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Liquid Crystals

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Liquid crystal of cobalt complex from 1-dodecyl-1H-benzimidazole

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A new cobalt complex of $[\text{Co}(\text{C}_{12}\text{H}_{25}\text{-bim})_2]\text{Cl}_2$ (bim=benzimidazole) was synthesised using a non-mesomorphic ligand and the structure was characterised by X-ray crystallography, infrared spectrum and elemental analysis. Single-crystal X-ray analysis revealed that the title complex adopted a U-shaped conformation with bilayer packing. The coordination environment of the Co atom was almost tetrahedral, comprising two nitrogen atoms of benzimidazole and two chlorine atoms. Differential scanning calorimetry and polarised optical microscopy results demonstrated that the title complex exhibited liquid crystalline property upon complexation. The cyclic voltammetry study showed that the title complex had a pair of redox peaks and one reduction peak.

Keywords: benzimidazole; crystal structure; liquid crystal property; cyclic voltammetry

1. Introduction

Liquid crystals (LCs) (1, 2) are a special type of liquid, in which molecules tend to self-assemble through various intermolecular forces. Metal containing liquid crystals (MLCs) (3) are LCs containing metal ions, in which LCs with additional properties such as geometry, colour, polarisability and magnetism can be found. MLCs are therefore important in basic science and advanced applications (4, 5). The metal ions may adopt various geometries and provide more variations of molecular geometry than traditional LCs. Moreover, metal ions are rich in oxidation states and have various electronic configurations. So the area of MLCs has become a research focus and has progressed tremendously in recent years (6). Lee et al. (7) reported MLCs of palladium(II) and copper(II) with *N,N'*-dialkylimidazolium, in which the crystal structure adopted a U-shaped conformation. Martin et al. (8) reported MLCs of zinc and cadmium with alkyltrimethylammonium ligand while Lee et al. (7) reported several MLCs of silver derived from 1-alkylimidazoles. Several nanoscaled MLCs, such as gold complexed with benzimidazole and imidazole ligands (9), and silver and gold complexed with 3-(4-dodecyloxybenzyl)-1-methyl-1H-imidazolium ligand (10) have recently been reported. To the best of our knowledge, few reports on MLCs including cobalt can be found in the literature, especially with examples of their crystal data. Herein, we report the fabrication of a new cobalt-based MLC of $[\text{Co}(\text{C}_{12}\text{H}_{25}\text{-bim})_2]\text{Cl}_2$ together with its crystal structure data.

2. Experimental

2.1. Chemicals and measurement

All chemicals were of analytical reagent grade and used directly without further purification. Elemental analyses were measured with a Perkin–Elmer 1400C analyser (USA). Infrared spectra were recorded on a Nicolet 170SX spectrometer (USA) using pressed KBr plates in the 4000 to 400 cm^{-1} ranges. Electronic spectra were taken on a UV-Vis spectrophotometer. Phase transition temperatures were determined by differential scanning calorimetry (DSC) at a scan rate of 10 $^{\circ}\text{C min}^{-1}$ using a DSC 204 thermal analysis data station. Optical characterisation was performed by using covered microscope slides on a ZEISS Axioplan2 imaging polarising microscope equipped with a Mettler FP 82 hot stage and a Mettler FP 90 central processor. Electrochemical experiments were carried out using an Autolab potentiostat/galvanostat (Eco Chemie, B.V., Utrecht, The Netherlands). Data acquisition and potentiostat control were accomplished with a computer, running GPES software Version 4.9. A three-electrode cell was used in the experiments. The working electrode was silver electrode ($\Phi=2\text{ mm}$). The counter electrode was a platinum wire. The reference electrode was an $\text{Ag}|\text{AgCl}|\text{KCl}$ (1 M), and all potentials reported in this work were measured versus this electrode (236.3 mV at 25 $^{\circ}\text{C}$). The electrochemical analyses were all carried out in DMF solution containing 0.1 M TBAP. The experiments were conducted in anaerobic conditions by bubbling with high-purity argon (99.999%). All measurements were performed at room temperature (25 \pm 2 $^{\circ}\text{C}$).

