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Octahedral metallo-mesogens of chromium, molybdenum and tungsten with 1,4,7-trisubstituted 1,4,7-triazacyclononane and three carbonyl groups as ligands

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Liquid crystalline complexes with chromium, molybdenum and with tungsten as metallic centres are reported. 1,4,7-Trisubstituted 1,4,7-triazacyclononane and three carbonyl groups are coordinated in an octahedral geometry. The observed mesophases are characterized as disordered rectangular columnar of a pyramidic type.

1. Introduction

Due to their interesting physical properties, thermotropic metallo-mesogens are the subject of rapidly increasing activities in liquid crystal research [1–4]. Until recently, they comprise in most cases a linear, square pyramidal or very often square planar coordination. Tetrahedral and octahedral complex geometries have been regarded till now as less favourable for obtaining metallo-mesogens [4]. Indeed, the number of relevant examples given in the literature is very small. Though Giroud-Godquin *et al.* [5], synthesized in 1982 an octahedral Fe(III) tris-β-diketonate, its mesomorphism has not yet been confirmed. On the other hand, the ferrocene structure in several metallo-mesogens, synthesized by different groups [6–11] can be regarded as formally octahedral or at least six-coordinate. Furthermore, it should be mentioned that a liquid crystalline Fe(III) complex, described by Galyatmetdinov [12, 2], is likewise formally six-coordinate (via Fe–Cl→Fe–Cl interactions), even though it is based on a five-coordinate metal centre. Another group of metallo-mesogens with an apparent octahedral coordination geometry was first described in 1987–1988: low molecular and polymeric phthalocyanine complexes with tin and silicon by Simon *et al.* [13–15], and Wegner *et al.* [16], and with the transition metal cobalt by Hanack *et al.* [17].

We reported recently the first example of a metallo-mesogen with the tridentate azamacrocyclic ligand *L* (see figure 1), i.e. the 1,4,7-trisubstituted 1,4,7-triazacyclononane [18]. With Ni(II) as metal centre, a liquid crystalline, octahedral metal complex was observed. The related 1,4,7-triazacyclononane, [9]aneN_3, and some 1,4,7-trisubstituted derivatives thereof are well-known ligands used in numerous, non-mesomorphic, mostly octahedral metal complexes [19, 20]. Furthermore, these kinds of tridentate azamacrocyclic ligands are not able to form different geometrical or

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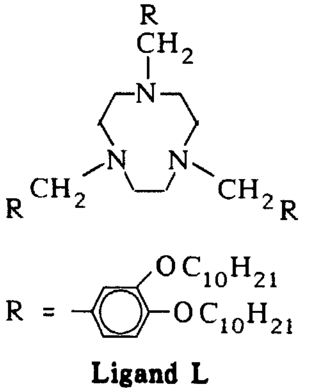


Figure 1. Schematic formula of the 1,4,7-trisubstituted 1,4,7-triazacyclonone, used as ligand *L*.

configurational isomers as is the case with larger saturated azamacrocycles (cyclam, hexacyclen) [21]. The new families of liquid crystalline complexes of cobalt, nickel and copper with cyclam or hexacyclene with one alkyl chain per side group, described by Ringsdorf *et al.* [22], or of zinc with cyclam and two alkyl chains per side group [23] do not seem to exceed this scope. Because of the small diameter of the [9]aneN_3 ring, in the case of trisubstituted derivatives such as 1,4,7-trimethyl-1,4,7-triazacyclononane (Me_3[9]aneN_3) [24] or 1,4,7-tribenzyl-1,4,7-triazacyclononane [25] only monofacial coordination is possible. Thus, the facial coordination of these saturated, azacyclic tridentate ligands seems to favour the formation of octahedral complexes with respect to the larger azacycloalkane compounds.

In the course of our examination of ligand *L* (see figure 1) for coordination in mesogenic metal complexes with different transition metals, we have prepared complexes with chromium, molybdenum and tungsten. Till now, only one type of metallomesogen with chromium or molybdenum, i.e. the corresponding dimetal tetracarboxylates, have been described by Chisholm *et al.* [26], and to our knowledge, the tungsten complex with *L* is only the second liquid crystalline compound with this transition metal [27].

