Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Styring, Peter , Tantrawong, Sukrit , Beattie, David R. and Goodby, John W.(1991) 'Magnetomesogens: Bis(1,3-di(4'-decoxyphenyl)propane-1,3-dionato)oxovanadium (IV)', Liquid Crystals, 10: 4, 581 — 584
To link to this Article: DOI: 10.1080/02678299108036445
URL: http://dx.doi.org/10.1080/02678299108036445

LIQUID CRYSTALS, 1991, VOL. 10, NO. 4, 581–584

Magnetomesogens: bis(1,3-di(4′-decoxyphenyl)propane-1,3-dionato)oxovanadium (IV)

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(*Received 22 April 1991; accepted 28 May 1991*)

β-Diketonate complexes of oxovanadium (IV) have been synthesized and their mesomorphic behaviour investigated. The title complex exhibits a short range monotropic columnar discotic phase, identified by its optical texture and by miscibility studies. The optical texture of the phase is retained on cooling to the crystal. As a consequence of the unpaired electron on vanadium the complexes are paramagnetic.

Interest in metal-containing liquid crystals (metallomesogens) has increased markedly over the past decade. Efforts have been directed mainly towards metallomesogens with low melting points and smectic C and nematic phases, presumably because of potential applications in electrooptic display devices. However, melting points have tended to be high (relative to structurally similar organic mesogens), the complexes are only sparingly soluble in liquid-crystalline hosts and the pure materials are usually thermally and electrically unstable. A system of notable exception is that of the dinuclear copper (II) carboxylates which show non-calamitic hexagonal columnar phases. Such materials have been processed in the mesophase to give highly oriented fibres [1]. Depending on the nature of the metallomesogen, it is possible in theory to develop conducting fibres, or molecular wires [2].

Galyametdinov and coworkers have reported a number of metal salicylaldimine complexes (**1**), including those of copper (II) and oxovanadium (IV) which show smectic C and smectic A mesophases [3,4]. Similar copper [5] and oxovanadium [6] complexes (**2**) have been reported by Serrano and coworkers which not only show smectic, but also nematic phases. Interestingly, the oxovanadium complexes can be aligned in their nematic phases by the application of a 1·4 T magnetic field and the alignment retained on cooling to the crystalline state. Whereas the copper (II) salicylaldimine complexes show calamitic mesomorphism, we have noted that the copper (II) β-diketonate complexes exhibit non-calamitic, discotic phases [7]. Elementary computer modelling suggested that similarly, oxovanadium (IV) β-diketonate complexes should show non-calamitic mesomorphism. Therefore, we undertook the synthesis of a series of substituted oxovanadium (IV) β-diketonate complexes (**3**) in order to evaluate their mesomorphic properties. In this preliminary communication we report the mesomorphic properties of a single member of this series, namely bis(1,3-di(4′-decoxyphenyl)propane-1,3-dionato)oxovanadium (IV), abbreviated to $4C_{10}OVO$. Although representative of this series, we note that this is only one example of many oxovanadium (IV) complexes that we have prepared which exhibit mesomorphism. Detailed results on these materials will be reported at a later date [8].

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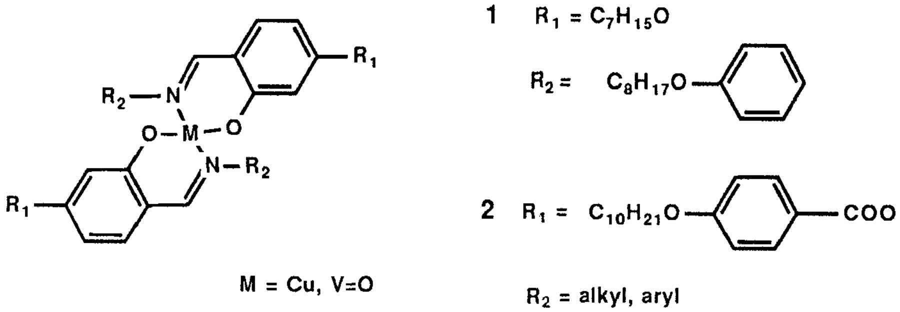

