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Columnar metallomesogens based on vanadyl(VI) and cobalt(II) complexes of *N*,*N′*-bis[3-(3,4-dialkoxyphenyl)-3-oxopropenyl]ethylenediamines

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The preparation, characterization and mesomorphic properties of vanadyl(VI) and cobalt(II) complexes derived from *N*,*N′*-bis[3-(3,4-dialkoxyphenyl)-3-oxopropenyl]ethylenediamines are described. These half-disk-shaped molecules exhibited columnar mesophases over a wide range of temperature, as characterized by DSC analysis and polarizing optical microscopy. The structure of the mesophases was also confirmed as columnar hexagonal (Col_{ho}) by powder XRD. The vanadyl complexes were found to have substantially higher clearing temperatures and wider mesophase temperatures than the analogous cobalt complexes. The influence of the metal centres on the mesomorphic temperatures may be attributed to better intermolecular dative association in the vanadyl complexes than in the cobalt complexes.

1. Introduction

Metallomesogenic structures obtained by incorporating metal centres into classical organic moieties have been used to generate metallomesogenic materials displaying a variety of novel molecular shapes and interesting mesomorphic properties [1, 2]. The metal centre incorporated into this type of coordinately unsaturated structure plays a significant role in determining the mesomorphic properties. Mesomorphism may potentially be obtained by incorporating certain single or multiple metal centres into non-mesogenic ligands. On the other hand the mesomorphic properties might be totally lost due to a change in molecular symmetry upon coordination to other types of metal ion. In general the overall geometries of the complex are determined by both the central metal and the organic moiety, and they can vary from square-planar to tetrahedral structures for metal complexes with coordination numbers of four. The compounds with square-planar (Cu^{2+}, Ni^{2+}, Pd^{2+}, Pt^{2+}) and square-pyramidal ($Fe\text{-}Cl^{2+}$, VO^{2+}) geometries generally give rise to liquid crystallinity, whereas, compounds with tetrahedral geometries are often not mesomorphic. Among them, examples with the Co^{2+} ion as the core group are relatively rare [1 (*a*), 3–7], probably due to its rapid oxidation to Co(III). Among known reported mesogenic structures containing the cobalt(II) ion are various derivatives such as aminopyridines [3], phthalocyanines [4], porphyrins [5], tetrapyrazinoporphyrazines [6] and tetra-azaporphyrins [7]. The cobalt(II) ion commonly forms more tetrahedral complexes than other transition metal ions. With ligands that are bidentate monoanions, tetrahedral complexes are formed in some cases, for example, with *N*-alkylsalicylaldiminato and bulky β-diketonato anions; however, with tetradentate ligands such as sal_2en and porphyrins, planar complexes are generally obtained.

In a previous paper [8], we reported the formation of columnar hexagonal phases by copper(II) and nickel(II) complexes derived from *N*,*N′*-bis[3-(3,4-dialkoxyphenyl)-3-oxopropenyl]ethylenediamines. Several complexes having similar structures derived from imineketone derivatives or Schiff's bases with various alkoxy side chains have been prepared and studied by other groups [9]. Continuing our research on metallomesogenic materials, we describe in this paper the preparation, characterization and mesomorphic properties of the vanadyl(VI) and cobalt(II) complexes (**1**, **2**) in order to understand better the effect of the metal ion incorporated on the formation of mesomorphic phases. These complexes are roughly half-disk-shaped, and correlated columnar phases formed by shape effects [9 (*a*, *c*)] and dative interaction between neighbouring complexes were

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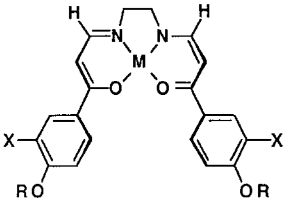
expected. The results indicate that both the cobalt and the vanadyl complexes form columnar hexagonal phases over a wide range of mesophase temperatures.

