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MESOMORPHIC TRANSITION METAL COMPLEXES.
4. DITHIENE COMPLEXES OF Ni, Pd, AND Pt.

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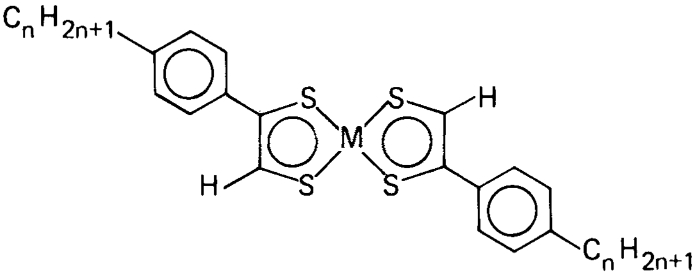
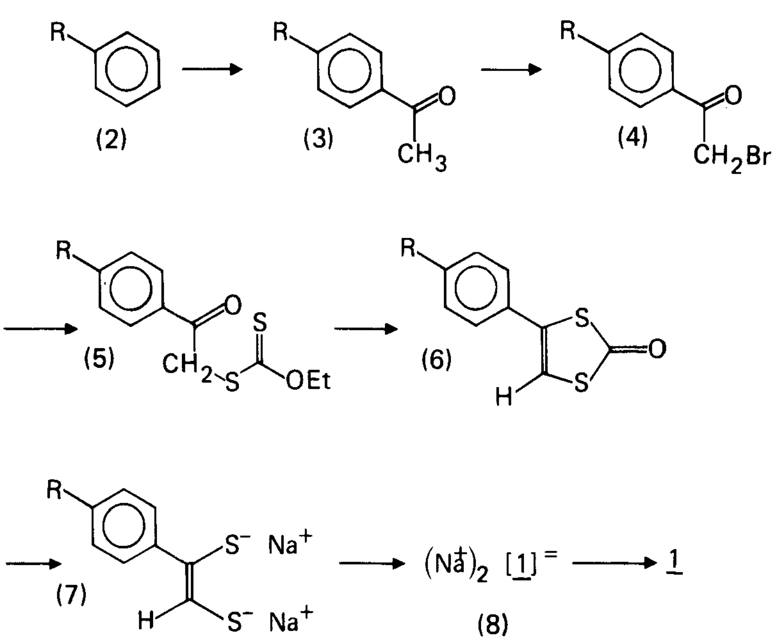
ABSTRACT: A rational synthesis of transition metal dithiene complexes with mesophorphic properties is reported. In addition to the nickel complexes described earlier, we have now obtained the Pd and Pt congerers. While the Ni and Pt complexes show, depending on the length of the para-n-alkyl chains, smectic or nematic mesophases, the Pd complexes have no mesomorphic properties at all. We suggest that the reason for the absence of a mesophase in the Pd complexes is caused by the formation of dimers.

We have recently reported that bis-styryldithiolato-nickel complexes, substituted with a linear p-alkyl group, can exhibit smectic or nematic mesophases.[2-4] Because, at that time, we wanted only to demonstrate the phenomenon that transition metal complexes can have mesophases, we used a convenient but crude synthetic procedure. In view of the interest in these infrared active liquid crystals, we have investigated a more appropriate synthetic method, which now has allowed us to prepare not only a variety of nickel complexes, but also dithienes of the more precious metals Pd and Pt. All these complexes are planar and have the general formula 1. In the following description, we will use an abbreviated notation, giving only the length of the linear p-alkyl chain and the nature of the central metal: C_4-Ni would be the nickel complex 1 with n-butyl groups as the substituents in the p-position of the styryl-dithiolato complex.



1: M = Ni,Pd,Pt
n = 4,5,6,7,8,9,10

Starting materials for the synthesis of complexes 1 were the alkyl benzenes with n-C_4H_9 to n-$C_{10}H_{21}$ chains (2). Friedel-Crafts acylation with acetyl chloride and $AlCl_3$ lead to the p-alkyl acetophenones 3, which were brominated by Br_2 in acetic acid or in carbon tetrachloride to the bromoacetyl derivatives 4. (In the previously published procedure,[2,4] these intermediates were treated first with P_4S_{10} and then with $NiCl_2$ in water to give the complexes in low yield.) Reaction of 4 with potassium ethyl xanthate in EtOH or CH_3CN produced the xanthates 5, which were cyclized by HBr in acetic acid to the dithiocarbonates 6. These were cleaved by sodium methoxide in methanol to the styryl dithiolates 7, which were reacted with the respective transition metal halides or tetrahalometallates to give, initially, the dianions 8 of the complexes 1. The neutral complexes were obtained by oxidation of 8 by air or by iodine. They were purified by column chromatography on SiO_2 with hexane as the eluent and by recrystallization from heptane.



