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Most of the nickel(II) complexes of tetradentate enaminoketone ligands obtained, although not strictly calamitic and with a rather low length to width ratio, form enantiotropic rod-like nematic and smectic A phases. Corresponding vanadyl(II) complexes exhibit only monotropic mesophases. The vanadyl complexes, due to their non-planar structure, are chiral with an asymmetry centre placed at the metal ion.

1. Introduction

Metallomesogens often possess molecular geometric shapes that are not readily attainable in purely organic materials. This provides opportunities to test the structural boundaries that support formation of liquid crystalline phases. Most liquid crystal molecules have an anisotropic rod-like or disc-like shape, which facilitates molecular ordering in a mesophase. We have designed and synthesised metallomesogens of an intermediate geometric shape, in which a transition metal ion is built into a single elongated tetradentate ligand. The complexes with the tetradentate ligands are known to be stable at high temperature and are resistant to moisture and air [1, 2]. The molecular structure of the compounds **1** is shown in the scheme. The structure is not strictly calamitic because of the nearly triangular shape of the central part of the mesogenic core—1,2-phenylene-diamine. To lengthen the core a phenyl ring is linked to one of the carbonyl groups. A terminal chain (R_3) substituted into the *para*-position of this phenyl ring mainly as an alkoxy group and another alkoxy group (R_1O) attached to the 1,2-phenylenediamine moiety are nearly collinear. These two alkoxy groups seem to set a long molecular axis. To break the molecular symmetry, an alkyl chain R_2 is linked to the second carbonyl group of the core. In the centre of the core, the transition metal ion: nickel(II) or vanadyl(II) (VO) is introduced. In the latter case, due to the low symmetry (C_s) of the organic ligand itself and the non-coplanar position of the vanadyl oxygen atom with respect to the donating atoms, the proposed vanadyl complex does not reveal any symmetry element (C_1). This allows us to expect some chiral
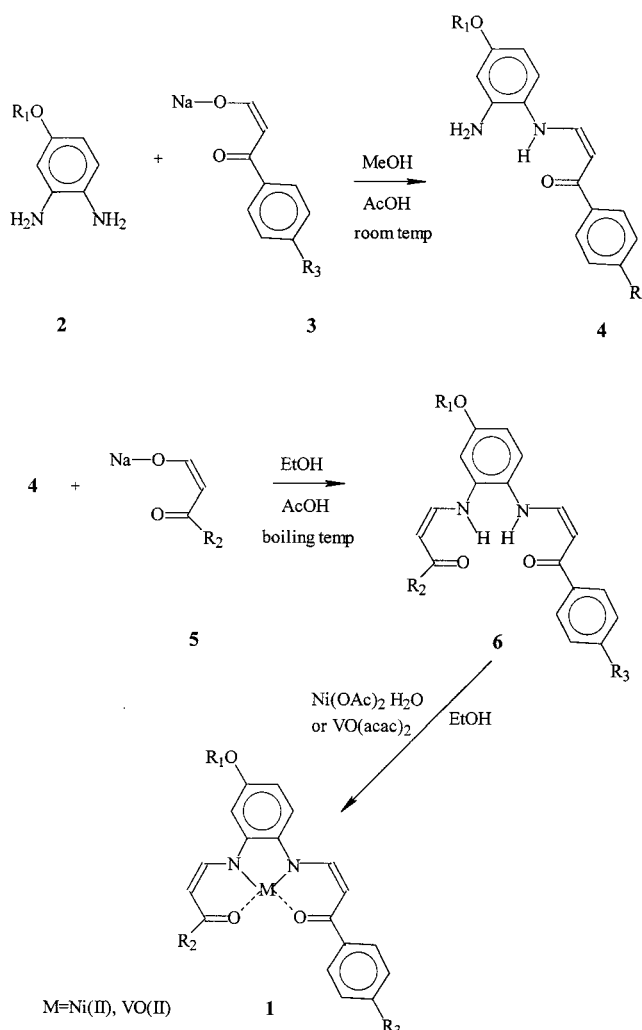
Scheme. Synthetic route for the tetradentate enaminoketone ligands and their complexes.