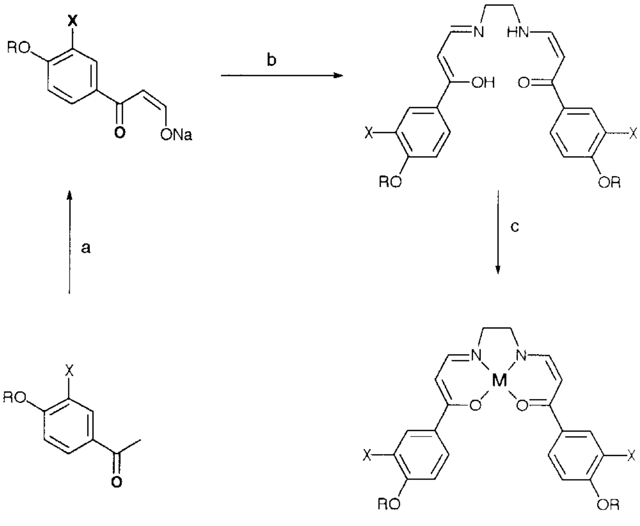


R = $(CH_2)_nH$; M = VO, Co
1 X = H
2 X = OR

2. Results and discussion

2.1. *Synthesis and characterization*

The synthetic pathways for the cobalt(II) and vanadyl(VI) complexes are summarized in the scheme. The reaction [8] of the Schiff's bases with vanadyl(II) acetate or cobalt(II) acetate tetrahydrate in boiling methylene chloride/methanol produced the complexes. Recrystallization twice from ethyl acetate or THF/methanol gave green solids for the vanadyl complexes and red solids for the cobalt complexes. The IR stretching band of the V=O group appeared at 983–987 cm^{-1} at room temperature or in the mesophase range and indicated a monomeric structure for the vanadyl compounds. Both complexes are paramagnetic and displayed only broad alkoxy signals in their ^{1}H and ^{13}C NMR spectra. The cobalt(II) complexes underwent decomposition on prolonged exposure to air due to partial oxidation to cobalt(III). A relatively broad X-band ESR signal at room temperature indicated and confirmed the presence of Co(II) species.



Scheme. Reaction conditions: (a) Ethyl formate (4.5 eq), Na (3.0 eq), stirred in Et_2O at RT, 12 h; (b) $NH_2(CH_2)_2NH_2$ (0.55 eq), CH_3COOH (3 drops), refluxing in CH_2CL_2, 12 h; (c) vanadyl or cobalt acetate (1.1 eq), refluxing in CH_2Cl_2/CH_3OH, 6 h, 72–83%.

2.2. *Mesomorphic properties*

The liquid crystalline behaviour for the metal complexes was studied by differential scanning calorimetry (DSC) and polarizing optical microscopy. The phase transitions and thermodynamic data for the complexes **1** and **2** are summarized in table 1. The vanadyl complexes exhibited columnar phases for series **1** with two longer alkoxy (n = 12, 16) side chains and series **2** with four alkoxy (n = 6, 8, 10, 12, 14, 16) side chains attached to the terminal phenyl rings. In series **2**, increasing the alkoxy carbon length lowered the clearing points, whereas the melting points initially decreased (n = 6–14) and then increased (n = 16). The effect of side chain length dependence in series of **1** was relatively small. Two transitions for crystal to columnar (Cr → Col_h)

Table 1. Phase behaviour of metal complexes **1** and **2**. n represents the number of carbons in the alkoxy chain. Cr = crystal phase; Col_{ho} = ordered columnar hexagonal phase; I = isotropic. The transition temperatures (°C) and enthalpies (in parenthesis, kJ mol^{-1}) were determined by DSC at a scan rate of 10.0°C min^{-1}.