2. Experimental

2.1. *Instruments*

FTIR: Bio Rad/Digilab FTS 40. ^{1}H, 13C NMR: Bruker AC 250, 250 MHz. FDMS: Finnigan MAT 95. Vapour pressure osmometer: Knauer. Elemental analysis: Mikroanalytisches Labor Beetz, Kronach. Polarizing microscopy: Leitz Laborlux 12 Pol, Mettler hot stage FP 82, photoautomat Wild MPS 45/51 S. DSC: Perkin–Elmer, DSC 7-temperatures were taken from peak maxima. X-ray: Siemens D-500 Goniometer.

2.2. *Materials*

The ligand *L* was synthesized according to the literature [9]. The compounds $M(CO_6)$ (M = Cr, Mo, W) (Merck-Schuchardt) and dimethylformamide (DMF) were purchased commercially.

By a literature method [25], the compounds $LM(CO)_3$ (M = Cr, Mo, W) were obtained by the reaction of the ligand *L* with $M(CO)_6$ in absolute DMF under a nitrogen atmosphere. The resulting precipitate was filtered off and recrystallized twice from hexane.

2.2.1. *LCr(CO)*$_3$

Reaction conditions: stirring 3 h at 100°C, then standing 12 h at room temperature. Yield: 61 per cent, yellow powder. ^1H NMR (acetone-d_6; decomposition in $CDCl_3$): δ (ppm) = 0·85 (t; 18 H), 1·1–1·6 (m; 84 H), 1·7–1·85 (m; 12 H), 2·35–2·55, 3·3–3·5 (2m; 12 H), 3·95–4·1 (2t; 12 H), 4·7 (s; 6 H), 6·9–7·15; 9 H). ^{13}C NMR (THF-d_8; decomposition in $CDCl_3$, poor solubility in acetone-d_6): δ (ppm) = 14·4, 23·5, 27·1, 30·3–30·6, 32·9, 52·3, 67·0, 69·6, 70·3, 114·1, 119·3, 125·5, 127·4, 150·1, 150·6, 210·3. IR (KBr; cm^{-1}): 2922, 2853 (vs; ν –CH_2, CH_3), 1892 (vs; ν CO sym.), 1772, 1730 (vs; ν CO asym.), 1600 (m; ν C=C arom.), 1269 (m; ν C–O ether). MS: see table 1. $C_{90}H_{153}N_3O_9Cr$ (1473·14) Calculated (per cent): C 73·37 H 10·47 N 2·86 Cr 3·53; Found (per cent): C 73·89 H 10·38 N 3·45 Cr 4·01. The complex is slowly oxidized in air.

2.2.2. *LMo(CO*$_3$*)*

Reaction conditions: stirring 3 h at 120°C, then standing 12 h at room temperature. Yield: 66 per cent, light yellow powder. ^1H NMR ($CDCl_3$): δ (ppm) = 0·85 (t; 18 H), 1·1–1·6 (m; 84 H), 1·7–1·85 (m; 12 H), 2·25–2·55, 3·2–3·45 (2m; 12 H), 3·9–4·05 (2t; 12 H), 4·6 (s; 6 H), 6·75–6·9 (m; 9 H), ^{13}C NMR (THF-d_8; slow decomposition in $CDCl_3$, poor solubility in acetone-d_6): δ (ppm) = 14·4, 23·6, 27·2, 30·3–30·7, 32·9, 52·6, 67·2, 69·6, 70·1, 114·1, 119·1, 125·7, 126·9, 150·1, 150·7, 214·7. IR (KBr; cm^{-1}): 2922, 2853 (vs; ν–CH_2, CH_3) 1896 (vs; ν CO sym.), 1760, 1730 (vs; ν CO asym.), 1600 (m; ν C=C arom.), 1269 (m; ν C–O ether). MS: see table 1. $C_{90}H_{153}N_3O_9Mo$ (1517·08); Calculated (per cent): C 71·25 H 10·16 N 2·78 Mo 6·32; Found (per cent): C 71·06 H 10·04 N 3·10 Mo 5·94. The complex is stable in air.