The pure nickel complexes are green in solution and form dark, almost black crystals of high reflectivity. The palladium complexes are bronze colored crystals, which dissolve with wine-red color. The platinum analogs are purple in solution as well as in the solid. All complexes were characterized by the usual analytical methods. Solutions of the complexes 1 in hexane show intense electronic transitions in the near infrared, with maxima near 850 nm for nickel, 865 nm for palladium and 780 nm for the platinum species.

The mesomorphic properties of the complexes 1 were investigated only by hot stage polarized light microscopy, except for the two compounds C_6-Ni and C_6-Pt, in which cases the microscopy was supplemented by differential thermal analysis, the relative peak size being used only to confirm the textures observed by microscopy. A more detailed investigation including x-ray diffraction analysis in order to classify the smectic phases will be reported later.

The most general observation is that all of the nickel and platinum complexes form well defined and stable mesophases, while, surprisingly at first, the palladium complexes do not seem to possess any mesomorphic properties at all. Of the complexes 1 with M = Pd, we have only prepared the two extreme cases C_4-Pd and C_{10}-Pd and found them to melt without any observable previous phase transition at 205°C and 207°C, respectively, to isotropic liquids which rapidly decompose. Since neither complex showed a mesophase, we abstained from preparing the other members C_5-Pd to C_9-Pd of this series.

For the Ni and Pt series, the results of our investigation of their mesomorphic properties are listed in the table below. The complexes with n-alkyl chains of six or less carbon atoms are nematic and those with longer chains are smectic. The only complex showing both mesophases is C_6-Ni, which is smectic between 139 and 169°C, and nematic above 169°C up to 181°C, where it becomes isotropic and then very rapidly decomposes.

Both the Ni and Pt series show the same break at a C_6 chain length between nematic or smectic mesophases. A break at that chain length is characteristic and occurs in many liquid crystal series.[5] On the other hand, a plot of the mesophase to isotropic transition temperature as a function of alkyl chain length generally shows an even/odd effect due to the conformation of the alkyl chains. Surprisingly, such an effect is not observed in the two series of complexes 1 with M = Ni and Pt. It seems, therefore, that the appearance of the mesophases is influenced by the alkyl chains but that their stability is independent of chain length.

Mesophases and Transition Temperatures (°C) of Bis-(alkyl-styryl-dithiolato)-Metal Complexes of Nickel and Platinum. Abbreviations: C = crystal-crystal transition, S = smectic, N = nematic, I = isotropic, D = decomposition.

Chain Length	Nickel	Platinum
C_4	117 N 175 I,D	145 C 158 N 202 I
C_5	133 N 185 I,D	167 N 202 I
C_6	139 S 169 N 181 I,D	175 N 200 I
C_7	130 S 185 I,D	169 S 199 I
C_8	121 S 191 I,D	150 S 209 I
C_9	108 S 191 I,D	146 S 205 I
C_{10}	103 S 189 I,D	140 S 202 I

The fact that the palladium complexes have no observable mesophases can be explained by the formation of dimers with so high a dissociation energy that the crystals melt to isotropic liquids before dissociation to the monomers, and with them the occurrence of mesophases, takes place. This suggestion gains in merit, which one considers that the unsubstituted bis(ethylenedithiolato)metal complexes of Pd and Pt form discrete dimers in the solid state, of which two the palladium complex is much more strongly bound.[6] The unsubstituted nickel complex is known[6] to show no tendency to dimerize. This trend is also reflected in the amount of cyclic electron delocalization (aromaticity) of these dithienes.[7]

It would be reasonable to assume that the intermolecular metal-metal interactions would also manifest themselves in the liquid crystalline phases, so that the formation of the more highly ordered smectic layers would be preferred. Thus, the occurrence of nematic nickel complexes would be expected, while for platinum as the central metal one would assume a preference for smectic mesophases or even the formation of dimers. The fact that nematic phases are indeed observed for the shorter chain members of both the nickel and platinum series is evidence for some competition between the different intermolecular interactions which determine the stability of the mesophases. In the case of the palladium complexes the attraction through metal-metal interaction clearly dominates, while in the other two cases the normal dispersive forces have a larger effect.

The point should also be made that all the above complexes can occur in their cisoid form as well as in the transoid form indicated in formula 1. We have so far been unable to isolate such isomers in any of these complexes. The sole indication for their existence comes from the ^{1}H-nmr spectra of the platinum complexes, which show two slightly different ^{1}H-^{195}Pt coupling constants. From semiempirical IEHT calculations on unsubstituted bis-(ethylenedithiolato)nickel we have estimated the barrier for cis-trans isomerization via a tetrahedral transition state to be above 10 kcal/mole. Further efforts are under way to clarify this question.

REFERENCES AND NOTES

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