Materials easily Orientated in a Magnetic Field: Paramagnetic Nematic Liquid Crystal Oxovanadium(IV) Complexes with Bidentate Schiff's Bases

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Bis-(*N*-R,4-decyloxybenzoyloxysalicylideneaminato)oxovanadium(IV) complexes (where R = n-C_mH_{2m+1} and m = 1,5,10 or R = $-C_6H_4-O-C_mH_{2m+1}$ and m = 1,2,5,10) showed a paramagnetic nematic mesophase (except for R = Me), and some complexes also showed smectic phases; the low viscosity of the mesophase allows the easy orientation of the molecules in a magnetic field, the orientation remaining in the state solid.

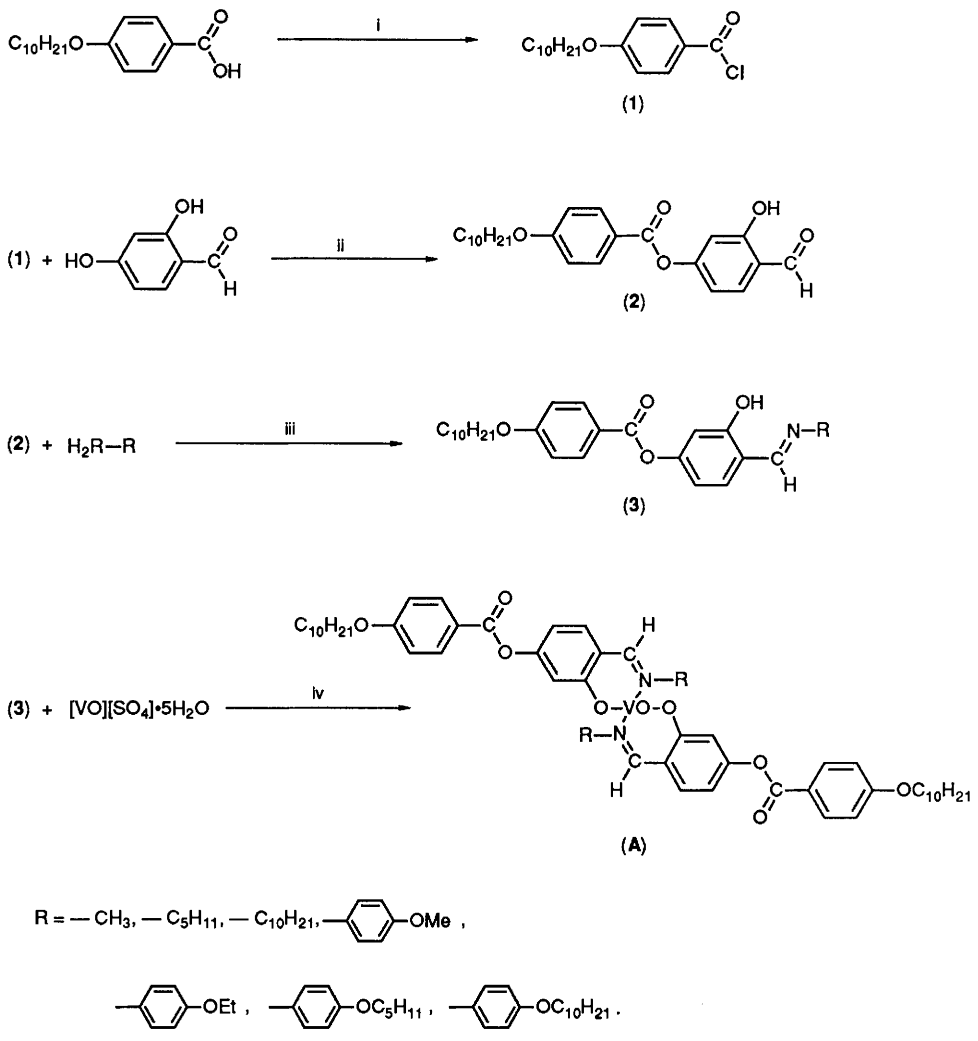
The introduction of transition metals into mesogens confers special magnetic and electro-optic properties to these materials.[1] Recent interest in metallo-mesogens has been focused on paramagnetic nematic liquid crystals.[2] We previously reported that bis-(N-C_mH_{2m+1}, 4-decyloxybenzoyloxysalicylideneaminato)copper(II) complexes are new materials which give wide paramagnetic nematic ranges.[3] All these complexes have a centrosymmetric square-planar geometry. Here we report that complexes (**A**), which have a square pyramidal geometry and contain a vanadium(IV) atom (as vanadyl group), exhibit liquid crystal properties forming a paramagnetic nematic mesophase and in some cases smectic phases as well.

