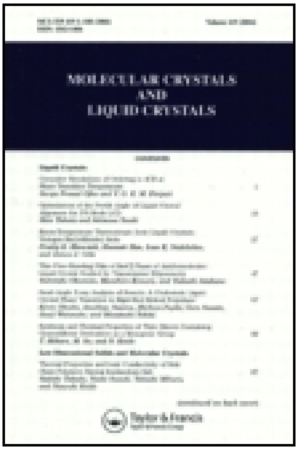

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Synthesis and Characterization of Some Manganese Complexes of 5,10,15,20-Tetrakis (4-n-Dodecylphenyl)Porphyrin

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Synthesis and Characterization of Some Manganese Complexes of 5,10,15,20-Tetrakis (4-*n*-Dodecylphenyl)Porphyrin

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The mesomorphic properties of 5,10,15,20-tetrakis(4-n-dodecylphenyl) porphyrin and its divalent metal complexes are well documented. Also, some trivalent metal complexes have been considered. In this work, the chloromanganese(III) complex of tetrakis(4-n-dodecylphenyl)porphyrin was synthesized and its thermotropic behaviour was observed. The tetracyanoquinodimethane(TCNQ) complex was also prepared by metathesis between chloro manganese porphyrin and $Li^+(TCNQ^{-\cdot})$. Magnetic susceptibility measurements were performed on this complex. The chloromanganese(III) complex showed a substantial depression of clearing point over the equivalent divalent complexes. However, although both crystalline and mesomorphic phases could be observed a reproducible phase transition was not seen. Furthermore, the clearing transition was irreversible under a heating/cooling rate of 5 deg/min. X-ray diffraction measurements showed an increase in the ordering of the mesophase upon heating.

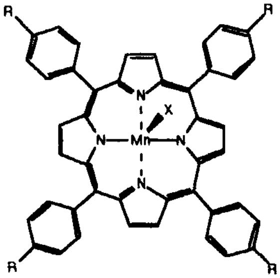
Keywords: TCNQ; magnetic susceptibility; porphyrin; metallomesogen; discotic

INTRODUCTION

Metallomesogens have attracted much attention in recent years because of the possibility of combining the properties of liquid crystals with those of transition metal ions[1]. In particular, metal ions such as copper(II), nickel(II), iron(II/III) and manganese(II/III) are of interest because of their magnetic properties[2]. Organization of these ions into molecular arrays(as in a liquid crystalline mesophase) may result in unique and potentially useful phenomena.

Complexes of transition metal ions with organic radical compounds have yielded several interesting examples of magnetic interactions[3] and the formation of molecular chains exhibiting ferromagnetic, ferrimagnetic and antiferrimagnetic properties is well documented[4].

Here we present initial results from the synthesis and analysis of chloro[5,10,15,20-tetrakis(4-n-dodecylphenyl)porphinato]manganese(III) and its corresponding 7,7',8,8'-tetracyanoquinodimethane complex. Hereafter, these complexes will be referred to as C_{12}TPPMnCl an C_{12}TPPMn·TCNQ. Their formulae are shown below.



R =$C_{12}H_{25}$; X=Cl^-, $TCNQ^{-\cdot}$

EXPERIMENTAL

Synthesis

The porphyrin free base($C_{12}TPPH_2$) was synthesized as previously described[5] and insertion of manganese(III) was accomplished by literature methods[6]. Yield of metalloporphyrin was >95%. The chloromanganese complex was recrystallized from dichloromethane/acetone at -20°C.

Synthesis of $Li^+(TCNQ^{-\cdot})$ and its reaction with C_{12}TPPMnCl were both by literature procedures[7]. The reaction between $Li^+(TCNQ^{-\cdot})$ and C12TPPMnCl rapidly yielded a product by precipitation as methanolic solutions of the compounds were mixed. This product was filtered and dried *in vacuo*. No porphyrin could be detected in the filtrate indicating the efficiency of conversion.