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2.2. The preparation and physical measurement of the title complex

Sodium ethylate (2.72 g, 40.0 mmol) was added absolute alcohol (40 ml) under vigorous stirring. After the sodium ethylate dissolved, benzimidazole (2.36 g, 20.0 mmol) and 1-bromododecane (6.5 ml, 120 mmol) was added to the mixture. After being refluxed for 20 h, the mixture was cooled to room temperature. The filter residue was removed and the ligand (C₁₂H₂₅-bim) was collected as a colourless block from the filtrate (mp 60 to 62°C). Yield: 82%.

The mixture of the ligand (C₁₂H₂₅-bim) (0.057 g, 0.2 mmol) and CoCl₂·6H₂O (0.024 g, 0.1 mmol) was added into absolute alcohol (20 ml) then refluxed for 0.5 h and a blue precipitate was obtained. Regular blue crystals suitable for X-ray analysis were formed in 2 days by slow evaporation from THF solution at room temperature (mp 83 to 93°C). Yield: 65%. The C, H and N contents were determined by elemental analysis (analysis calcd for C₃₈H₆₀Cl₂CoN₄ (%) C 64.89, H 8.54, N 7.97; found: C 64.86, H 8.56, N 7.95).

In the infrared spectra, the bands at 2921 and 2851 cm⁻¹ may be assigned to the C–H stretching vibration of the alkyl chains. Several bands appearing in the 1557–1465 cm⁻¹ range were contributions from the stretching vibrations of the aromatic rings. The band at 1394 cm⁻¹ was attributed to the C–N stretching vibration of the imidazole ring. A medium-intensity band at 753 cm⁻¹ was present in the spectrum, which could be tentatively assigned to a vibration involving a Co(II)–N stretch vibration (11).

A summary of the key crystallographic information is given in Table 1. Reflection data and reflections for the unit cell determination were measured at 20°C using Mo K_α radiation (λ=0.71073 Å) with a graphite monochromator. The technique used was ω-scan with θ limits 1.33° < θ < 25.00° for the title complex. Empirical absorption correction was carried out by using the SADABS (12) program. The structure of [Co(C₁₂H₂₅-bim)₂]Cl₂ was solved by direct methods and refined by least squares on F_{obs}² by using the SHELXTL (13) software package. All non-H atoms

Table 1. Crystal data and structure refinement for the title compound.

Empirical formula	C ₃₈ H ₆₀ Cl ₂ CoN ₄
Formula weight	702.73
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P1
a (Å)	9.140 (2)
b (Å)	14.000(3)
c (Å)	16.090(3)
α (deg)	4.19(3)
β (deg)	80.90(3)
γ (deg)	82.42(3)
V (Å ³)	1947.5(7)
Z	2
Calculated density (Mg m ⁻³)	1.198
Absorption coefficient (mm ⁻¹)	0.608
F(000)	754
θ range for data collection (deg)	1.33 to 25.00
Limiting indices	-10 ≤ h ≤ 10, -15 ≤ k ≤ 14, -19 ≤ l ≤ 8
Reflections collected/unique	8375/6288 [R _{int} =0.1845]
Completeness to θ=25.00	91.6%
Data/restraints/parameters	6288/0/407
Goodness-of-fit on F ²	0.903
Final R indices [I > 2σ(I)]	R ₁ =0.1066, wR ₂ =0.1629
R indices (all data)	R ₁ =0.3992, wR ₂ =0.2811
Largest diff. peak and hole (e·Å ⁻³)	0.369 and -0.321

were anisotropically refined. The hydrogen atoms were located by difference synthesis and refined isotropically. The final conventional $R(F)=0.1066$ and $wR(F^2)=0.1629$ for 8375 reflections $I > 2\sigma(I)$ with weighting scheme, $w=1/[\sigma^2(F_o^2)+(0.0603P)^2+0.0000P]$, where $P=(F_o^2+2F_c^2)/3$. The molecular graphics were plotted using SHELXTL. Atomic scattering factors and anomalous dispersion corrections were taken from *International Tables for X-ray Crystallography* (14).

3. Results and discussion

3.1. Crystal structure of complex

The molecular structure of the title complex with the atomic numbering scheme is shown in Figure 2.