As a result of their molecular structure, the complexes have a net electric dipole moment along their C_2 symmetry axis which is perpendicular to the plane that contain the ligands. This may have important consequences regarding the nature of the molecular packing and the physical properties of the mesophases formed by these compounds.[4] We also believe these complexes are of special interest because they are the first nematogenic vanadyl chelates with Schiff's bases described to date.[5]

The complexes were obtained following the route illustrated in Scheme 1 by refluxing a mixture of a solution of the ester (**3**) (2 mmol) in ethanol with a solution of $[VO][SO_4]\cdot5H_2O$ (1 mmol) in water, using a method described in the literature.[6]

The final products as well as the intermediates were all characterized by microanalysis for which satisfactory results were obtained and by IR and UV–visible spectroscopy. The stability of the complexes was studied by thermogravimetric analysis using a Perkin-Elmer TGS-2 equipped with a system 4 Microprocessor at a heating rate of 10 °C/min, under nitrogen; none showed a weight loss below 274 °C, thereby confirming the absence of water molecules.

Their phase behaviour was examined with an optical



Scheme 1. *Reagents and conditions*: i, $SOCl_2$, dimethylformamide, reflux, 2 h; ii, CH_2Cl_2, Et_3N, room temp., several hours; iii, EtOH, AcOH, reflux; iv, $EtOH/H_2O$, NaOAc, reflux, 1 h.

microscope equipped with a polarizing light source, a Mettler FP82 hot stage, and a Mettler FP 80 central processor. Transition temperatures and enthalpies were measured using a Perkin-Elmer DSC-2 differential scanning calorimeter with a heating or cooling rate of 10 K/min [the apparatus was calibrated with indium (156.6 °C; 28.4 J/g) and tin (232.1 °C; 60.5 J/g) as standards]. The phase transitions and the enthalpy changes corresponding to the first scan are summarized in Table 1.

All the complexes synthesized, except for R = Me, are mesogens.

The mesophases shown by the complexes were identified as smectic C (S_C) and nematic (N) by their optical textures, which are similar to those observed for classical rod-like organic compounds.[7]

The nematic mesophases showed a marbled texture on heating and Schlieren texture on cooling. The smectic C mesophase is clearly identified on cooling from the nematic phase by the Schlieren textures. Typical transition bars are also observed during the smectic C to nematic transition when the two phases appear. Preliminary *X*-ray diffraction studies on the nematic phase are consistent with these microscopic observations.

The compounds with R = $-C_6H_4-OEt$, $-C_6H_4-OC_5H_{11}$, and $-C_6H_4-OC_{10}H_{21}$ exhibit an additional birefringent phase, labelled S_{crys}, which is stable in the ranges 199.3—207.4, 173.9—224.8, and 161.1—227.0 °C respectively. Experiments performed on this phase indicate that it is not crystalline; for example the sample does not show fractures but rather a considerable deformation resembling the properties of a gum when mechanical stress is applied.

The complexes with R = $-C_6H_4-OEt$ and $-C_6H_4-OMe$ decompose after the complex has become isotropic.

The enthalpies of the nematic to isotropic transition are similar to those of other rod-like organic mesogenic compounds. The enthalpies for the transition S_{crys} to the nematic or to the smectic C phase are large which means that the S_{crys} phase is very ordered.