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properties in the vanadyl liquid crystals and the possible appearance of cholesteric, ferroelectric or antiferroelectric phases for pure enantiomeric materials.

2. Experimental
2.1. *Synthesis*

All the compounds **1** were prepared in a similar manner as described in [2]. The starting materials are well known substances and their synthesis is routine. A sketch of the applied synthetic procedure to obtain the complexes **1** is presented in the scheme. An appropriate 4-alkoxy-*1,2*-phenylenediamine **2** (1 mmol) and a formyl ketone derivative **3** (1 mmol) dissolved in methanol ($\sim 50 \, \text{cm}^3$) and neutralized with acetic acid reacted at room temperature selectively. The aroylvinyl group is joined only to the amine functionality in position 1, resulting in a crystalline intermediate **4**, which was purified by recrystallization from octane. (Yield $\sim 80\%$). A reaction between the remaining amino group of compound **4** (1 mmol) and another formyl ketone derivative **5** (1 mmol) proceeded similarly to the first step but at the boiling point of ethanol, giving rise to the tetradentate ligand **6**. To the mixture, without separation of **6**, a metal salt—nickel(II) acetate or vanadyl(II) acetyl-acetonate—(1 mmol) dissolved in hot ethanol was added. After boiling for 5 min and then cooling, the resulting precipitates **1** were filtered off and recrystallized from octane. (Yield $\sim 50\%$). The elemental C, H and N analyses for the complexes **1** were satisfactory, as shown by the examples below.

For {1-[3′-(4″-methoxyphenyl)-3′-oxo-1′-propenyl-amino]-2-[3‴-oxo-1‴-butenylamino]-4-octyloxybenzeno}-nickel(II) (see the table, compound 3): found C 64.42, H 6.63, N 5.30; calc. for $C_{28}H_{34}N_2O_4Ni$ (521.3), C 64.50, H 6.59, N 5.37%.

For {1-[3′-(4″-methoxyphenyl)-3′-oxo-1′-propenyl-amino]-2-[3‴-oxo-1‴-butenylamino]-4-octyloxybenzeno}-oxovanadium(IV) (see the table, compound 4): found C 63.38, H 6.51, N 5.19; calc. for $C_{28}H_{34}N_2O_5V$ (529.6), C 63.50, H 6.48, N 5.29%.

The ^{1}H NMR spectra (in CDCl$_3$) of the intermediates **4** and of the Ni(II) complexes **1** were obtained (Varian UNITY plus 500 MHz). They are consistent with the assumed structures without any sign of additives or impurities. As examples, we quote:

^{1}H NMR for **4** 1-[3′(4″-methoxyphenyl)-3′-oxo-1′-propenylamino]-2-amino-4-octyloxybenzene: δ 0.86–0.92 (m, 3 H, $(CH_2)_6 CH_3$), 1.24–1.80 (m, 12 H, $OCH_2(CH_2)_6$), 3.78 (s, 2 H, NH$_2$), 3.86 (s, 3 H, OCH$_3$), 3.89 (t, $J = 6.3$ Hz, 2 H, OCH$_2$), 5.95 (d, $J = 8.3$ Hz, H, H$^{2'}$), 6.33–6.37 (m, 2 H, H^{3,5}), 6.92–6.97 (m, 3 H, H$^{6,3'',5''}$), 7.28 (dd, $J = 12.2, 8.3$ Hz, H, H$^{1'}$), 7.90–7.94 (m, 2 H, H$^{2'',6''}$), 11.84 (d, $J = 12.2$ Hz, H, NH);