2.2.3. *LW(CO)*$_3$

Reaction conditions: stirring 3 h at 90°C, then standing 12 h at room temperature. Yield: 66 per cent, light yellow powder. ^1H NMR ($CDCl_3$): δ (ppm) = 0·85 (t; 18 H), 1·1–1·6 (m; 84 H), 1·7–1·85 (m; 12 H), 2·35–2·55, 3·3–3·45 (2m; 12 H), 3·9–4·05 (2t; 12 H), 4·65 (s; 6 H), 6·75–6·9 (m; 9 H). ^{13}C NMR ($CDCl_3$): δ (ppm) = 14·0, 22·6, 26·0, 29·3–29·6, 31·9, 51·7, 66·6, 69·0, 69·0, 69·9, 113·1, 118·2, 124·9, 125·0, 148·7, 149·7, 208·6. IR (KBr; cm^{-1}): 2922, 2853 (vs; –CH_2, CH_3), 1886 (vs; ν CO sym.), 1768, 1720 (vs; ν CO ν asym.), 1600 (m; ν C=C arom.), 1269 (m; ν C–O ether). MS: see table 1. $C_{90}H_{153}N_3O_9$ W (1604·99) Calculated (per cent): C 67·35 H 9·61 N 2·63 W 11·45; Found (per cent): C 67·67 H. 9·75 N 2·81 W 10·6. The complex is stable in air.

Table 1. Mass values obtained for the *LM*(CO)$_3$ complexes. M, metal centre; FDMS, field desorption mass spectrometry; VPO, vapour pressure osmometry; GPC, gel permeation chromatography; V_e, elution volume.

	Molar masses/g mol^{-1}			GPC
M	Calculated	FDMS	VPO	V_e/ml
Cr	1473·14	1473·0 2944·7		25·1
Mo	1517·08	1518·7 3033·64	1560	25·3
W	1604·99	1603·8 3209·8		25·3

3. Results

3.1. *Complex structure*

FTIR spectroscopic measurements in solution (CH_2Cl_2) reveal two characteristic carbonyl absorptions, the ν (CO) symmetric mode A_1 and the ν (CO) asymmetric mode E. All absorption values are summarized in table 2. In the solid state, the A_1 absorptions are shifted towards lower wave numbers, and the E mode is split into two absorptions. All values agree well with those found for the corresponding complexes with 1,4,7-tribenzyl-1,4,7-triazacyclononane [25]. According to this, the solution spectra are typical for a 9ane[N_3]Mo$(CO)_3$-core, possessing local C_{3v} symmetry, i.e. octahedral coordination geometry. In the solid state, the degeneracy of the E mode is lifted towards a lower symmetry, i.e. a distortion of the coordination geometry. In general, the positions of the absorption maxima indicate a high double bonding character between the metal and the carbon atom (back donation) [28].

The FD mass spectra reveal two main peaks. Table 1 summarizes all values obtained. To differentiate between the mass ion and the cluster ions that are possible in FDMS and eventually occur [29], additional vapour pressure osmometry on the Mo complex has been performed using toluene as solvent. Including GPC measurements, all values (table 1) confirm the first main peak of the FD mass spectra as that of the mass ion. This corresponds in all cases to a mononuclear, monofacial complex.

Monofaciality also agrees well with the results, obtained by ^{13}C NMR measurements and elemental analysis.

Therefore, the schematic structure of the complex can be established as shown in figure 2.

Table 2. ν(CO) absorptions of the *LM* $(CO)_3$ complexes.

M	CH_2Cl_2-solution	KBr-pellet
Cr	1902 (A_1)†, 1767 (E)‡	1892 (A_1)†, 1772, 1730
Mo	1906 (A_1)†, 1767 (E)‡	1896 (A_1)†, 1760, 1730
W	1896 (A_1)†, 1757 (E)‡	1886 (A_1)†, 1768, 1720

† A_1: ν (CO) symmetric mode (cm^{-1}).
‡ E: ν (CO) asymmetric mode (cm^{-1}).