Both kinds of complex (*N*-aryl and *N*-alkyl) show paramagnetic mesophases as indicated by EPR spectroscopy. In particular, the EPR spectra of complexes with R = n-C_5H_{11} and R = $-C_6H_4-OC_5H_{11}$ were recorded at temperatures

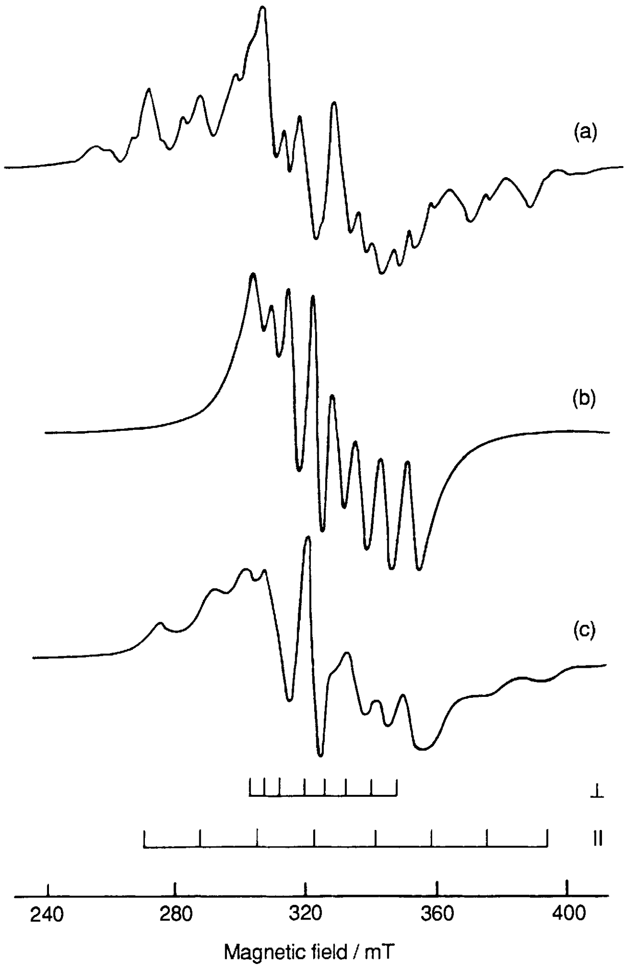


Figure 1. EPR spectra for complex (**A**; R = n-C_5H_{11}) (a) room temperature, powder sample; (b) 115 °C, nematic phase after heating to 150 °C and cooling in the presence of a magnetic field of 1.4 T; (c) 150 °C, isotropic liquid phase.

Table 1. Optical, thermal, and thermodynamic data for oxovanadium complexes.

R[a]	Transition	T/°C	ΔH/kJ mol^{-1}
Me	C–I	157.9	39.33
C_5H_{11}	C–N	109.4	89.86
	N–I	131.0	4.88
$C_{10}H_{21}$	C–S_C	91.7	84.64
	S_C–N	103.1	3.37
	N–I	118.4	1.11
–C_6H_4–OMe	C–N	208.6	79.30
	N–I	281.7	3.14
–C_6H_4–OEt	C–C′	78.2	3.92
	C′–S_{crys}	199.3	69.60
	S_{crys}–N	207.4	
	N–I	280.9	1.34
–C_6H_4–OC_5H_{11}	C–S_{crys}	173.9	35.65
	S_{crys}–N	224.8	29.78
	N–I	266.5	1.06
–C_6H_4–$OC_{10}H_{21}$	C–S_{crys}	161.1	50.68
	S_{crys}–S_C	227.0	43.29
	S_C–N	239.7	8.58
	N–I	247.1	2.31

[a] Aromatic substituents are *para*-substituted.

between room temperature and a temperature slightly higher than the clearing point, before and after several heating–cooling cycles, in either the presence or the absence of a magnetic field.

These molecules are easily orientated in the presence of a magnetic field and show positive anisotropy of the magnetic susceptibility. Figure 1 gives the spectra for complex R = n-C_5H_{11} in polycrystalline, nematic, and isotropic phases. The complex spectrum of the solid becomes more simple in the nematic phase when the molecules are orientated by the magnetic field. This spectrum can be described by a standard axial spin Hamiltonian whose parameters do not change with temperature: $g_{\parallel} = 1.945 \pm 0.005$ and $g_{\perp} = 1.978 \pm 0.005$; $A_{\parallel} = 485 \pm 5$ and $A_{\perp} = 180 \pm 5$ MHz. These values agree well with those reported for other $(VO)^{2+}$ complexes.[8] It is noteworthy that the molecular orientation is maintained even in the isotropic phase in spite of the high molecular motion and in the solid state after cooling in presence of a magnetic field. More studies are in progress.