^{1}H NMR for **1** {1-[3′-(4″-methoxyphenyl)-3′-oxo-1′-propenylamino]-2-[3‴-oxo-1‴-butenylamino]-4-octyloxybenzeno}nickel(II): δ 0.86–0.92 (m, 3 H, $(CH_2)_6 CH_3$), 1.24–1.80 (m, 12 H, $OCH_2(CH_2)_6$), 2.20 (s, 3 H, OCCH$_3$), 3.84 (s, 3 H, OCH$_3$), 3.92 (t, $J = 6.3$ Hz, 2 H, OCH$_2$), 5.48 (d, $J = 6.3$ Hz, H, H$^{2'''}$), 6.08 (d, $J = 6.3$ Hz, H, H$^{2'}$), 6.60 (dd, $J = 9.3, 2.5$ Hz, H, H^5), 6.88 and 7.84 (AA′BB′, 4 H, H$^{2'',3'',5'',6''}$), 6.92 (d, $J = 2.5$ Hz, H, H^3), 7.31–7.35 (m, 2 H, H$^{6,1'''}$), 7.48 (d, $J = 6.3$ Hz, H, H$^{1'}$).
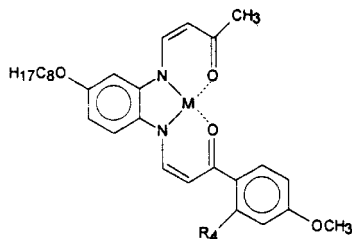
2.2. *Measurements*

For the identification of the mesophases, microscopic examinations of liquid crystalline textures were performed. A Zeiss Jenapol-U polarizing microscope equipped with a Mettler FP82HT hot stage was used. To determine phase transition temperatures, besides those obtained by the microscopic observations, calorimetric measurements were made using a Perkin-Elmer DSC7. Thermograms were taken from routine runs of the calorimeter mainly at a scanning heating rate of 5 K min^{-1}. If necessary other scanning rates (up or down) were applied and thermal effects were recalculated at the standard rate. X-ray scattering data were obtained from a DRON spectrometer, IR spectra were recorded by a Nicolet Magna IR 500 spectrophotometer and EPR spectra were taken in the X-band on a Radiopan spectrometer. Molecular dimensions were estimated by molecular modelling (HYPERCHEM).

3. Results and discussion

The mesomorphic properties—e.g. the phase sequences and phase transition temperatures—for the nickel(II) and vanadyl(II) complexes synthesized are gathered in the table. The octyloxy chain was used in the R_1O–group, since for this homologue the minimum in the melting temperature was usually observed [3]. Most of the nickel compounds reveal a simple polymorphism and form low ordered, liquid-like phases: the uniaxial smectic A and nematic phases. The broadest temperature range liquid crystalline phase (about 43 K of SmA phase) is observed for the nickel(II) complex *5* with both terminal groups (R_1O– and R_3) as octyloxy, directed along the molecular axis, and containing the shortest possible side chain ($R_2 = CH_3$). Elongation of the alkyl side chain does not destroy the mesomorphic properties entirely, but makes the liquid crystalline temperature range narrower. Use of a terminal alkoxy chain R_3 longer than eight carbon atoms does not improve the mesophase stability. Branching the chain of R_3 in compound *18* suppresses the clearing temperature and destabilizes the smectic phase. When an electron acceptor cyano group is introduced as R_3, it removes π-electrons from the mesogenic core and leads to a lowering the order of the phenyl–carbonyl bond that makes the core more flexible.

Table. Melting points, phase sequences, phase transition temperatures (in °C) and phase transition enthalpy changes (in parentheses, J g^{-1}) for the compounds synthesized.