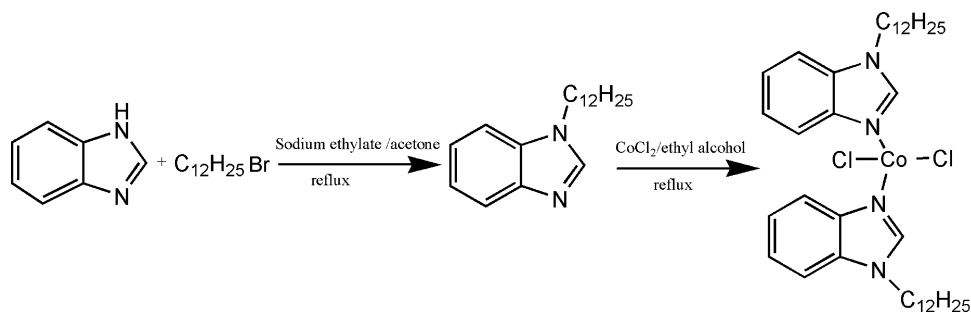


Figure 1.

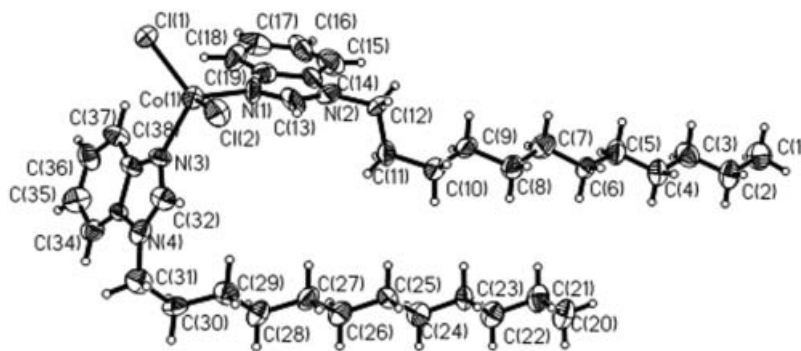


Figure 2. ORTEP drawing of the title complex (30% thermal ellipsoids) with partial atomic numberings.

Selected bond distances and bond angles are listed in Table 2.

The cation adopted a U-shaped conformation, in which the two trans-benzimidazole planes were twisted with an angle of 67.97° . The molecular geometry of the title complex was similar to the structure of $[\text{Ag}(\text{C}_{12}\text{H}_{25}\text{-im})_2][\text{NO}_3]$ (8). The centre Co adopted a distorted tetrahedron geometry by coordinating to two nitrogen atoms from benzimidazole and two chlorine atoms, respectively. The bond distances of Co(1)–N(1) [1.96(2) Å], Co(1)–N(3) [2.01(1) Å] and Co(1)–Cl(1) [2.220(4) Å] were comparable with those reported for $[\text{Co}(\text{R-bim})_2]$ [2.106 Å] (15) and $[\text{Co}(\text{R-im})_2]$ [2.218 Å] (16) complexes. The bond angles of N(1)–Co(1)–N(3) [$112.0(5)^\circ$], N(1)–Co(1)–Cl(1) [$108.7(5)^\circ$], N(1)–Co(1)–Cl(2) [$102.2(5)^\circ$] and Cl(1)–Co(1)–Cl(2) [$121.0(2)^\circ$] were comparable with the corresponding values in a similar complex (17). The angles of the alkyl chain to its connected benzimidazole plane were very different, with angles of 49.42° and 83.85° , but the

two arms pointed in the same direction. Molecules of the title complex were packed in an interdigitated bilayer fashion with a layer thickness of 17.3 Å. Every molecule was associated with neighbouring molecules through four Co–Cl...H–C hydrogen bonding interactions. Each bilayer was further linked to neighbouring bilayers through C–H...Cl hydrogen bonds (~ 2.7 Å), which formed a lamellar structure with a separation of 3.3 Å between bilayers (Figure 3). Recently, C–H...Cl hydrogen bonds have attracted much interest since the hydrogen bond acceptor capability of terminal metal-bound chlorine (M–Cl) was found to be stronger than the C–Cl analogues (18, 19). Some selected hydrogen bond lengths and bond angles are listed in Table 3. There was a weak C–H...Cl intramolecular hydrogen bond with the donor and acceptor distance of 3.347 Å for C(13)...C(12). There were also two weak potentially C–H...Cl hydrogen bond intermolecular interactions, and the donor and acceptor distances were 3.654 Å and 3.661 Å for C(31)...C(11) and C(31)...C(12),

Table 2. Selected bond lengths [Å] and angles [$^\circ$] of the title compound.