1	VO	$n = 8$			Cr	$\underset{139.2\ (51.4)}{\overset{166.6\ (22.4)}{\rightleftharpoons}}$	I
		12	Cr	$\underset{54.4\ (2.64)}{\overset{57.7\ (2.84)}{\rightleftharpoons}}$	Col_{ho}	$\underset{141.7\ (27.1)}{\overset{148.8\ (26.3)}{\rightleftharpoons}}$	I
		16	Cr	$\underset{57.6\ (1.53)}{\overset{62.9\ (6.00)}{\rightleftharpoons}}$	Col_{ho}	$\underset{143.3\ (13.6)}{\overset{150.0\ (13.1)}{\rightleftharpoons}}$	I
	Co	$n = 16$			Cr	$\underset{95.3\ (62.5)}{\overset{116.0\ (61.2)}{\rightleftharpoons}}$	I
2	VO	$n = 6$	Cr	$\underset{92.2\ (5.82)}{\overset{101.7\ (5.87)}{\rightleftharpoons}}$	Col_{ho}	$\underset{154.9\ (25.9)}{\overset{164.3\ (26.4)}{\rightleftharpoons}}$	I
		8	Cr	$\underset{81.4\ (0.25)}{\overset{88.1\ (0.33)}{\rightleftharpoons}}$	Col_{ho}	$\underset{153.5\ (26.1)}{\overset{160.6\ (25.1)}{\rightleftharpoons}}$	I
		10	Cr	$\underset{<25.0}{\overset{<25.0}{\rightleftharpoons}}$	Col_{ho}	$\underset{150.0\ (17.0)}{\overset{156.3\ (16.2)}{\rightleftharpoons}}$	I
		12	Cr	$\underset{<25.0}{\overset{<25.0}{\rightleftharpoons}}$	Col_{ho}	$\underset{150.1\ (25.7)}{\overset{157.6\ (24.6)}{\rightleftharpoons}}$	I
		14	Cr	$\underset{<25.0}{\overset{<25.0}{\rightleftharpoons}}$	Col_{ho}	$\underset{149.7\ (15.2)}{\overset{156.1\ (15.2)}{\rightleftharpoons}}$	I
		16	Cr	$\underset{39.8\ (17.7)}{\overset{54.9\ (27.0)}{\rightleftharpoons}}$	Col_{ho}	$\underset{143.3\ (12.2)}{\overset{150.0\ (11.3)}{\rightleftharpoons}}$	I
	Co	$n = 6$			Cr	$\underset{100.9\ (29.3)}{\overset{113.7\ (29.7)}{\rightleftharpoons}}$	I
		8			Cr	$\underset{102.6\ (24.5)}{\overset{112.9\ (24.1)}{\rightleftharpoons}}$	I
		12	Cr	$\underset{56.4\ (2.83)}{\overset{61.4\ (2.45)}{\rightleftharpoons}}$	Col_{ho}	$\underset{91.4\ (5.56)}{\overset{102.6\ (5.21)}{\rightleftharpoons}}$	I
		14	Cr	$\underset{57.6\ (4.13)}{\overset{63.7\ (4.39)}{\rightleftharpoons}}$	Col_{ho}	$\underset{93.4\ (7.43)}{\overset{103.9\ (7.13)}{\rightleftharpoons}}$	I
		16	Cr	$\underset{59.1\ (6.75)}{\overset{66.8\ (8.61)}{\rightleftharpoons}}$	Col_{ho}	$\underset{91.4\ (8.05)}{\overset{99.9\ (8.03)}{\rightleftharpoons}}$	I

and for columnar to isotropic ($\mathrm{Col_h} \rightarrow \mathrm{I}$) were typically observed for these vanadyl derivatives. DSC studies gave crystal to mesophase transition temperatures in the range 57.7–62.9°C for series **1** and 25.0–101.7°C for series **2**, with transition enthalpies in the range 0.33–27.0 kJ mol^{-1}. The clearing points were all in the range 148.8–164.3°C, with relatively large enthalpies of 13.1–26.4 kJ mol^{-1}. These larger enthalpies indicated a highly ordered state of arrangement in the columnar phases. In fact, for some of the vanadyl complexes **2** with longer carbon lengths ($n = 10$, 12, 14) the mesophases supercooled to room temperature, and this behaviour was also confirmed by DSC. Pseudo-focal-conic or fan-shaped textures were observed on cooling from the isotropic state for each complex and generally this is characteristic of a columnar phase, as shown in the figure.