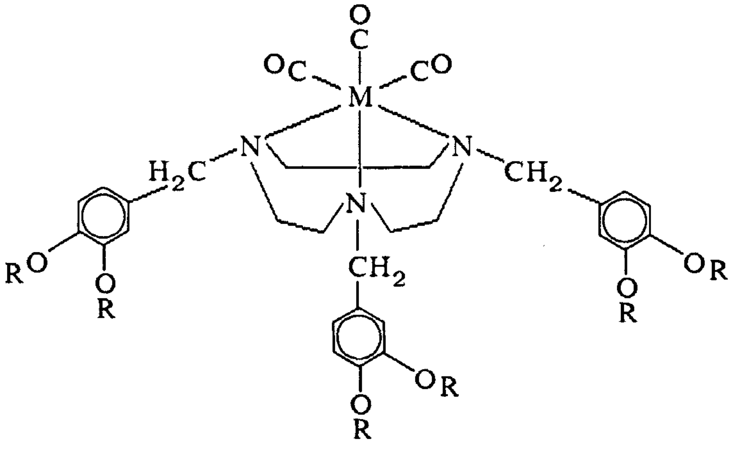


Figure 2. Schematic structure of the *LM*(CO_3) complexes.

3.2. *Thermal behaviour and mesophase structure*

3.2.1. *Polarizing microscopy and DSC*

The thermal properties of the freeze-dried compounds have been investigated by polarizing microscopy and differential scanning calorimetry (DSC). Table 3 shows the corresponding phase transition temperatures on second and further heatings. In all cases a solid–solid transition appears around 57°C, and the melting to the mesophase occurs in the region 62·5 to 67°C. In contrast to this behaviour, the clearing temperature is strongly influenced by the nature of the metallic centre. T_C increases from 174·5°C for the chromium complex to 227·5°C for the tungsten compound. The clearing enthalpies are remarkably high in all cases.

On cooling from the isotropic melt, first a dendritic growing of the texture can be observed with a final development of pseudo-focal-conic domains (see figure 3 (*a*)–(*c*)). This is typical for columnar mesophase structures.

3.2.2. *X-ray measurements*

The wide angle X-ray diagram (see figure 4(*a*)) shows in all cases just a halo, indicative of the presence of short range order. The small angle diffraction is characterized for all samples by the presence of one strong reflection and two weaker ones (see figure 4 (*b*)). The spacings derived from the scattering diagrams are given in table 4. It is obvious that they cannot be attributed to a hexagonal lattice. Indeed, they fit rather a rectangular lattice (table 4). Additional evidence for the correctness of such an assignment comes from the comparison of the scattering behaviour with that for the related triazacyclononane metallo-mesogen with Ni(II) as metal centre [18]. In this

Table 3. Phase transition temperatures (in °C) and (in parentheses) enthalpies (kJ mol^{-1}) for the $LM(CO)_3$ complexes.

M	C_1†		C_2†		Rect. column‡		I§
Cr	●	57·5 (32·3)	●	62·5 (22·9)	●	174·5 (13·6)	●
Mo	●	57·5 (29·6)	●	67·0 (22·9)	●	195·0 (20·8)	●
W	●	57·0	●	62·5 (42·3)¶	●	227·5 (14·0)	●

† C_1, C_2, crystal phases.
‡ Rect. column, disordered rectangular columnar phase.
§ I, isotropic phase.
¶ ΔH value for C_1 and C_2 transitions.

Table 4. Scattering distances *d* and indications of the X-ray (*hk*) reflections for the $LM(CO)_3$ complexes.

Cr *d*/Å	Mo *d*/Å	W *d*/Å	*hk*
	27·5		01
22·2	21·9	21·9	11
19·7	19·3	19·9	20
14·2	13·9	14·1	02