Chemical Analysis

C_{12}TPPMnCl: UV/Vis(CH_2Cl_2): λ(nm)(ε/10^3mol^{-1}dm^{3}cm^{-1}): 376(56), 403(48), 479(108.6), 531(5.7), 584(9.3), 621(13.2). FT-IR(KBr) (cms^{-1}): 3134, 3085(w) (porphyrin s,as-(υC-H), 3020(w) (phenyl υC-H), 2953-2852(vs) (aliphatic υC-H), 1610 (υC=C, υC=N), 1500(m) (aromatic ring breathing), 1468(m) (δCH_2), 1458(m) (δCH_3(a)), 1374(w) (δCH_3(s)), 1017(vs)(υC-C, υC-N) , 815(sh) (porphyrin C-H out-of-plane bending), 805(m) (phenyl C-H out-of-plane bend), 714(m) (ρ(CH_2)$_4$-). ^{1}H-n.m.r.($CDCl_3$) (ppm): 0.89(br., terminal $C\underline{H}_3$), 1.31(br. ,-($C\underline{H}_2$)$_9$-), 1.84(br., -Ph$CH_2C\underline{H}_2$-R), 3.159(br., -Ph$C\underline{H}_2$-), 8.15(v. br., aromatic protons). C12TPPMn·TCNQ: UV/Vis(CH_3OH): λ(nm)(ε/10^3mol^{-1}dm^{3}cm^{-1}): 378(55), 404(59), 419(54), 470(74.8), 519(7), 568(10.5), 603(10.3), 680(8), 741(18.7), 758(16.2). FT-IR(KBr)(cms^{-1}): IR spectrum similar to chloromanganese complex except: 2189, 2161(vs), 2126(m) (υCN). ^{1}H-n.m.r. ($CDCl_3$): 0.89(br., terminal $C\underline{H}_3$), 1.3(br. -($C\underline{H}_2$)$_7$-)), 1.45(br., $C\underline{H}_2$-C_8H_{17}), 1.63(br., $C\underline{H}_2$-C_9H_{19}), 1.80(br., $C\underline{H}_2$-$C_{10}H_{21}$), 2.95(br., $C\underline{H}_2$-$C_{11}H_{23}$), 7.80(br., aromatic H).

RESULTS AND DISCUSSION

Thermal analysis of C_{12}TPPMnCl did not reveal simple behaviour. Whilst the clearing point could consistently be observed on the first heating it was absent in subsequent heatings. Also, although a stable mesophase formed at room temperature a reproducible response for the crystal-mesophase could not be observed. Usually, broad transitions were observed over a range between 10 and 30°C upon heating or cooling which are thought to correspond to the crystal-mesophase transition..

DSC measurements of C_{12}TPPMn·TCNQ revealed several phase transitions. A crystal-crystal phase transition at 80°C is followed by transition to mesophase at 183°C observed by polarized-light microscopy. The clearing transition at 220°C is accompanied by decomposition and no further DSC response can be illicited. The identity of the mesophase between 183° and

220°C is still unknown because of the lability of the complex in air at high temperatures. However, heating the sample at 120°C results in the formation of a discotic lamellar mesophase and it is thought that this phase forms following some transformation of the TCNQ moiety. The results of thermal analyses are summarised:

<u>C_{12}TPPMnCl :</u>

C (13°C(var),~16 kJmol^{-1}) D_L (92.2 °C, 8.5 kJmol^{-1}) Iso.

<u>C_{12}TPPMn.TCNQ:</u>

C_1(80.2°C, 53.7kJmol^{-1}) C_2 (183°C, 1.3kJmol^{-1}) D_x (220.5, 56.1kJmol^{-1})Iso

X-ray powder diffraction patterns of C_{12}TPPMnCl indicate a discotic lamellar structure for the mesophase and reveal an extremely low value of the d_{100} spacing. Usually, this value is around 31Å for complexes of $C_{12}TPPH_2$ corresponding to the distance between the ends of adjacent alkyl chains of one molecule(fully extended model). However, in this case, d_{100} is equal to 23.6Å which is even shorter than the low value of d_{100} also observed in the aluminium μ-oxo dimer of this porphyrin(28.8Å)[8]. Increase of the face-to-face intermacrocyclic distance caused by the presence of a ligand in the fifth coordination space allows increased intra- and interlamellar interdigitation of the n-alkyl chains thus reducing the observed value of d.

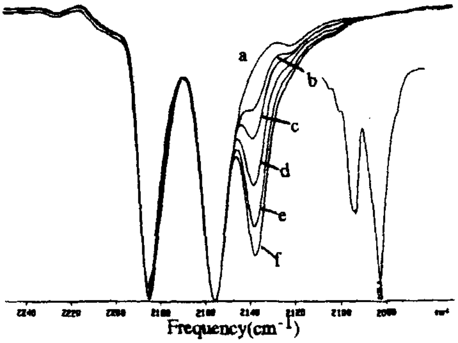


FIGURE 1 Changes in nitrile bands on formation of D_L phase in C_{12}TPPMn·TCNQ. a) T=0, b) T=60, c) T=85, d) T=100, e) T=120 f) T=155. Inset shows final product.