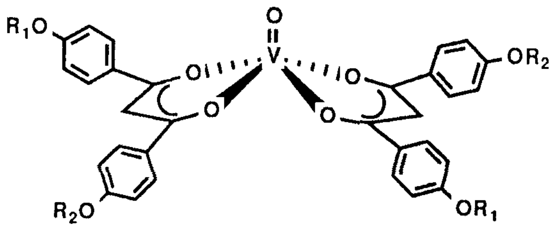

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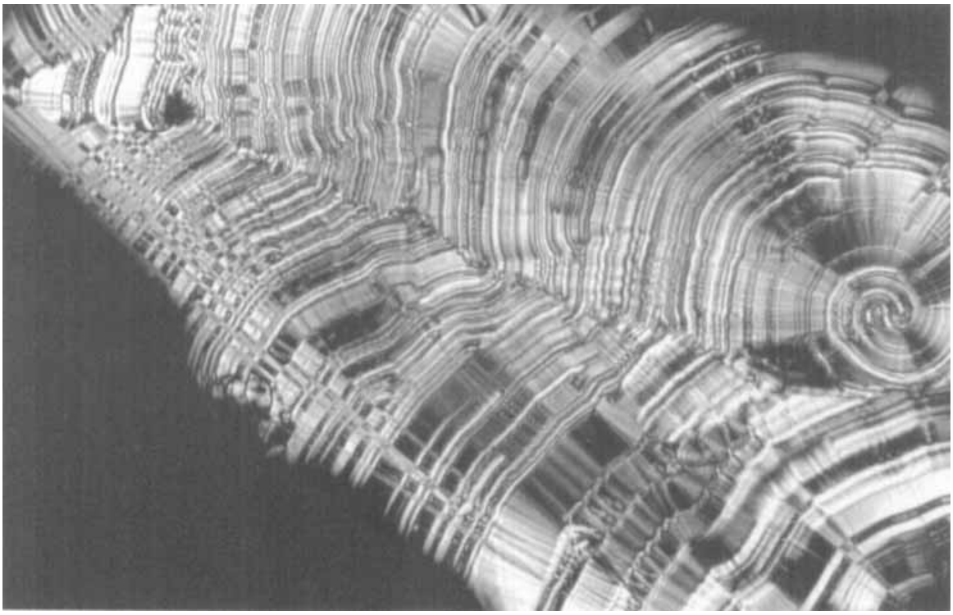
The ligand, 1,3-di(4′-decoxyphenyl)propane-1,3-dione, was prepared according to previously reported procedures [9] and characterized from ^{1}H NMR, IR and mass spectra. The complex was prepared from oxovanadium (IV) sulphate using a modification of the method described by Rowe and Jones [10]. The resulting green coloured complex was recrystallized several times from hot acetone and characterized by elemental analysis and from the IR spectrum. Elemental analysis: calculated (found) for $C_{70}H_{102}O_9V$; C 73·85 per cent (74·86 per cent), H 9·03 per cent (9·10 per cent). Attempts to analyse for vanadium content by inductively coupled plasma spectroscopy were frustrated by the low solubility of the complex in strong mineral acids. However, we feel that the accuracy of the carbon and hydrogen elemental analyses is sufficient to confirm the purity of the complex, while the presence of vanadium was confirmed by the magnetic moment measurements described later. The solid state IR spectrum (KBr disc) was consistent with complexation of diketone ligands around a V=O centre. The unsymmetrical carbonyl stretches around 1600 cm^{-1} in the ligand were resolved in the complex and of essentially equal intensity, and a new absorption was observed at 994 cm^{-1} (sharp), characteristic of the V=O stretch. The latter value is consistent with that observed [11] in the solid state spectrum of VO(acac)$_2$ of 997 cm^{-1}. Isothermal magnetic studies were performed at 19°C on crystalline samples using a Johnson Matthey susceptibility balance of the Gouy type. The paramagnetic moment of the complex, uncorrected for the diamagnetic contributions of the ligands, was determined to be 1·19 ± 0·09 BM, whereas the corrected value was calculated to be 1·80 ± 0·9 BM. This is consistent with vanadium in the IV oxidation state ([Ar]3d^{1}4s^2), and thus possessing a single unpaired electron and is close to the spin-only value for the paramagnetic moment of 1·73 BM. Initially it was thought that the complex might be polymeric in nature, at least in the crystal form, due to axial intermolecular oxygen–vanadium interactions. This proposition was discounted as a result of our experimental studies as the V=O stretching frequency of a polymer would be expected to be lower [12], in the range 800–850 cm^{-1}, and the paramagnetic dipole moment would also be substantially reduced.

