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MESOMORPHIC TRANSITION METAL COMPLEXES
3. SMECTIC AND NEMATIC NICKEL DITHIENES.

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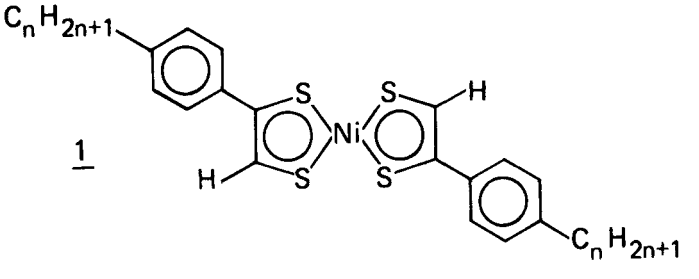
ABSTRACT: The synthesis and characterization of the first nematic transition metal complex and of smectic complexes of the dithiene type are described.

We have recently described[2] the synthesis and characterization of transition metal complexes which show smectic mesophases. These compounds belong to the class of ethylene dithiolato complexes (Dithienes)[3] and are p-alkyl derivatives of bis-(styryldithiolato) nickel (1). The chemically quite inert and photochemically stable dithienes are interesting materials because of their electron acceptor properties and their unusual electronic structure. They all show strong (ε above 25000) absorption bands at wavelengths longer than 700 nm.



1

1a: n = 10, 1b: n = 9, 1c: n = 8, 1d: n = 4.

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We now wish to report the synthesis of two new derivatives of complexes with the structure 1, one with C_{10} chains (1a) and the other with C_4 chains (1d). We find that, in addition to the smectic materials, nematic transition metal complexes of this type do indeed exist.

The synthesis of these materials was carried out in a sequence similar to the one described earlier.[2] The complexes were purified by column chromatography (silica gel, hexane) and recrystallized from heptane. They were characterized by elemental analysis and by their nmr and electronic spectra. All complexes of the type 1 are green in solution and form shiny black crystals.

The complex 1a, carrying a C_{10} chain, shows a transition to a smectic phase at 108°C and 121°C observed[2] for the C_9 and C_8 analogs, respectively. The smectic phase of 1a is stable to 189°C, where the material becomes isotopic. Above this temperature, however, thermal decomposition is rapid.

Compound 1d, with a C_4 chain in the p-position of the styryl dithiolato ligand appears to be the first nematic transition metal complex[4] ever to be reported. Its transition to a nematic phase occurs at 117°C. The nematic nature of this phase was confirmed by microscopic examinations of the texture and by solid state[5] ^{13}C nmr at 120°C. The complex decomposes at approximately 200°C without first becoming isotropic.

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In view of the fact that dithiene complexes tend to utilize their metal d-orbitals for intermolecular bonding, leading in some cases to the formation of dimers and other aggregates, the occurrence of a nematic material of this type is unexpected. Compared to nematic materials, smectic compounds show a stronger intermolecular interaction vertical to the plane of the molecule. The appearance of smectic phases in the dithienes of type 1 would therefore be expected. That the C_4 substituted complex 1d indeed forms a nematic phase, is a good indication that the intermolecular interactions are dominated by the entire molecular system rather than by metal-metal bonding.

The complexes 1a - 1d all have strong absorption bands at 850 nm. This suggests their use in mixtures with other liquid crystals or by themselves in display or other devices, where they could be addressed by an infrared laser. Since in the dithienes the conversion of photochemical to thermal energy is very efficient, these new materials should be useful in various switching applications. Some experiments along these lines are currently in progress.

We thank Dr. R. J. Cox and Dr. J. Lyerla of this laboratory for the characterization of the mesophases.

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