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Di[2-(4-substituted-phenyl)-3-mercapto-propenato]-nickel(II) complexes. Metallo-mesogens exhibiting broad nematic ranges

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Di[2-(4-substituted-phenyl)-3-mercapto-propenato]-nickel(II) complexes

Metallo-mesogens exhibiting broad nematic ranges

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Di[2-(4-substituted-phenyl)-3-mercapto-propenato]-nickel(II) complexes have been synthesized and investigated. All of them are mesomorphic; they have nematic phases with wide ranges and typical Schlieren textures.

Liquid crystalline transition metal complexes are of great current interest. The incorporation of a metal centre into a liquid crystal molecule not only offers an interesting approach to many new technical applications [1], but also can be used as a possible way to test new structures and geometries capable of forming mesophases, in order to improve our understanding of the liquid crystalline state.

Stilbazoles [2], phthalocyanines [3], β-diketones [4, 5] and malondialdehydes [6], for example, have been used for the preparation of new metallo-mesogens. In our search for suitable ligands, we noticed, that monothio-β-diketones have not been taken into consideration for this purpose until now, although they form very stable square planar nickel(II) chelates [7, 8]. The synthetic route we chose is shown in figure 1 and corresponds to a literature method [9] for similar monothio-ketones. In this way we were able to obtain 4-substituted-phenylmonothio-malondialdehydes (**V**). Because those compounds are rather unstable, we converted the compounds **V** into the corresponding nickel(II) chelates **VI** directly. The final products, as well as the intermediates, were characterized by NMR, elemental analysis, and UV and IR spectroscopy. The spectroscopic data were typical for materials with the given structures, and in the tables, elemental analytical data are given for one homologue from each of the two series prepared. The chelates **VI** have a violet, almost black colour and all of them are mesomorphic. Unfortunately, we could not determine the crystal structure of our chelates. However, X-ray investigations of analogous chelates [10, 11] have revealed that those O,S-chelates have the *cis*-configuration and we propose this configuration also for the di[2-(4-substituted-phenyl)-3-mercapto-propenato]-nickel(II) complexes **VI**.

The phase behaviour was examined by optical microscopy (Nikon Optiphot-2, Linkam THM 600/S) and confirmed by DSC (Perkin–Elmer DSC 7). The transition temperatures and enthalpies for the complexes **VI** are listed in tables 1 and 2. Figure 2

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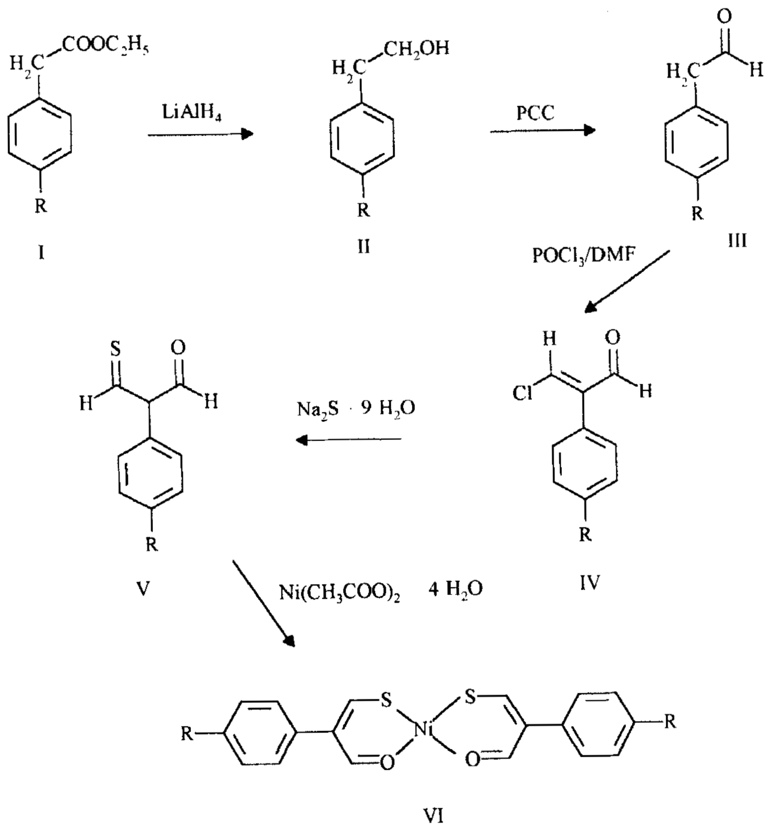