Complex No.	R_1	R_2	R_3	R_4	M	Melting point	Phase sequence, phase transition temperatures and enthalpies
1	CH$_3$	CH$_3$	OC$_8$H$_{17}$		Ni	168.5 (56.0)	—
2	H$_{17}$C$_8$	CH$_3$	H		Ni	137.2 (30.6)	—
3	H$_{17}$C$_8$	CH$_3$	OCH$_3$		Ni	143.1 (29.1)	N–159.5 (0.43)–I
4	H$_{17}$C$_8$	CH$_3$	OCH$_3$		VO	165.2 (51.2)	N–145.3 (0.5)–I
5	H$_{17}$C$_8$	CH$_3$	OC$_8$H$_{17}$		Ni	123 (14.6)	SmA–166.5 (0.64)–N–168.3 (4.3)–I
6	H$_{17}$C$_8$	CH$_3$	OC$_8$H$_{17}$		VO	158.1 (41.5)	SmA–162.8 (5.2)–I
7	H$_{17}$C$_8$	C$_5$H$_{11}$	OC$_8$H$_{17}$		Ni	155.3 (32.3)	Microscopy reveals a narrow range N phase
7a	H$_{17}$C$_8$	C$_9$H$_{19}$	H		Ni	131.3 (47.0)	SmA–121.7 (7.4)–I
8	H$_{17}$C$_8$	C$_9$H$_{19}$	OCH$_3$		Ni	160.2 (54.4)	SmA–135[a]–N–140.5–I
9	H$_{17}$C$_8$	C$_9$H$_{19}$	OC$_8$H$_{17}$		Ni	138.1 (32.1)	SmA–144.1 (0.78)–N–147.3 (1.3)–I
10	H$_{17}$C$_8$	C$_9$H$_{19}$	OC$_8$H$_{17}$		VO	150.2 (31.9)	—
10a	H$_{17}$C$_8$	C$_9$H$_{19}$	OC$_{11}$H$_{23}$		Ni	158 (32)	SmA–131[a]–N–135.1 (0.6)–I
11	H$_{17}$C$_8$	C$_9$H$_{19}$	OC$_{12}$H$_{25}$		Ni	129.3 (23.8)	SmA–132.1 (.05)–N–137.6 (1.1)–I
13	H$_{17}$C$_8$	C$_9$H$_{19}$	CN		Ni	130.7 (64.8)	—
14	H$_{17}$C$_8$	C$_9$H$_{19}$	CN		VO	163 (56.2)	N–100[a]–I
15	H$_{17}$C$_8$	C$_{11}$H$_{23}$	H		Ni	115.2 (18.2)	SmA–122.4 (7.3)–I
16	H$_{17}$C$_8$	C$_{11}$H$_{23}$	OCH$_3$		Ni	145.0 (40.5)	SmA–139.7 (4.4)–I
17	H$_{17}$C$_8$	C$_{11}$H$_{23}$	OC$_8$H$_{17}$		Ni	121.5 (28.9)	SmA–143.0 (0.4)–N–143.7 (4.0)–I
18	H$_{17}$C$_8$	C$_{11}$H$_{23}$	OCH$_2$CH(CH$_3$)C$_2$H$_5$		Ni	118.0 (18.4)	SmA–138 (3.8)–I
19	H$_{17}$C$_8$	ΦOC$_8$H$_{17}$[b]	OC$_8$H$_{17}$		Ni	168.7 (23.8)	—

	R_1	R_2	R_3	R_4	M	Melting point	Phase sequence, phase transition temperatures and enthalpies
20	H$_{17}$C$_8$	CH$_3$	CH$_3$	F	Ni	127.3 (44.2)	N–116.0 (0.9)–I
21	H$_{17}$C$_8$	CH$_3$	CH$_3$	F	VO	136.5 (57.2)	N–113.7 (0.9)[a]–I N phase supercooled to room temperature
22	H$_{17}$C$_8$	CH$_3$	CH$_3$	H$_3$CO	Ni	132.6 (79.6)	N–66.7 (0.44)–I N phase supercooled to room temperature
23	H$_{17}$C$_8$	CH$_3$	CH$_3$	H$_3$CO	VO	63.4 (3.1)	— I phase supercooled to room temperature

[a] From microscopy
[b] Φ = phenyl

This results in a monotropic nematic phase only (*13*, *14*) and reflects the crucial role of delocalized, conjugated π-electrons on the mesogenic properties of a core composed of a few aromatic parts [4].

Shortening the terminal chain of R_1O– in the best liquid crystalline compound, *5*, gives compound *1*, which does not exhibit mesophases. This shows that shortening the length of the terminal chain (R_1) attached to the very stiff part of the core destroys mesophases much more drastically than cutting down the length of the chain (R_3) (*3*) substituted at the phenyl ring which is slightly stiffened by conjugation with the remaining part of the core.

The vanadyl complexes were shown to form liquid crystalline phases much more reluctantly than the nickel complexes. When mesomorphic (see the table), the phases are either weakly enantiotropic smectic A or monotropic nematic. The mesogenity of the vanadyl compounds is most evident when the related nickel complexes exhibit sufficiently broad mesophase temperature ranges.