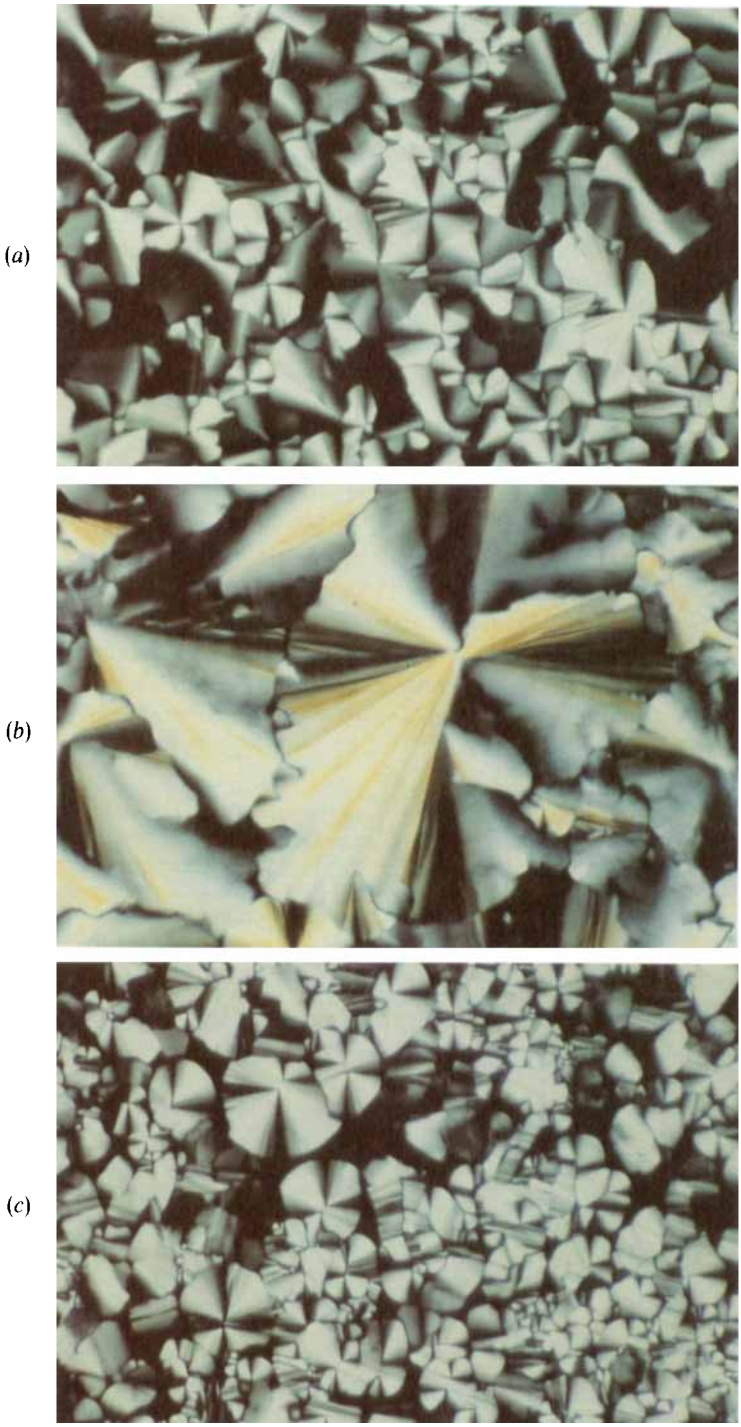


Figure 3. Optical textures for the complexes, between crossed polarizers, after cooling from the isotropic melt; (*a*) $L\mathrm{Cr(CO)_3}$ at 140°C; (*b*) $LM_o\mathrm{(CO)_3}$ at 175°C; (*c*) $LW\mathrm{(CO)_3}$ at 110°C.