2.3. *Cobalt(II) complexes*

Thermal phase data for all the cobalt complexes **1**,**2** are listed in table 1. The formation of columnar phases by the cobalt complexes was dependent on both side chain density and carbon length of the alkoxy side chains. Longer carbon lengths ($n = 14$ or 16) for the alkoxy side chains and/or more side chains seemed to stabilize the mesomorphic state strongly. Cobalt complex **2** with four longer alkoxy side chains ($n = 12$, 14, 16) exhibited similar columnar hexagonal phases to the vanadyl complexes, but cobalt complex **1** ($n = 16$) with two alkoxy side chains was not liquid crystalline. The clearing points in series **2** were significantly lower than those for the vanadyl analogues, and this lowering might be attributed to the better molecular planarity at the vanadyl than at the cobalt centre core. The assignment of a columnar hexagonal phase was confirmed by the X-ray powder diffraction data. For example, vanadyl complex **2** ($n = 14$), displayed the diffraction pattern of a two-dimensional hexagonal lattice [9 (*a*–*c*)] with an intense peak at 36.13 Å at 130°C. This type of diffraction pattern is characteristic of the hexagonal columnar ($\mathrm{Col_h}$) phase [8, 9 (*a*–*c*)] and the results corresponded to an intercolumnar distance (a parameter of the hexagonal lattice) of 41.72 Å. An additional weak halo at mid-angle of *d*-spacing ≈ 6.04 Å was observed for this compound. The presence of a distinct peak at *c*. 5.24 Å indicated a relatively ordered mesophase, consistent with the large enthalpies for the columnar to isotropic transitions obtained by DSC. This peak corresponded to a more regular period within the columns than for other similar disordered $\mathrm{Col_h}$ systems. However, the cobalt(II) complexes gradually decomposed under prolonged exposure to the X-ray beam.

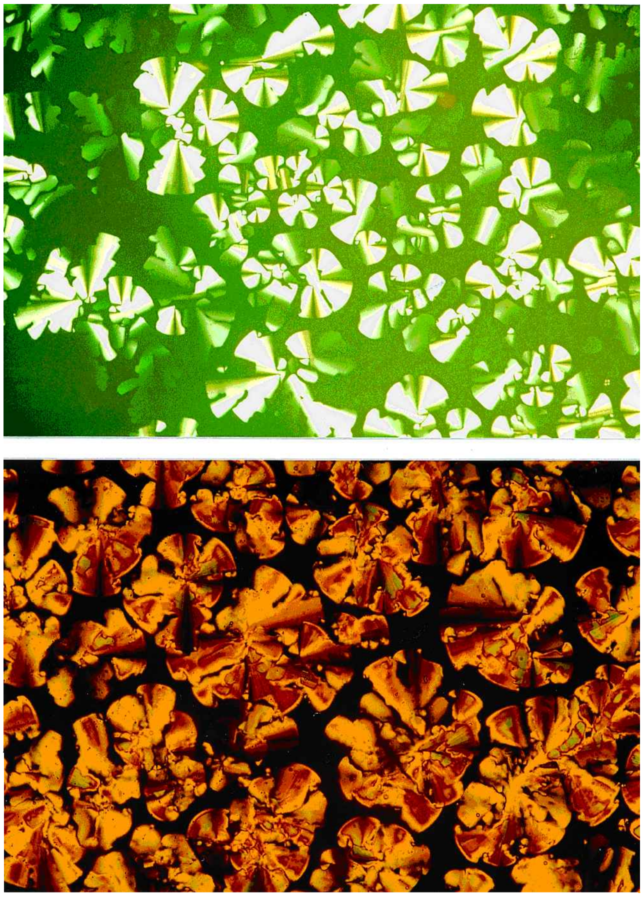


Figure. Optical textures (100×) of $\mathrm{Col_{ho}}$ phases observed for vanadyl complex **2** ($n = 10$) at 147°C (top) and cobalt complex **2** ($n = 12$) at 87°C (bottom).