In C_{12}TPPMn·TCNQ, a discotic lamellar mesophase forms when the sample is heated at 120°C for several hours. Observation of the infrared spectra during this process indicate serious changes in the chemical structure. In particular, nitrile stretching frequencies are altered and a band assigned to C=N stretching appears at 1650cm^{-1}. Alteration of the nitrile stretching bands is illustrated in Figure 1. The identity of the product obtained by heating this complex at 120°C will be reported elsewhere.

Electronic Spectrophotometry

UV/Vis spectrophotometry provides a useful probe into the structure of the TCNQ complex. C_{12}TPPMn·TCNQ dissolves in a variety of solvents by virtue of its aliphatic chains and the vacant coordination space of the manganese porphyrin.

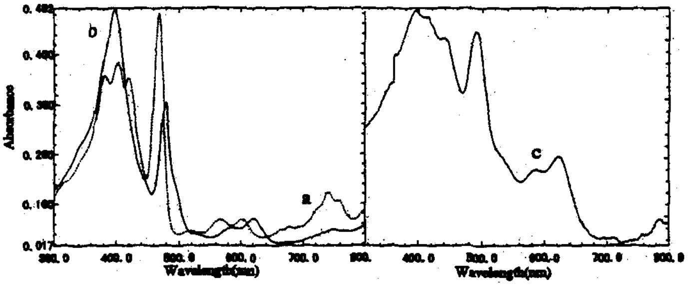


FIGURE 2 Electronic Spectra of C_{12}TPPMn·TCNQ a) in methanol, b) in dichloromethane, c) solid.

Solutions in methanol are basically the product of adding the spectrum of TCNQ$^{-\cdot}$ to the spectrum of the manganese(III) porphyrin. Complete dissociation of the complex occurs with the metalloporphyrin cation coordinating two molecules of methanol(giving a characteristic pattern of the short wavelength porphyrin absorption)[9]. In less polar solvents, however, the absorptions due to porphyrin cation and TCNQ$^{-\cdot}$ are reduced and there is a strong increase in the absorption at 395nm. We believe that this is largely due to the association of the porphyrin cation and TCNQ$^{-\cdot}$ resulting in a reduction in intensity of the porphyrin-metal charge transfer band around 470nm[10]. Previously, the intensity of this band has been found to depend on the axial ligand coordinating the manganese atom.[11)

Magnetic Susceptibility

Figure 3 shows magnetic susceptibility data for C_{12}TPPMn·TCNQ (χT *vs* T). Several results arise from this data. Firstly, the pronounced minimum at 62K and the sharp maximum at 10K reveal the ferrimagnetic chain structure of this complex[12].

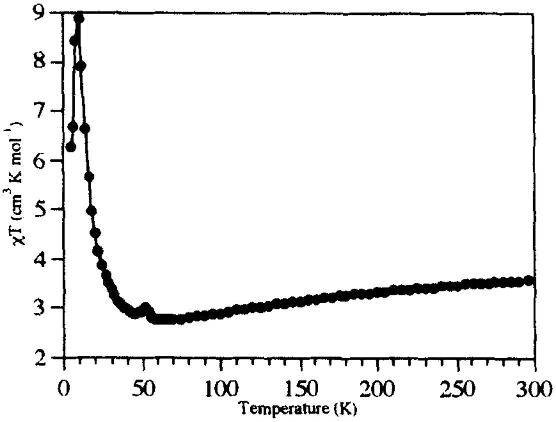


FIGURE 3 χT vs T plot for C_{12}TPPMn·TCNQ.

Additionally, there is a maximum μ_{eff} of 8.43μ_B (at 10K) which indicates the presence of long-range magnetic ordering in this compound[13]. The room temperature effective magnetic moment is 5.35μ_B which is close to the expected value for independent S=2 and S=1/2 systems(5.2μ_B). In a plot of 1/χ *vs* T, the data can be fit to the Curie-Wiess expression with θ = −44K indicating an antiferromagnetic interaction. Thus, this complex behaves in a similar manner to some of the substituted manganoporphyrin derivatives of tetracyanoethylene[13, 14].

CONCLUSION

In conclusion, we have synthesized the complexes C_{12}TPPMnCl and C_{12}TPPMn·TCNQ both of which exhibit discotic mesophases over certain temperature ranges. The TCNQ complex is unstable at elevated temperature and the product of thermal treatment at 120°C exhibits a discotic lamellar mesophase. The TCNQ complex has magnetic characteristics typical of a ferrimagnetic chain structure with an antiferromagnetic interaction.

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