Bond lengths		Bond lengths	
Co(1)–N(1)	1.96(2)	Co(1)–N(3)	2.01(1)
Co(1)–Cl(1)	2.220(4)	Co(1)–Cl(2)	2.236(4)
N(1)–C(13)	1.26(2)	N(1)–C(19)	1.43(2)
N(2)–C(13)	1.31(2)	N(2)–C(14)	1.33(2)
N(3)–C(32)	1.33(2)	N(3)–C(38)	1.42(2)
N(4)–C(32)	1.318(17)	N(4)–C(33)	1.366(18)
N(4)–C(31)	1.434(17)		
N(1)–N(2)–C(6)	124.1(4)	N(3)–N(2)–C(6)	125.9(4)
Bond angles		Bond angles	
N(1)–Co(1)–N(3)	112.0(5)	N(1)–Co(1)–Cl(1)	108.7(5)
N(3)–Co(1)–Cl(1)	109.4(4)	N(1)–Co(1)–Cl(2)	102.2(5)
N(3)–Co(1)–Cl(2)	103.3(5)	Cl(1)–Co(1)–Cl(2)	121.03(19)
C(13)–N(1)–C(19)	102.4(16)	C(13)–N(1)–Co(1)	123.8(16)
C(19)–N(1)–Co(1)	133.8(14)	C(13)–N(2)–C(14)	107.2(18)
C(13)–N(2)–C(12)	131(2)	C(14)–N(2)–C(12)	121.2(18)
C(32)–N(3)–C(38)	105.5(14)	C(32)–N(3)–Co(1)	123.7(14)
C(38)–N(3)–Co(1)	130.8(13)	C(32)–N(4)–C(33)	107.7(18)
C(32)–N(4)–C(31)	126.0(16)	C(33)–N(4)–C(31)	126.2(18)

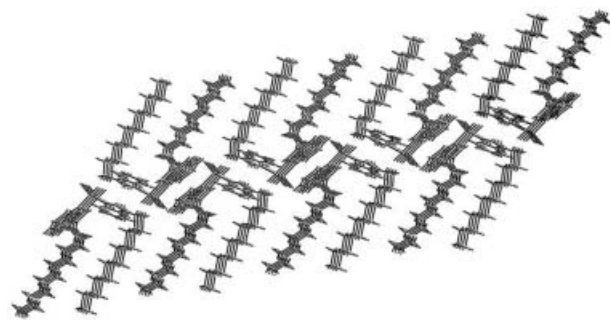


Figure 3. Crystal packing view along the b-axis. Symmetry operations used to generate equivalent atoms.

respectively. There were seven types of π - π stacking interactions between imidazole rings and phenyl rings and the centre-to-centre distances were in the range from 3.566 to 3.740 Å. The shortest interplanar distances above were in the range of 2.958 to 2.958 Å. In the solid state, the intermolecular interactions in this structure stabilised the crystal structure. Also, the intermolecular interactions may be responsible for the higher melting temperature and the liquid crystalline property.

3.2. UV-Vis spectra

A comparison result of the UV-Vis spectra of the ligand ($C_{12}H_{25}$ -bim) and the title complex is shown in Figure 4. The ligand in acetonitrile solution showed absorption peaks at 218, 250, 268 and 275 nm, which were indicative of benzimidazole ring chromophore moieties present in the ligand. The peaks of the complex seldom shifted compared with that of the ligand. However, a significant hyperchromicity was shown, which may be due to existence of a ligand-to-metal charge transfer transition, which indicated that nitrogen atom of the ligand coordinated to the cobalt atom.

3.3. Liquid crystal property.

The liquid crystal property of the title complex was studied by DSC and polarised optical microscopy (POM). The DSC heating trace is shown in

Table 3. Hydrogen bond distances [Å] of the title compound.

