Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Oxovanadium(IV) Metallomesogens Derived from 1,3-Diketonate Ligands: The Importance of Ligand Design

Sukrit Tantrawong [a] & Peter Styring [a]
[a] School Of Chemistry, The University of Hull, Hull, HU6 7RX, UK

Version of record first published: 04 Oct 2006

To cite this article: Sukrit Tantrawong & Peter Styring (1997): Oxovanadium(IV) Metallomesogens Derived from 1,3-Diketonate Ligands: The Importance of Ligand Design, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 302:1, 309-314

To link to this article: http://dx.doi.org/10.1080/10587259708041842

Mol. Cryst. Liq. Cryst., 1997, Vol. 302, pp. 309–314
Reprints available directly from the publisher
Photocopying permitted by license only

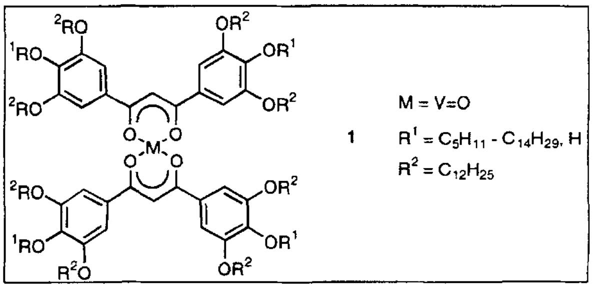
OXOVANADIUM(IV) METALLOMESOGENS DERIVED FROM 1,3-DIKETONATE LIGANDS: THE IMPORTANCE OF LIGAND DESIGN

SUKRIT TANTRAWONG AND PETER STYRING
School Of Chemistry, The University of Hull, Hull HU6 7RX, UK.

Abstract The effects of structural modification of the chelating ligand on mesophase stability in a number of oxovanadium(IV) complexes has been studied. Enantiotropic phases are observed when the complexes exhibit small long-range associations together with anti-ferromagnetic dimerisation. If either case is not satisfied, monotropic phases are observed. The calamitic nature of the observed phases in rationalised in the context of results obtained from molecular simulation experiments on the parent ligands.

INTRODUCTION

The last ten years have witnessed extraordinary advances in metal-containing liquid crystal (metallomesogen) science and many reviews have appeared in the literature[1]. The range of metal centres available to the chemist for incorporation in metallomesogen systems has increased considerably in that time, due in part to the careful design of new pro-mesogenic ligands. Bidentate chelating ligands have been used extensively and wide ranging chemical, physical and structural studies have been carried out on copper(II) complexes of 1,3-diketonate ligands in particular. In recent years, Swager[2], Maitlis[3] and ourselves[4] have reported analogous complexes using the oxovanadium (IV) metal ion (**1**) which show discotic mesomorphism. In this paper we will look at the importance of ligand design in the synthesis of calamitic oxovanadium(IV) metallomesogens.