Special attention was paid to the Ni and VO complexes with the aroyl moiety additionally *ortho*-substituted by fluorine (*20*, *21*) or a methoxy group (*22*, *23*). Relative to the non-substituted compounds (*3*, *4*), both melting and clearing temperatures are strongly depressed. However, the clearing temperatures are suppressed more than the melting points, and only monotropic nematic phases are observed. It is due to the introduced steric hindrance that the phenyl ring is twisted out of the plane of the enaminoketone group. This effect is more pronounced for the methoxy group, which is larger than fluorine. For the methoxy vanadyl complex *23*, this results in a molecular conformation that completely prevents liquid crystal formation, although compound *23* has a low melting point and the isotropic phase can be easily supercooled. For the vanadyl fluoro substituted complex *21*, the nematic phase can be supercooled to room temperature and is stable even for a few days.

It has been reported in the literature [5] that the smectic A phase created by nickel or vanadyl mesogenic complexes might involve a dimeric structure attributed to Ni…Ni or V=O…V=O interactions. To examine the possibility of dimer formation in the liquid crystalline phases of our compounds, X-ray, IR and EPR studies were carried out. The X-ray spectrum obtained for the smectic A phase of the nickel compound *9* is typical. A low angle peak related to the inter-layer distance (28.7 Å) and a single broad diffuse signal corresponding to the in-layer molecular distance (2.4 Å) were detected. The thickness of the smectic layer is, as usual, a little smaller than the molecular length (33.5 Å) calculated along the R_1O–, –R_3 terminal chains. The lack of any doubled high angle signal shows that the distance between molecules in the smectic layers is approximately

the same. Thus the existence of dimeric molecules in the smectic A phase must be excluded for the flat core nickel compounds studied.

As for the vanadyl complexes, the IR spectra for complex *4* in the solid state and in solution in dichloromethane were obtained. The positions of the peaks $w_{=O} = 987\,cm^{-1}$ and $w_{=O} = 990\,cm^{-1}$ related to V=O bond stretching for the solid and the solution, respectively, are very similar and correspond to monomeric vanadyl molecules [6]. Since dimer interactions do not appear in the crystal phase, we can assume that these specific interactions would not appear in the less organized liquid crystalline phases. Thus, we may conclude that the mesophases are formed by single molecules.

Additional confirmation of the monomeric structure of the compound *4* was taken from the EPR investigation. The EPR spectrum of the vanadyl complex in chloroform reveals eight well-separated peaks, which are typical for single vanadyl molecules. The EPR spectrum of the crystal or the nematic phase displays one broad non-informative signal, which is common for undiluted paramagnetic substances.

The supposed chiral properties of the oxovanadium complexes were proved by analysing the ^{1}H NMR spectrum of an isopropyl group attached as R_2 to a vanadyl compound. The examination of the isopropyl moiety signal is a well-known method for confirming the existence of a chiral centre in a molecular structure [7]. We synthesized two non-liquid crystalline model compounds with $R_1 = CH_3$, $R_2 = C(CH_3)_3$, $R_3 = CH_3$ and with $R_1 = CH_3$, $R_2 = CH(CH_3)_2$, $R_3 = CH_3$. For the first chiral substance, the three methyl groups of the *tert*-butyl substituent R_2 are equivalent and in the NMR spectrum a single broad peak at 1.68 ppm is observed (see the figure-*a*). This signal was used as an NMR standard position of a methyl moiety close to the vanadyl ion, which as a paramagnetic group always broadens and changes the positions of NMR peaks. In the second asymmetric complex, the geminal methyl groups of the isopropyl R_2 moiety produce two separate signals due to the different chemical shift related to each of the methyl groups. The positions of the two signals are identical for either of two enantiomers and were found to be 1.46 and 1.65 ppm (see the figure-*b*). The appearance of these two peaks in the NMR spectrum confirms the chiral properties of the oxovanadium complex in the NMR time scale.