D-H...A	symm	D-H	H...A	D...A	D-H...A
C(13)-H(13A) ...Cl(2)		0.93	2.79	3.3471	120
C(31)-H(31A) ...Cl(1)	$-x, 1-y, -z$	0.97	2.69	3.6537	172
C(31)-H(31B) ...Cl(2)	$1-x, 1-y, -z$	0.97	2.72	3.6607	165

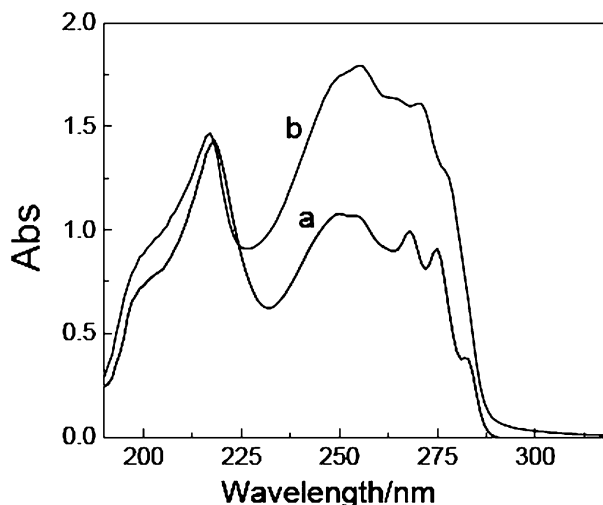
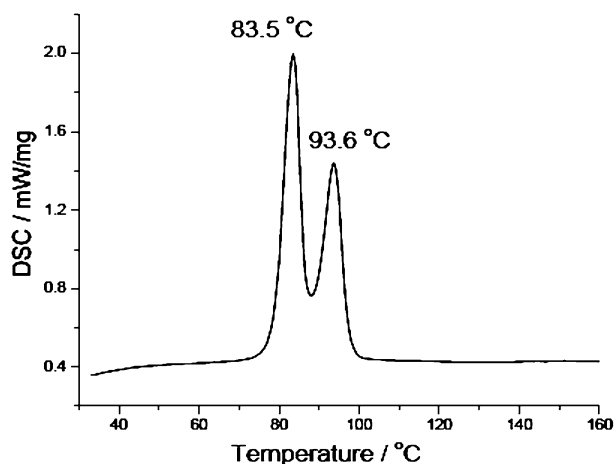


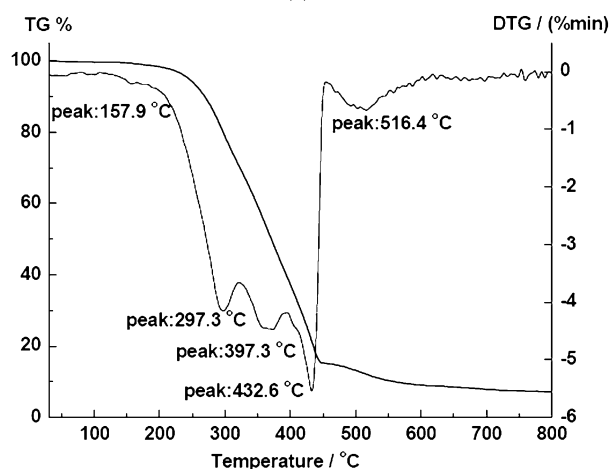
Figure 4. UV-Vis spectra of 5.0×10^{-5} M the ligand (a) and 5.0×10^{-5} M the title complex (b) in acetonitrile solution.

Figure 5(a). The first heating cycle exhibited two endothermic transitions at 83.5°C and 93.6°C. The first transition was one peak with a total ΔH value of 36.51 kJ mol⁻¹, while the second transition peak had a ΔH value of 25.26 kJ mol⁻¹. The first peak corresponded to the transition of crystal phase to mesophase. The second peak, having a relatively small ΔH value, corresponded to the transition of mesophase to isotropic liquid. The subsequent cooling and heating processes did not give reproducible results; presumably thermal decomposition occurred during the first heating cycle. In order to confirm this, a thermogravimetric analysis was done (Figure 5(b)). The result showed that the title complex has a little decomposition of about 0.98% at 157.3°C. The title complex greatly decomposed when subsequently heated from 200°C to 600°C. The residual may be cobalt with a value of 8.0%, which is smaller than the theoretical value of 8.3%. Also, the title complex had higher melting point and higher clearing point than the analogues (8, 9), but had a narrower mesophase range than that of those complexes.