Studies carried out in order to determine the biaxiality of the nematic mesophase were unsuccessful. This nematic mesophase was uniaxial in the case of R = –C_6H_4–OC_5H_{11} and the sample with R = n-C_5H_{11} could not be well orientated.

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References

1 Ch. Piechocki, J. Simon, A. Skolious, D. Guillon, and P. Weber, *J. Am. Chem. Soc.*, 1982, **104**, 5245; S. Takahashi, Y. Takai, H. Morimoto, and K. Sonogashira, *J. Chem. Soc., Chem. Commun.*, 1984, 3; M. P. Eastman, M. L. Horng, F. Freiha, and K. W. Shen, *Liq. Cryst.*, 1987, **2**, 223; J. S. Moore and S. I. Stupp, *Polymer Bull.*, 1988, **19**, 251; P. Espinet, J. Etxebarria, M. Marcos, J. Perez, A. Remón, and J. L. Serrano, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1065.

2 Ch. Chandrasekhar, B. K. Sadashiva, and B. S. Srikanta, *Mol. Cryst. Liq. Cryst.*, 1987, **151**, 93; S. Chandrasekhar, B. R. Ratna, B. K. Sadashiva, and V. N. Raja, *Mol. Cryst. Liq. Cryst.*, 1988, **165**, 123; Yu. G. Galymetdinov, A. Z. Zakieva, and I. V. Ovchinnikov, *Izvest Akad. Nauk. SSSR, Ser. Khim.* (Engl. translation), 1986, (2), 491; Yu. G. Galymetdinov, G. I. Ivanova, and I. V. Ovchinnikov, *Izvest. Akad. Nauk. SSSR, Ser. Khim.*, 1989, **183**, 1931.

3 M. Marcos, P. Romero, and J. L. Serrano, *J. Chem. Soc., Chem. Commun.*, 1989, 1641.

4 P. Palffy-Muhoray, M. A. Lee, and R. G. Pestchek, *Phys. Rev. Lett.*, 1988, **60**, 2303.

5 During the preparation of this paper we found two reports by Yu. G. Galymetdinov, G. I. Ivanova, and I. V. Ovchinnikov on bis(4-heptyloxy-2-hydroxy-*N*-4-octyloxybenzylideneaminato-(oxo)vanadium(II): *Z. Obshch. Khim.*, 1984, **54**, 2796, in which the particular phase identity was not reported, and Yu. G. Galymetdinov, I. G. Bikchantaev, and I. V. Ovchinnikov, *ibid.*, 1988, **58**, 1326 (*Chem. Abstr.*, 1988, **109**, 202093n), where the mesophase exhibited by the complex is described as smectic A.

6 M. Pasquali, F. Marchetti, C. Floriani, and S. Merlino, *J. Chem. Soc., Dalton Trans.*, 1977, 139.

7 D. Demus and L. Richter, 'Textures of Liquid Crystals,' Verlag Chemie, New York, 1978; G. W. Gray and J. W. Goodby, 'Smectic Liquid Crystals,' Leonard Hill, 1984.

8 D. L. Griscom, *J. Non-Cryst. Sol.*, 1980, **40**, 211; C. P. Stewart and A. L. Park, *J. Chem. Soc., Dalton Trans.*, 1972, 11661; H. G. Hecht and T. S. Johnson, *J. Chem. Phys.*, 1967, **46**, 23; B. R. McGarvey, *J. Phys. Chem.*, 1967, **71**, 51; V. K. Jain, V. P. Seth, and R. K. Malhotra, *J. Phys. Chem. Sol.*, 1984, **45**, 529; P. J. Alonso, E. Zorita, and R. Alcalá, *ibid.*, 1985, **45**, 1351.