3. Summary

Association of the metal ions within neighbouring molecules in this type of coordinately unsaturated structure plays an important role in the formation of mesomorphic phases. This systematic investigation of the mesomorphism exhibited by various metallomesogenic compounds has helped our understanding of the effect of core–core interactions on the formation of columnar phases. The vanadyl(VI) and cobalt (II) complexes prepared have also been used to study the difference in behaviour for the mesomorphic properties exhibited by previously prepared copper(II) and nickel(II) complexes.

4. Experimental

All chemicals and solvents were reagent grade from the Aldrich Chemical Co. ^{1}H and ^{13}C NMR spectra were measured on a Bruker DRS-200. DSC thermographs were obtained using a Perkin-Elmer DSC-7, calibrated with pure indium. Polarizing optical microscopy was carried out with a Nikon MICROPHOT-FXA with a Mettler FP90/FP82HT hot stage system. X-ray powder diffraction studies were performed using an INEL MPD-diffractometer, with a 2.0 kW Cu-Kα

X-ray source, and equipped with an INEL CPS-120 position sensitive detector and a variable temperature capillary furnace with an accuracy of ± 0.10°C in the vicinity of the capillary tube. Elemental analysis results for carbon and hydrogen were obtained with a Heraeus CHN-O-Rapid elemental analyser; the results are listed in table 2.

The *N*,*N*′-bis[3-(4-alkoxyphenyl)-3-oxopropenyl]-ethylenediamines and *N*,*N*′-bis[3-(3,4-dialkoxyphenyl)-3-oxopropenyl]ethylenediamines were prepared as described previously [8]. Some typical characterization data are given below.

4.1. *N,N′-Bis[3-(4′-hexadecyloxyphenyl)-3-oxopropenyl]ethylenediamine*

Light yellow solid, yield 86%, m.p. 172.0°C. ^{1}H NMR (ppm, $CDCl_3$): 0.85 (t, $J = 6.10$ Hz, $-CH_3$, 6H), 1.15–1.40 (m, $-CH_2$, 52H), 1.76 (t, $J = 6.51$ Hz, $-CH_2$, 8H), 3.38 (m, $-CNCH_2$, 4H), 3.96 (t, $J = 6.11$ Hz, $-OCH_2$, 4H), 5.63 (d, $J = 5.42$ Hz, −COCH, 2H), 6.69 (m, −CHN, 2H), 6.79 (d, $J = 8.21$ Hz, $-C_6H_4$, 4H), 7.78 (d, $J = 8.10$ Hz, $-C_6H_4$, 4H), 10.23 (m, −CNH, 2H). ^{13}C NMR (ppm, $CDCl_3$): 14.14, 22.60, 25.09, 29.20, 29.28, 31.74, 50.22 ($N-CH_2$), 68.03 (OCH_2), 90.75 (CH=), 113.91 ($C_{3'}$), 129.01 ($C_{2'}$), 131.90 ($C_{1'}$), 153.80 ($C_{4'}$), 161.69 (C=N), 189.62 (C=O).