The mesophase was also examined by optical observation. The fan-like texture of the title complex at 87°C is shown in Figure 6. The ligand ($C_{12}H_{25}$ -bim) was non-mesomorphic; however, upon complexation, the title complex exhibited liquid crystalline property. A typical fan-shape texture with the presence of homeotropic domains was observed when the sample was not subjected to mechanical stress. Optical observations confirmed the presence of a single mesophase for the title complex, which only occurred during the first heating cycle. In cooling processes no mesophase appeared and the sample became viscous even at room temperature. The



(a)



(b)

Figure 5. (a) DSC heating curve (5 K min^{-1}) of the title complex. (b) DG-DTG curve (10 K min^{-1}) of the title complex.

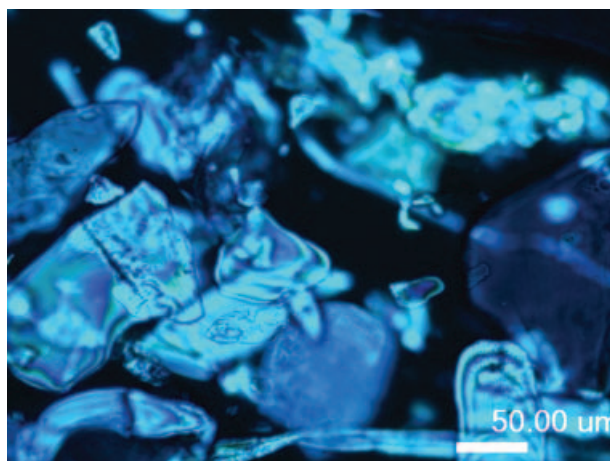


Figure 6. Polarised optical micrograph of the title complex at 87°C .

results of DSC and POM therefore suggest the presence of a cholesteric mesophase of the title complex. The cholesteric phase was a highly ordered mesophase. The molecules in the cholesteric phase were arranged in layers and have on average their long molecular axis perpendicular to the layer planes. This result also coincided with crystal packing of the title complex.

3.4. Electrochemical characterisation of the title complex

The result of the cyclic voltammogram (CV) of the ligand and the title complex is shown in Figure 7. Curve (a) was the CV of $2.80 \times 10^{-5} \text{ M}$ of the ligand in DMF solution containing 0.1 M TBAP and curve (b) was that of $2.80 \times 10^{-5} \text{ M}$ of the title complex. The ligand had two reduction peaks at -0.864 V ($\text{P}_{2\text{a}}$) and -0.640 V (P_1), while no oxidation peak appeared. The reduction peaks of the ligand may be the reduction peaks of two nitrogen atoms of benzimidazole. The title complex had two reduction peaks and one oxidation peak at -0.847 V ($\text{P}_{2\text{b}}$), -0.449 V and -0.332 V , respectively. The peak potentials of $\text{P}_{2\text{a}}$ and $\text{P}_{2\text{b}}$ had no significant shift, which might indicate the reduction peak of the nitrogen atom with linking alkyl chains. The peak of P_1 in the ligand might be the reduction peak of the other nitrogen atom of benzimidazole, but this peak did not appear in the CV of the title complex, which possibly indicates that the nitrogen atom coordinated to the cobalt atom. The title complex had a pair of redox peaks at -0.449 V and -0.332 V , with the formal potential (E^0) at approximately -0.391 V , corresponding to the electrochemical process of Co(II)/Co(I) (I/I). The separation of the cathodic