1

M = V=O

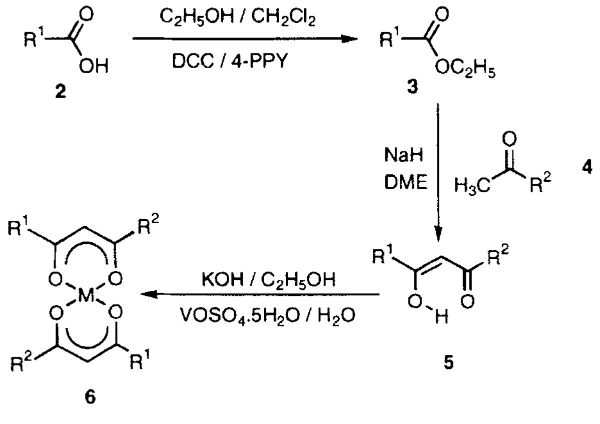
$R^1 = C_5H_{11} - C_{14}H_{29}$, H

$R^2 = C_{12}H_{25}$

EXPERIMENTAL PROCEDURE

The ligands and complexes were prepared according to the procedure outlined in Scheme 1. The appropriate ethyl carboxylic ester (3) was prepared from ethanol and the carboxylic acid (2) together with N,N-dicyclohexylcarbodiimide (DCC) and 4-pyrrolidinopyridine (4-PPY) in dichloromethane. The esters were purified by column chromatography in yields of 80 % or greater. Condensation of 3 with an appropriate methyl ketone (4) in 1,2-dimethoxyethane using sodium hydride as base followed by acidic work-up gave the 1,3-diketone (5) in yields of typically 30 % after repeated recrystallisations from ethanol. The complexes were formed by reaction of 5 in ethanol with ethanolic potassium hydroxide at ambient temperature followed by addition of an ice-cold solution of oxovanadium(IV) sulfate pentahydrate in water. The target complexes (6) were isolated in good yields as green micro-crystals after repeated recrystallisations from acetone. Satisfactory analyses (Table 1) were achieved for each complex, the abbreviations for which are found in Table 2.

SCHEME 1 Synthesis of the 1,3-diketonate complexes



DISCUSSION

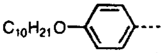
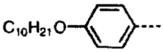
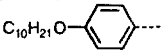
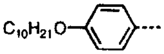
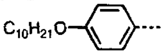
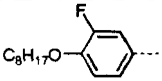
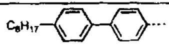
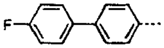
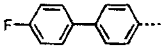
The mesomorphic properties (Table 2) of the intermediate ligands and complexes were determined by polarised light microscopy (Olympus BH-2) using a Mettler FP52 microfurnace and FP5 temperature controller. Transitions were confirmed calorimetrically using a Perkin Elmer DSC7-PC with indium metal as the reference standard. The complexes prepared may be divided in to two sub-groups: those in where R^1 possesses a single aromatic ring, and those where R^1 contains two rings.

TABLE 1 Analytical data for the oxovanadium(IV) complexes

Complex	Yield / %	$\nu_{V=O}$ / cm^{-1}	μ / μ_B	% C Calc (Found)	% H Calc (Found)
10OP7	69	955	1.45	71.4 (71.7)	9.6 (9.5)
10OP9	43	955	1.52	72.3 (72.6)	9.8 (9.8)
10OP11	61	965	1.55	73.5 (73.4)	9.8 (10.1)
10OP13	39	960	1.63	74.1 (74.0)	10.2 (10.3)
10OP7CH	49	980	1.65	74.6 (74.3)	10.1 (9.9)
8OFP8	68	965	1.60	68.1 (68.4)	9.1 (8.8)
7BCH8	81	980	1.49	75.2 (75.2)	11.6 (11.3)
7PCH8	60	995	1.83	76.7 (76.6)	8.6 (8.5)
8BP8	67	995	1.71	77.2 (77.1)	9.0 (9.1)
FBP9	75	995	1.52	76.7 (76.8)	7.7 (7.5)
FBP7BCH	59	970	1.46	76.3 (76.0)	8.2 (8.3)

For the single ring systems, monotropic smectic phases were observed in all cases where R^2 was a simple n-alkyl chain, smectic A for short chain lengths and smectic A and C for longer chain lengths. If R^2 was a 4-n-heptylcyclohexyl unit (10OP7CH), an enantiotropic smectic A phase resulted with an additional monotropic smectic C phase. The overall length of this complex is comparable with 10OP11 and the molecular weight is the same as in 10OP13, yet the melting point is stabilised by 43 and 40 °C respectively. We have attributed the increased mesophase stability of 10OP7CH to rotational damping of the alkyl chain by the inclusion of the more rigid cyclohexane ring close to the co-ordinating core which allows for better molecular packing in the smectic layers. Additionally, the frequency of the V=O stretch in the IR spectrum of 10OP7CH indicates very little intermolecular O...V association while the lower values obtained for each of the other one ring systems suggests a stronger interaction. Lateral fluorination of the phenyl ring has little effect on phase stability as can be observed in complex 8OFP8 which exhibits a monotropic smectic A phase.