Separation of the racemic mixtures obtained by synthesis into pure enantiomers is in progress.

4. Conclusions

The tetradentate enaminoketone complexes described, although forming exclusively rod-like phases (SmA and N),
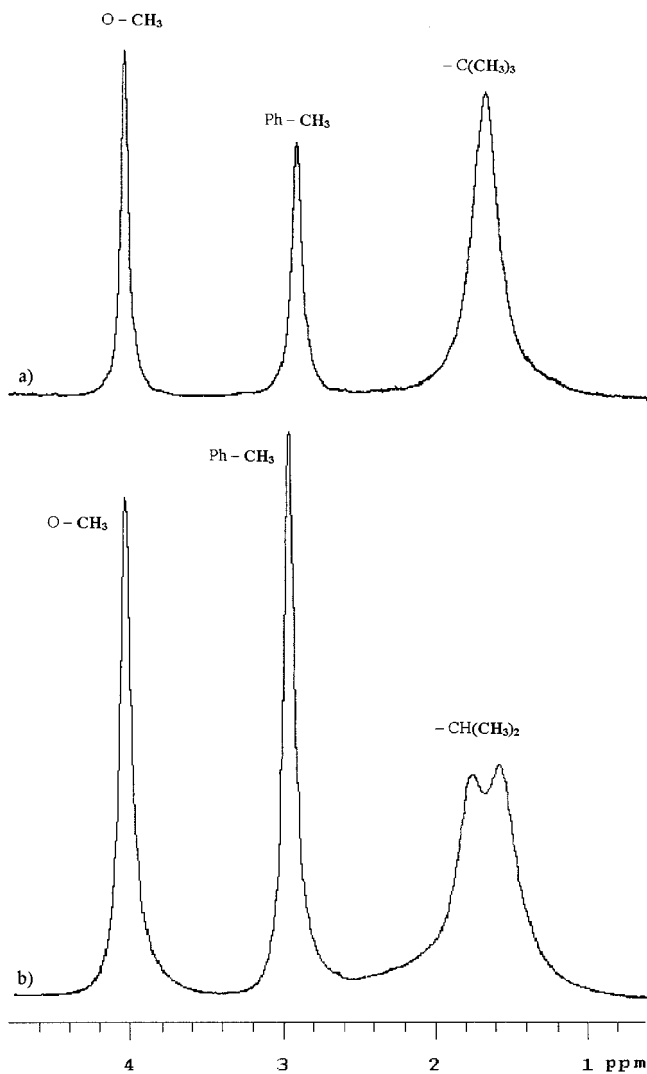
Figure. ^{1}H NMR signals of the vanadyl complex with $R_1 = CH_3$, $R_3 = CH_3$ and (*a*) $R_2 = C(CH_3)_2$ (*b*) $R_2 = CH(CH_3)_2$.

do not have a strictly calamitic molecular anisotropic shape because of their rather wide mesogenic core. The protruding moiety (with the R_2 chain) substantially disturbs arrangement of the molecules into meso-phases, but does not entirely eliminate liquid crystalline properties. The compounds studied exhibit a very low length to width ratio that weakly promotes mesogenicity

[8]. For the mesomorphic nickel complex *3* there was found a value for the L/D ratio as low as 2.3, whereas the substance *2* with a slightly smaller L/D ratio of 2.2 does not exhibit liquid crystal properties at all. These two ratios indicate the structural boundaries for formation of calamitic phases by the complexes studied.

For the compounds presented, it is supposed that in the SmA or N phases, the molecular rotation axis (C_∞) is situated along the R_1 and R_3 chains. The lateral substituent R_2, when sufficiently long, seems to be aligned parallel to the R_3 chains.

The vanadyl complexes generally give monotropic liquid crystalline phases. Their worse mesogenic properties, in comparison with the flat nickel complexes, can be attributed to the bowl-like shape of the molecular coordination plane and especially to the protruding V=O group. The resulting steric hindrances probably cause the lowering of the clearing temperatures. However, the properties of the vanadyl compounds remain promising and worthy of further studies because of the opportunity to obtain new chiral mesogens containing the asymmetric centre at the metal ion.

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