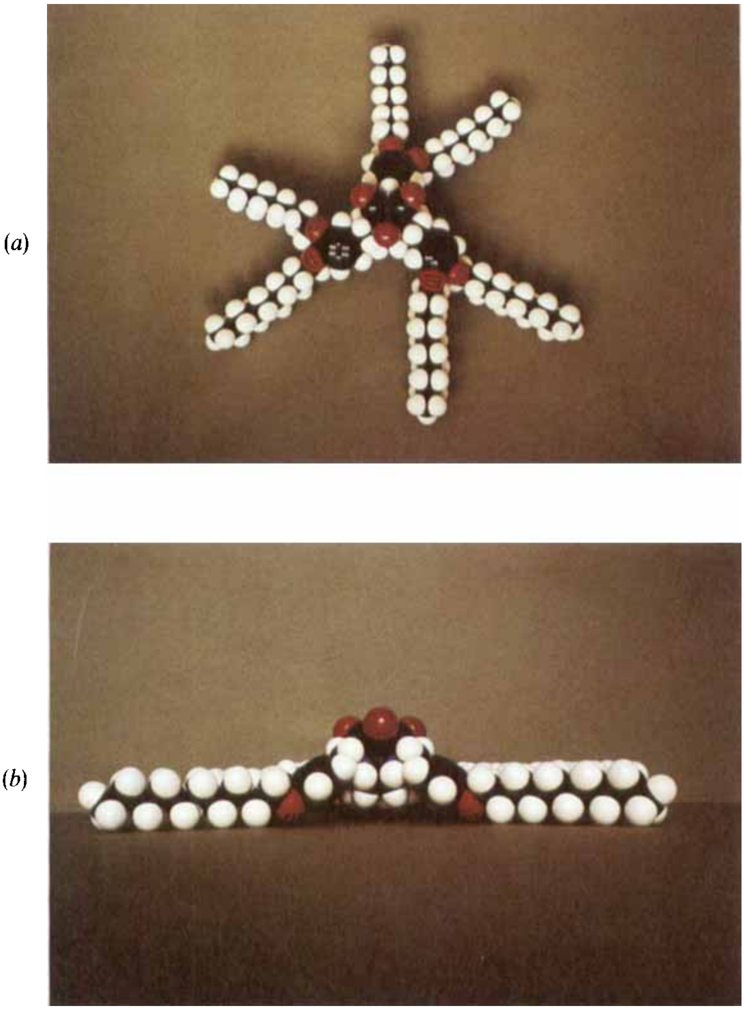
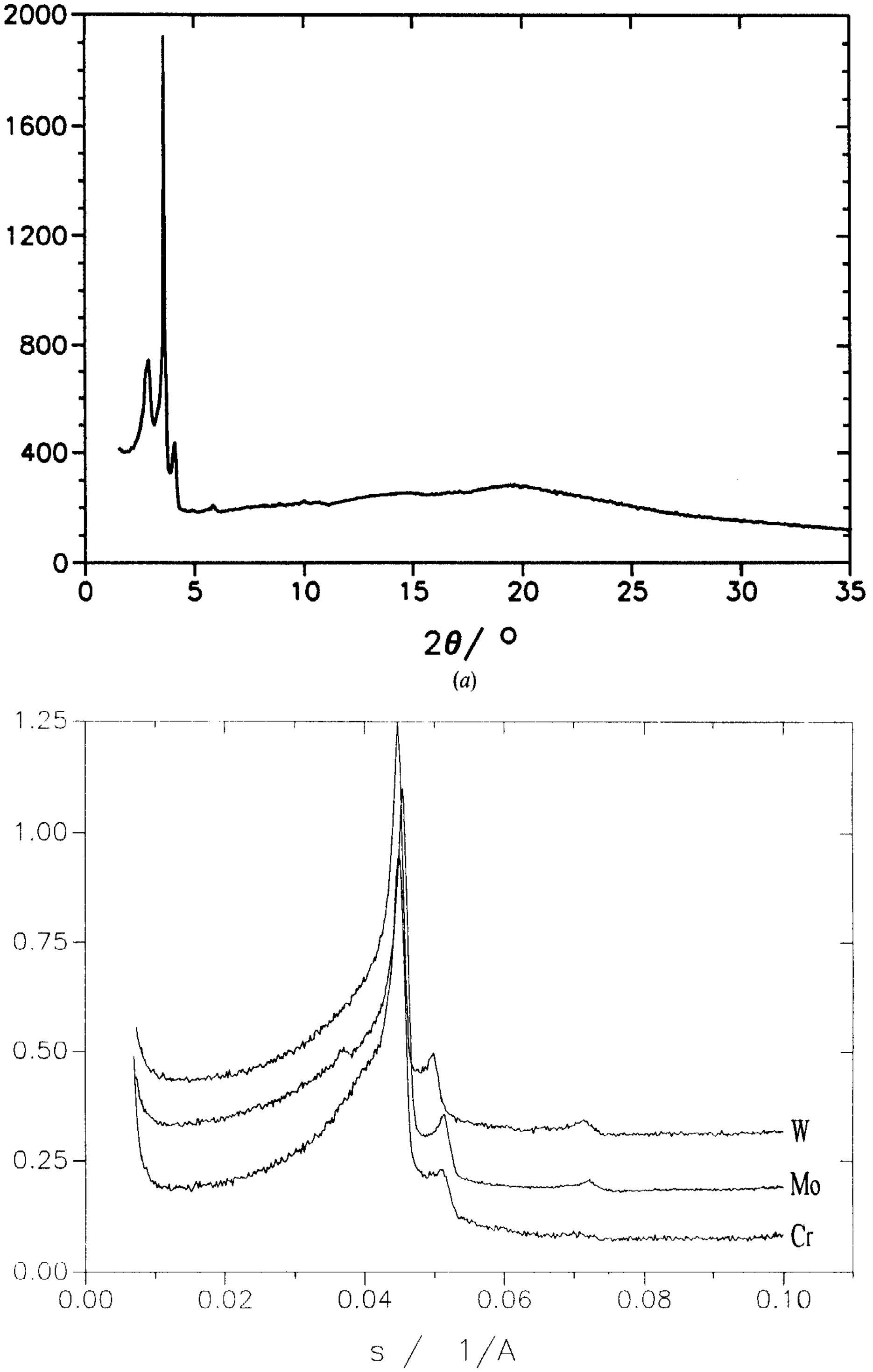