TABLE 2 Transition temperatures of the oxovanadium(IV) complexes

Complex	R[1]	R[2]	Transition Temperatures (°C)
10OP7		C_7H_{15}---	K 51 (S_A 39.6) Iso
10OP9		C_9H_{19}---	K 64 (S_A 49.8) Iso
10OP11		$C_{11}H_{23}$---	K 67 (S_C 49.2 S_A 63.4) Iso
10OP13		$C_{13}H_{27}$---	K 70 (S_C 51.2 S_A 57.5) Iso
10OP7CH			K 110 (S_C 82.3) S_A 117.9 Iso
8OFP8		C_8H_{17}---	K 64 (S_A 54.5) Iso
7BCH8		C_8H_{17}---	K 108 (S_A 64.0) N 128.0 Iso
7PCH8		C_8H_{17}---	K 122 (S_A 94.0 N 117.7) Iso
8BP8		C_8H_{17}---	K 132 (S_A 105.0 N 125.7) Iso
FBP9		C_9H_{19}---	K 97 (S_A 82.3) N 98.8 Iso
FBP7BCH			K 185 N >290 Dec.

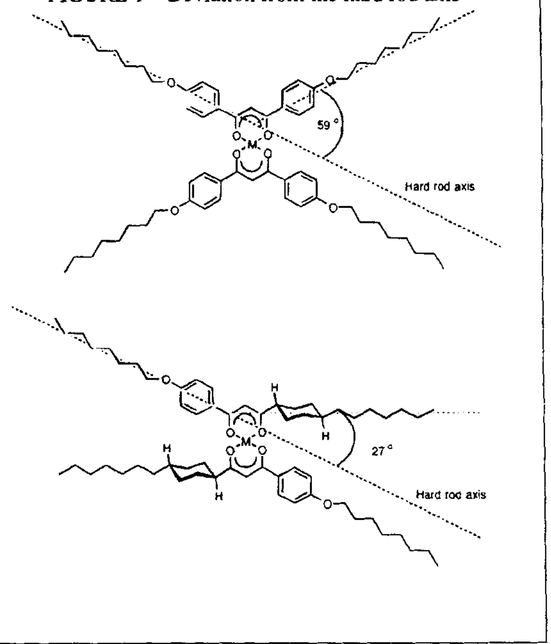
For all the one ring systems, the measured paramagnetic moment (μ) corrected for the strong diamagnetic contributions of the ligands are somewhat reduced in comparison with the spin only value of 1.73 μ_B expected for the V^{4+} ion with the electronic configuration [Ar] $3d^1$. This would indicate a degree of anti-ferromagnetic coupling between molecules of the type observed in structurally related oxovanadium(IV) complexes, resulting from a sideways direct σ metal-metal anti-ferromagnetic interaction. This produces magnetically isolated exchange-coupled pairs in which the unpaired d electron from each vanadium atom is assigned to the $3d_{xy}$ orbital.[5] The observed reduction in μ[6] can be confirmed using the Bleaney-Bowers susceptibility equation[7] which gives a calculated value for exchange-coupled pairs as typically 1.4 μ_B at 27 °C.