Figure 1. Reaction scheme.

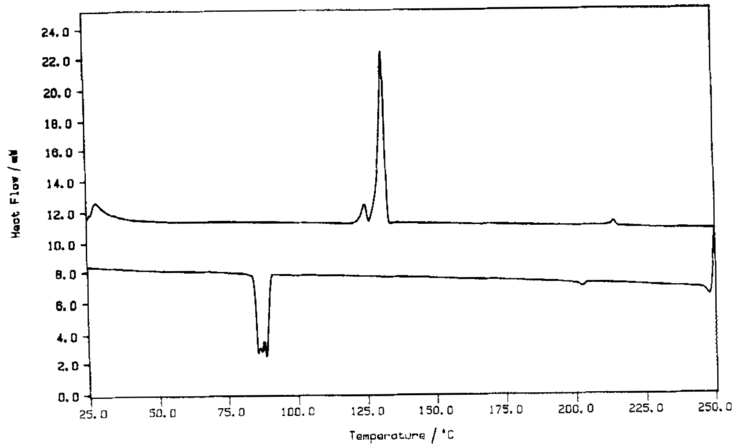

Figure 2. Differential scanning calorimetry thermogram for compound **VIg**. Heating rates (cooling and heating) were 20°C min^{-1}.

Table 1. Transition temperatures (°C) and enthalpies (kJ mol^{-1}) in parentheses for the nickel(II) complexes **VI** with $R = C_nH_{2n+1}$.

Compound	*n*	C		N		I
VIa	2	●	171	●	192	●
VIb	3	●	122	●	224 (dec)	●
			(21·9)			
VIc	6	●	114	●	173	●
			(27·0)		(0·4)	

Elemental analysis for **VIb**: Found C 61·04, H 5·78, S 13·24, Ni 12·15 per cent. $C_{24}H_{26}O_2S_2Ni$ (469·28 g mol^{-1}) requires C 61·42, H 5·58, S 13·66, Ni 12·51 per cent.

Table 2. Transition temperatures (°C) and enthalpies (kJ mol^{-1}) in parentheses for the nickel (II) complexes with $R = C_nH_{2n+1}O$.

Compound	*n*	C		N		I
VId	3	●	155	●	232	●
			(23·0)		(0·5)	●
VIe	4	●	134	●	227	●
			(27·5)		(1·4)	
VIf	5	●	113	●	231	●
		●	(27·7)	●	(1·9)	●
VIg	6	●	129	●	211	●
			(29·9)	●	(0·6)	●

Elemental analysis for **VIe**: Found C 58·81, H 6·02, S 11·95, Ni 11·12, per cent. $C_{26}H_{30}O_4S_2NI$ (529·33 g mol^{-1}) requires C 58·99, H 5·71, S 11·09, Ni 11·09 per cent.

shows a typical example of a DSC thermogram. All the nickel(II) compounds **VI** exhibit relatively low melting temperature and wide nematic ranges. The phases have typical Schlieren textures. The enthalpies of the nematic/isotropic transitions are similar to those of ordinary calamitic liquid crystals. The observed properties confirm our assumption, that complexation of the 4-substituted-phenylmonothiomalondialdehydes leads to molecules with an almost ideal rod-like shape. Since many more interesting O,S-chelates are conceivable, easily accessible and likely to be mesomorphic, these investigations justify further examination of this type of compound.

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