuring a sample of 2 with the Xpert powder diffractometer. The recorded diffractogram (Figure 4.6) showed the presence of a significantly more ordered texture than a pure liquid phase, but far less ordered than a pure crystalline phase (Figure 4.7). It could be possible that this diffractogram (Figure 4.6) belongs to a liquid crystalline phase.

1H NMR studies of complex 2, at different concentrations, strongly indicate that only the aromatic protons interact with each other in solution. This could mean that the aromatic rings of the terpyridine ligands undergo stacking interactions (i.e. self-association), which supports the conformation of the simulated dimer depicted in Figure 4.9b. Unfortunately, from all the collected data concerned about the studied liquid crystalline phases of 2, it is impossible to conclude the statistical orientations of the discrete monomers in space without speculation. However, the structure shown in Figure 4.10 is in line with all data obtained. The fact that the molecules form a layered structure is reinforced by the shape of the single crystals obtained after drying (Figure 4.4): the plate shape is characteristic of the organisation in layers. The axis of the dimers is tilted with respect to the bilayer, which implies that the director (i.e. the mean orientation of the dimer axes) is also tilted, which corresponds to a smectic C phase.
It is unlikely that very small amounts of CH$_2$Cl$_2$ molecules (weight ratio complex 2:solvent > 1:2.5) can influence dramatically the organisation and orientation of complex 2 molecules, implying that the textures of the wet liquid crystalline and dry solid crystalline phases are very similar. Hence, the organisation and orientation of complex 2 in the liquid crystalline phase could be very similar to the organisation in single crystal plates (Figure 4.4) and to the simulated structures depicted in Figures 4.9 and 4.10.

The $^1$H NMR spectrum of the single crystals of complex 2, collected after several months standing at room temperature under air atmosphere, is exactly the same as for freshly synthesised powder of complex 2. This means that the studied structures are not affected by polymerisation processes.

Clearly, complex 3 showed no liquid crystalline behaviour. Based on the results, described in this chapter, for complex 4 it is not possible to conclude whether it has the capacities to display liquid crystalline behaviour, since relevant microscope observations were performed with impure samples of complex 4. However, based on similar $^1$H NMR signals and co-elution from SEC of complex 4 and compound A, it is highly likely that both products are chemically and physically similar to each other. From the fact that this mixture is an oil, it can be suggested that both compounds are an oil.
For the synthesis of cholotropic liquid crystals, certain criteria must be met, as explained earlier. Concerning the relative size of the rigid and flexible parts needed for liquid crystalline behaviour, it is clear that G2 is suitable to form, together with complex 1, chotropic liquid crystals. In contrast, G1 and G3 do not show, together with complex 1, any liquid crystalline behaviour. Likely, G1 is too small and G3 too large to form a good combination, with complex 1 to display liquid crystalline behaviour.

The approach presented in this chapter proves that the oxidative addition reactions can not only alter dramatically liquid crystalline phases but can also be used to form mesogenic liquid crystalline phases directly from non-mesogenic precursors. The reaction described here is easy to perform and allows one to use a wide variety of precursors to generate different types of mesogens. Thus, it provides a useful alternative to the standard strategy of first preparing a mesogenic ligand and then coordinating it to a metal.

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References.