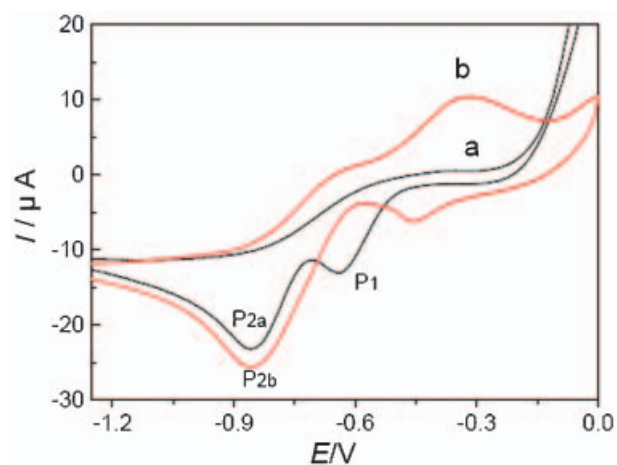


Figure 7. Cyclic voltammograms of $2.80 \times 10^{-5} \text{ M}$ the ligand (a) and $2.80 \times 10^{-5} \text{ M}$ the title complex in DMF solution containing 0.1 M TBAP (b). Scan rate: $50 \text{ mV} \cdot \text{s}^{-1}$.

and anodic peak potential, $\Delta E = 0.117 \text{ V}$, $i_{pa}/i_{pc} = 1.86$, indicated that the electrochemical behaviour of the title complex on a silver electrode was a quasi-reversible process. CV results also showed that the reduction peak current of the ligand (P_{2a}) and the title complex (P_{2b}) increased linearly with v in the range from 50 to 150 mVs^{-1} , with correlation coefficients of 0.996 and 0.998, respectively, characteristics of surface adsorption-controlled processes (20).

As the scan rate increases, the reduction peak potential shifts negatively. For an irreversible reduction process, the number of electrons transferred per molecule (n) could be calculated from the following relation (21):

$$|E_p - E_{p/2}| = 1.857RT/\alpha nF, \quad (1)$$

where E_p is the peak potential, $E_{p/2}$ the half peak potential, α is the electron transfer coefficient (generally, $0.3 < \alpha < 0.7$), F is the Faraday constant ($96,487 \text{ Coulombs mol}^{-1}$), R is the universal gas constant ($8.314 \text{ JK}^{-1} \text{ mol}^{-1}$), and T is temperature Kelvin. The $|E_p - E_{p/2}|$ of the ligand and the title complex were 86 and 91 mV, respectively, so according to Equation (1), the numbers of electron transfers were calculated to be 0.54 and 0.52, when α was assumed to be 0.5, thus approximating to 1. This suggested that the most probable reduction sites and numbers of electron transfers for the ligand and the title complex did not change on the time scale of the measurements.

Integration of reduction CV peaks at low scan rates gives the number of moles of electroactive free ligand and the title complex (γ) from the relation (20): $Q = nFA\gamma$, where Q is the integrated charge, n is the number of electrons transferred, F is the Faraday constant, and A is the electrode area. Here, $n = 1$, for the ligand and the title complex, $A = 0.0314 \text{ cm}^2$. At a scan rate of 50 mVs^{-1} , the values of Q were $5.826 \times 10^{-5} \text{ C}$ and $1.440 \times 10^{-4} \text{ C}$ for the ligand and the title complex, respectively. From the data, the values of γ were $1.92 \times 10^{-8} \text{ mol cm}^{-2}$ and $4.7 \times 10^{-8} \text{ mol cm}^{-2}$ for the ligand and the title complex, respectively. The surface coverage of the title complex was more than that of the ligand.

4. Conclusions

The synthesis, structural characterisation and electrochemistry of a novel liquid crystal $[\text{Co}(\text{C}_{12}\text{H}_{25}\text{-bim})_2]\text{Cl}_2$ has been established. The crystal structure revealed that the cation adopted a U-shaped conformation with bilayer model packing and a distorted tetrahedron geometry. The thermodynamic parameters

suggest that both the melting and the clearing temperatures of the title complex are higher than those of the Ag(I) and Au(I) analogues. The presence of plenty of C–H...Cl hydrogen bonds and ring π – π interactions in the title complex may be responsible for the higher melting temperature. Further study on the novel liquid crystal complexes of other metals are in progress.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC reference number 687594. Copies of this information may be obtained free of charge from The Director, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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