Figure 5. CPK model of $LM(CO)_3$ complexes; (a) viewed from above; (b) side view.

case, we observed a quite similar small angle diagram at temperatures some degrees below the clearing temperature, although we were able to observe there still more reflections [30]. All likewise fitted a rectangular lattice. Therefore, we conclude that the metallo-mesogens described here display a disordered rectangular columnar phase. The cell parameters are given in table 5. They vary only very slightly, i.e. 0·01 Å K^{-1}, with temperature.

3.3. *Discussion*

The CPK model of the complexes (see figure 5) shows that the triazacyclononane ring must have lost its flexibility by being coordinated to the metallic centre. Furthermore, the substituted benzyl groups are more or less fixed to the complex centre at a certain angle. Therefore, the inner part of the complex can be described as pyramidic or conic as schematically shown in figure 6. The tricarbonyl assembly is



(*a*)

(*b*)

Figure 4. X-ray diagrams for the $LM(CO)_3$ complexes at 20°C: (*a*) Wide angle diagram $M = Mo$; (*b*) Small angle (SAXS) diagrams for $M = Cr$, Mo, W.

Table 5. Lattice constants for the $LM(CO)_3$ complexes measured at 353 k (Cr) and 348 K (Mo, W).

Lattice constants/Å	Cr	Mo	W
a	39·4	38·5	39·8
b	28·4	27·9	28·0

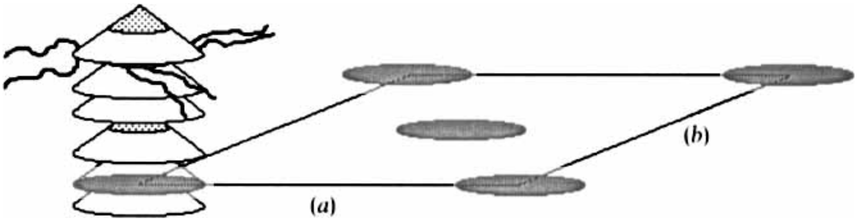


Figure 6. Schematic model for the stacking of $LM(CO)_3$ complexes into the rectangular columnar disordered mesophase structure (a, b = lattice constants).

symbolized as the dotted top of the cone. Furthermore, figure 6 shows the possible schematic arrangement for the stacking of the complex molecules in the rectangular columnar disordered mesophase structure.

4. Summary and conclusions

In summary, we have presented three examples of a new group of metallo-mesogens, which exhibit the following characteristics:

(1) Chromium, molybdenum and tungsten complexes exhibit a d^6 electronic configuration. Mesomorphic complexes of metals with such an electron number are very rare. Only some Fe(II) and Ru(II) mesogens have been realized [2]. In the future, it will be interesting to investigate the oxidation behaviour of the metal centres and the influence on mesomorphism.

(2) The triazacyclononane ligand L is responsible for the formation of the monofacial, octahedral complex. In general, the rarely realized octahedral coordination geometry in metallo-mesogens is highly desirable, because in principle, an octahedral ligand field should either be able to influence the electronic state of several transition metals in an interesting manner [20], or should lead to a special geometrical shape for the complex. In our case, mononuclear, diamagnetic, 18 electron complexes have been obtained. The three carbonyl ligands should create a dipole along the C_3 axis of the complex, as can be deduced from a similar situation found in butadiene iron tricarbonyl metallo-mesogens [31]. From this and the pyramidic shape of the complex, we may assume that a permanent polarization, different from that in a tilted, chiral columnar phase [32], leading to ferroelectric or antiferroelectric behaviour, depending on the interaction between the columns [33–36, 27], may be found for metallo-mesogens of the novel type described. More investigations concerning this field will be made in the future.

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