Mesomorphism was studied initially by thermal optical microscopy using a Zeiss Universal polarized light microscope equipped with either a Mettler FP 52 hot stage and FP 5 temperature controller or a Linkam THM600 hot stage and PR600 temperature controller. Transition temperatures were confirmed by differential scanning calorimetry using a Perkin–Elmer DSC7/IBM system. On heating, $4C_{10}OVO$ melted directly into the isotropic liquid at 165°C. However, depending on the cooling rate employed, it was possible to observe without question a short range monotropic discotic phase. At cooling rates of $5^\circ C\,min^{-1}$ and above crystallization occurred directly from the isotropic liquid. When the rate was reduced to $3^\circ C\,min^{-1}$ a columnar discotic phase was observed, the texture developing as platelets which then became banded, as shown in figure 1. The texture was retained on cooling, even on standing for several days at room temperature. Close examination of the optical texture suggests that the discotic phase is probably a hexagonal columnar (D_h) phase which is consistent with the molecular shape. The DSC trace showed a single endotherm at $T_{onset}=162{\cdot}8^\circ C$ at a heating rate of $10^\circ C\,min^{-1}$ ($\Delta H=61{\cdot}7\,kJ\,mol^{-1}$, $\Delta S=17{\cdot}0\,J\,K^{-1}\,mol^{-1}$). When the sample was cooled at $3^\circ C\,min^{-1}$, two partially resolved exotherms were observed with the following onset temperatures: $T_{DI}=140{\cdot}7$ and $T_{CD}=136{\cdot}8^\circ C$ ($\Delta H_{(combined)}=61{\cdot}9\,kJ\,mol^{-1}$, $\Delta S_{(combined)}=18{\cdot}2\,J\,K^{-1}\,mol^{-1}$). The higher temperature peak corresponded to the transition from isotropic liquid to the liquid crystal phase and the lower temperature peak to crystallization. Optically there was little difference between the textures of the mesophase and crystal phase suggesting that the liquid-crystalline order is retained on crystallization. In order to confirm the identity of the discotic phase, miscibility studies were carried out with standard materials. Contact preparations were studied on cooling from the isotropic phase of $4C_{10}OVO$. By using thin films in a strong light source it was possible to obtain good



The optical texture of the D_{ho} phase in $4C_{10}OVO$ formed on cooling from the isotropic liquid (magnification ×35).

transmission and therefore excellent textures. A homogeneous texture, without discontinuity, was observed at the interface of a contact preparation between $4C_{10}OVO$ and tetrakis(tetradecanato)copper (II) [13] in the mesophase range of both complexes. This confirms the existence of a hexagonal columnar (D_h) phase in $4C_{10}OVO$. Similar mesomorphic behaviour was observed in other membranes of this series of compounds [8].

The fact that the optical texture persists on cooling into the crystal phase suggests that molecular orientation is retained in the crystal phase, which is similar to the situation found in Giroud-Godquin's copper (II) carboxylate fibres. This may lead to interesting properties in the crystal phase, for example, ferroelectricity or second harmonic generation as a consequence of the axial vanadium–oxygen dipole. Because of the unusual nature of these mesogens we have embarked on further studies in order to characterize fully the structure of the mesophase. This will be achieved by a combination of single crystal and low angle X-ray diffraction in the first instance, then by EXAFS in the columnar and crystal phases. The fact that oxovanadium (IV) complexes are intrinsically paramagnetic naturally suggests these materials as candidates for temperature dependent magnetic studies.

We are grateful to Thorn EMI plc and STC plc for funding the lectureship to PS, the Thai Government for support in the form of the studentship to ST and the procurement of the Ministry of Defence (RSRE) for support to DRB.

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