When a two ring substituent is used at R^1, the overall thermal stability of the complexes increases. The 4-n-heptylbicyclohexyl substituted complex (7BCH8) exhibits an enantiotropic nematic phase and a monotropic smectic A phase. The same phases are again observed in the 4-n-heptylphenylcyclohexyl (7PCH8) and 4-n-octylbiphenyl (8BP8) substituted complexes, however both have become monotropic. If a 4-fluorobiphenyl substituent is used at R^1 then an enantiotropic nematic phase and a monotropic smectic A phase are observed for R^2 = n-nonyl (FBP9) and an enantiotropic nematic phase alone is observed for R^2 = 4-n-hexylbicyclohexyl (FBP7BCH). The V=O stretching frequency in the IR spectra of each of the two ring systems shows little or no deviation from that expected for a pure monomeric species (997 cm^{-1}) suggesting minimal intermolecular O...V interactions. The values of μ observed for the two ring complexes which exhibit monotropic mesomorphism are close to the expected spin-only values. However, the three complexes in this sub-group which show enantiotropic nematic phases exhibit values of μ which are significantly reduced. This would indicate a degree of anti-ferromagnetic coupling between molecules as described previously. If T_{NI} is sufficiently stabilised (FBP7BCH), then thermal disruption of the O...V interactions can take place at a temperature below the clearing point and therefore an enantiotropic nematic phase is observed despite the low value observed for ν in the IR spectrum.

At first glance, it appears strange that the complexes discussed exhibit calamitic mesomorphism yet complexes of structure **1** exhibit discotic columnar phases. Molecular mechanics simulations performed on the parent ligands using a combination of Cerius^2 on a Silicon Graphics workstation and Nemesis for Windows show that for the diaryl ligands used in the synthesis of **1** there is a deviation of 59° from the hard rod axis, whereas in the ligand of 10OP7CH the deviation is only 27°. A schematic representation is shown in Figure 1. The latter is more conducive to calamitic phase formation and the resulting complex is observed as an elongated 'H' shape with a molecular length of 33 Å and a width of approximately 7 Å at the periphery of the molecular core, neglecting normal rotation of the n-alkyl chains.

It would appear that the use of ligands which promote disruption of long-range ordering of the V=O dipoles, as reflected in the high values of the V=O IR stretching frequency(ν), and which also promote anti-ferromagnetic, dimeric coupling of the molecules, resulting in a value of the effective paramagnetic moment close to the spin-only value of 1.73 μ_B, promotes enantiotropic phase formation. If intermolecular O...V inter-actions are too strong (low ν), thermal breakdown of the association results in a direct transition to the isotropic liquid and phase formation can only occur on supercooling, as intermolecular interactions again become stronger and anti-ferromagnetic pairing can occur. Enantiotropic phases may be observed in systems with reasonably strong intermolecular interactions if the T_{NI} is sufficiently stabilised (FBP7BCH).

FIGURE 1 Deviation from the hard rod axis



REFERENCES

1. (a) A.M. Giroud-Godquin and P.M. Maitlis, Angew. Chem. Int. Ed. Engl., 30, 375 (1991); (b) P. Espinet and J.L. Serrano, Coord. Chem. Rev, 117, 275 (1992); (c) P.M. Maitlis and S.A. Hudson, Chem. Rev., 93, 861 (1993); (d) D.W. Bruce in 'Inorganic Materials' D.W Bruce and D. O'Hare (Eds.), Wiley and Sons, Chichester, 1992; (e) 'Metallomesogens', J.L. Serrano (Ed.), VCH, Weinheim, 1996.
2. A. Serrette, P.J. Carroll and T.M. Swager, J. Am. Chem. Soc., 114, 1887 (1992).
3. S.N. Poelsma, A.H. Servante, F.P. Fanizzi and P.M. Maitlis, Liq. Cryst., 16, 675 (1994).
4. (a) S. Tantrawong, P. Styring, D.R. Beattie and J.W. Goodby, Liq. Cryst., 10, 581 (1991); (b) S. Tantrawong, P. Styring and J.W. Goodby, J. Mater. Chem., 3, 1209 (1993).
5. A.P. Ginsberg, E. Koubek and H.J. Williams, Inorg. Chem., 5, 1656 (1966).
6. V.V. Zelentsov, Russ. J. Inorg. Chem., 7, 670 (1962).
7. B. Bleaney and K.D. Bowers, Proc. R. Soc. London A, 214, 451 (1952).