4.2. *N,N′-bis[3-(3,4-dihexadecyloxyphenyl)-3-oxopropenyl]ethylenediamine.*

Yellow needle-like crystals, yield 75.0%, m.p. 98.1°C. ^{1}H NMR (ppm, $CDCl_3$): 0.87 (m, $-CH_3$, 12H), 1.12–1.45 (m, $-CH_2$, 104H), 1.82 (m, $-CH_2$, 8H), 3.36 (m, $-CNCH_2$, 4H), 3.91–4.12 (m, $-OCH_2$, 8H), 5.63 (d, $J = 5.70$ Hz, −COCH, 2H), 6.80 (m, −CHN, 2H), 6.83 (d, $J = 6.31$ Hz, $-C_6H_3$, 2H), 7.37 (d, $J = 2.90$ Hz, $-C_6H_3$, 2H), 7.45 (s, $-C_6H_3$, 2H), 10.19 (m, −CNH, 2H). ^{13}C NMR (ppm, $CDCl_3$): 13.97, 22.67, 25.85, 29.11, 29.28, 29.49, 31.89, 50.10 (NCH_2), 68.87 ($-OCH_2$), 69.02 ($-OCH_2$), 90.78 (CH=), 111.94 ($C_{5'}$), 111.99 ($C_{2'}$), 120.78 ($C_{6'}$), 132.32 ($C_{1'}$), 148.64 ($C_{3'}$), 151.81 ($C_{4'}$), 153.62 (C=N), 189.47 (C=O). IR (thin film): 1637, 1589, 1544, 1518, 1465, 1377, 1336, 1271, 1220 cm^{-1}.

Table 2. Elemental analysis (%) for compounds **1** and **2** with calculated values in parentheses.

Compound		*n*	C	H
1	VO	8	67.68 (67.11)	8.77 (8.41)
		12	70.79 (70.09)	8.57 (8.82)
		16	72.69 (72.11)	9.70 (9.54)
	Co	16	73.13 (72.78)	9.36 (9.63)
2	VO	6	68.18 (67.24)	8.79 (8.46)
		8	70.23 (69.54)	9.57 (9.20)
		10	72.15 (71.32)	9.96 (9.78)
		12	72.94 (72.35)	10.31 (10.24)
		14	74.39 (73.92)	10.34 (10.61)
		16	74.34 (74.90)	10.49 (10.92)
	Co	6	70.67 (70.16)	9.59 (9.29)
		8	71.09 (71.89)	10.17 (9.85)
		12	73.84 (73.28)	10.66 (10.31)
		14	74.64 (74.41)	10.58 (10.68)
		16	75.91 (75.33)	10.83 (10.99)

4.3. *Vanadyl complexes of N,N′-bis[3-(3,4-dihexadecyloxyphenyl)-3-oxopropenyl]ethylenediamine*

N,*N*′-Bis[3-(3,4-dihexadecyloxyphenyl)-3-oxopropenyl]-ethylenediamine (0.50 g, 0.40 mmol) was dissolved in methylene chloride (5.0 ml) and a hot methanol solution of vanadyl acetate (0.037 g, 0.20 mmol) was added. Upon addition, green solid became suspended in the solution, and the mixture was gently heated at reflux for 6 h. The green solid was filtered off, and recrystallized from methylene chloride methanol; yield 79%. IR (thin film): 1616, 1574, 1524, 1499, 1470, 1437, 1385, 1364, 1267, 1205, 1134, 1070, 1020, 987, 954, 864, 766, 721, 590 cm^{-1}. Elemental analysis results are given in table 2.

4.4. *Cobalt complexes of N,N′-bis[3-(3,4-dihexadecyloxyphenyl)-3-oxopropenyl]ethylenediamine*

N,*N*′-bis[3-(3,4-dihexadecyloxyphenyl)-3-oxopropenyl]-ethylenediamine (0.50 g, 0.40 mmol) was dissolved in 5.0 ml of methylene chloride and a solution of cobalt(II) acetate tetrahydrate (0.049 g, 0.20 mmol) in methanol was added. The reaction mixture was gently heated at reflux for 6 h. The solution was evaporated to dryness to give a dark red solid. Red crystals were obtained after recrystallization from ethyl acetate; yield 80%. IR (thin film): 1574, 1512, 1470, 1439, 1379, 1346, 1277, 1207, 1165, 1138, 1076, 1016, 877, 802, 748, 723 cm^{-1}. Elemental analysis results are given in table 2.

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