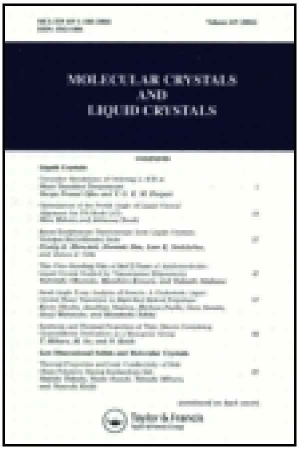

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Synthesis of Potentially Self-Assembling Liquid Crystalline Macrocyclic Complexes: Detection of a New Glassy State

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SYNTHESIS OF POTENTIALLY SELF-ASSEMBLING LIQUID CRYSTALLINE MACROCYCLIC COMPLEXES: DETECTION OF A NEW GLASSY STATE.

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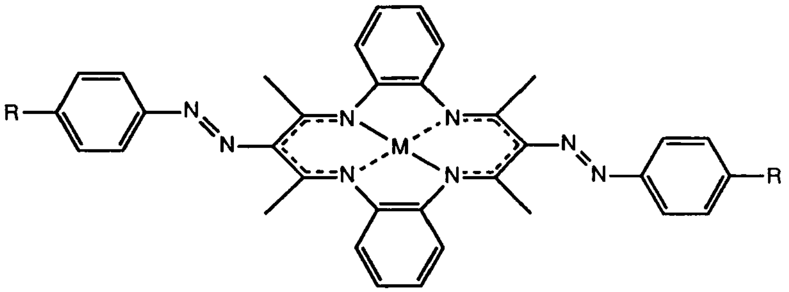
Abstract

In studies aimed at generating new self-assembling macrocyclic complexes for conductivity and modified electrode studies we prepared new azotetra-azaannulene macrocycles and their Ni complexes. The temperature-dependent behaviour of these compounds as studied by DSC showed that while some were sensitive to decomposition, others readily formed a stable glassy material of the kind that has been observed in mesogenic organic compounds with bulky side groups. We have also investigated the self-assembly of these molecules onto gold electrode surfaces. The Co macrocyclic complex adsorbs such that the metal centre is no longer accessible to O_2.

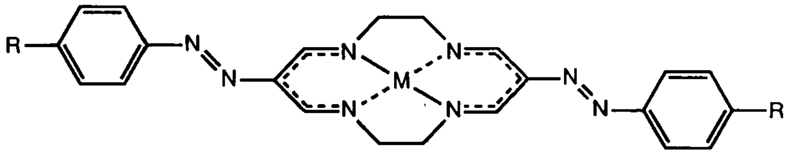
INTRODUCTION

Macrocyclic complexes have been studied in a wide range of molecular electronics applications, including liquid crystals,[1] novel electronic conductors[2] and monolayer films.[3] We are also interested in the modification of electrode surfaces by macrocycle complexes in order to exploit their useful redox properties.[4] Recently, we have synthesized tetraazaannulene complexes of the type shown in Fig. 1. While the unsubstituted members of the family have been shown to be planar,[5] these complexes and ligands have a saddle-shaped structure due to steric interactions between the methyl groups on the ring and the benzene protons. This confers a high solubility and low melting points on the complexes. In this work we wished to discover whether lateral substitution of the ring by mesogenic phenylazo groups (complexes Ia-d, M=Ni, H_2 and

Co) brought about liquid crystalline behaviour. We report the synthesis and thermal behaviour of these materials, together with preliminary work on modified electrodes formed by a self-assembly method.



M = Ni
R = **Ia**(H),**Ib**(C_4H_9),**Ic**($O\text{-}C_8H_{17}M = H_2$,Ni and Co) and **Id**($O\text{-}C_{14}H_{29}$)



II M = Ni ,R = $O\text{-}C_{14}H_{29}$

Figure 1 Structures of synthesized tetraazamacrocydes.

SYNTHESIS

The starting material, Ni(TMTAA) (7, 16-Dihydro-6,8,15,17-tetramethyldibenzo[b,i]-[1,4,8,11]tetraazacyclotetradeainato(2–)nickel(II)) is readily prepared by the template reaction between nickel acetate, pentan-2,4-dione and 1,2-diamino benzene.[6] The aromatic amines were commercially available (for Ia and Ib) or synthesized from p-hydroxyacetanilide and the alkyl bromide.[7] The diazonium salt was then coupled to the macrocycle.[8] Compound II was prepared from the azomalondialdehyde,[9] ethylene-diamine and nickel acetate template reaction.[10] This slightly different strategy to compounds I was necessary because the corresponding nickel dien complex is difficult to completely ring-close. Ic(M=Co) was prepared from Ic($M=H_2$) by reacting with cobalt acetate.[11] Ic($M=H_2$) was prepared from TMTAA (*via* demetallation of TMTAA) and the diazonium salt.

The compounds were characterized by ^{1}H NMR, F.T.I.R. (KBr disk) and UV-Vis spectroscopy (Table 1). The NMR of the free ligand Ic($M=H_2$) showed evidence of tautomerism.[9,12] Its solid-state ^{13}C CP-MAS NMR (Fig. 2a) also shows five different methyl group environments which are clearly distinguishable from the CH_2 carbons in the non-quatenary suppression (NQS) spectrum, (Fig.2b). Thus all three tautomers are found in the solid state.

TABLE I ^{1}H NMR Data for New Macrocyclic Ligands and Complexes

Ia	2.65 (s,12H),6.75 6.9(m,8H),7.3(s,2H),7.4(t,4H),7.6(d,4H)
Ib	0.9(t,6H),1.2-1.7(m,12H),2.6(s,12H),6.8(dm,8H),7.25(t,4H) ,7.55(d,4H)
Ic(M=Ni)	0.85(s,6H),1.32.1(m,24H),2.6(s,12H),4.0(s,4H),6.7(m,4H), 6.85(m,4H),6.9(m,4H),7.6(m,4H) paramagnetic
Ic($M=H_2$)	0.9(t,6H),1.2(s,16H),1.4(s,4H),1.8(d,4H),2.2s 2.3s 2.4s 2.5s 2.6s(12H) 3.9(m,4H),6.9(m,16H),11(s,1H),14.3(bs,1H),16.3(s,1H)
Id	0.85(t,6H),1.3-1.8(m,48H),2.7(s,12H),4.0(t,4H),6.7(m,4H),6.85(m,4H) 6.92(d,4H),7.6(d,4H)
II	0.9(t,6H),1.3s,1.55s(48H),3.5(t,4H),4.0(t,4H)6.9(d,4H),7.5(d,4H), 7.7(s,4H)

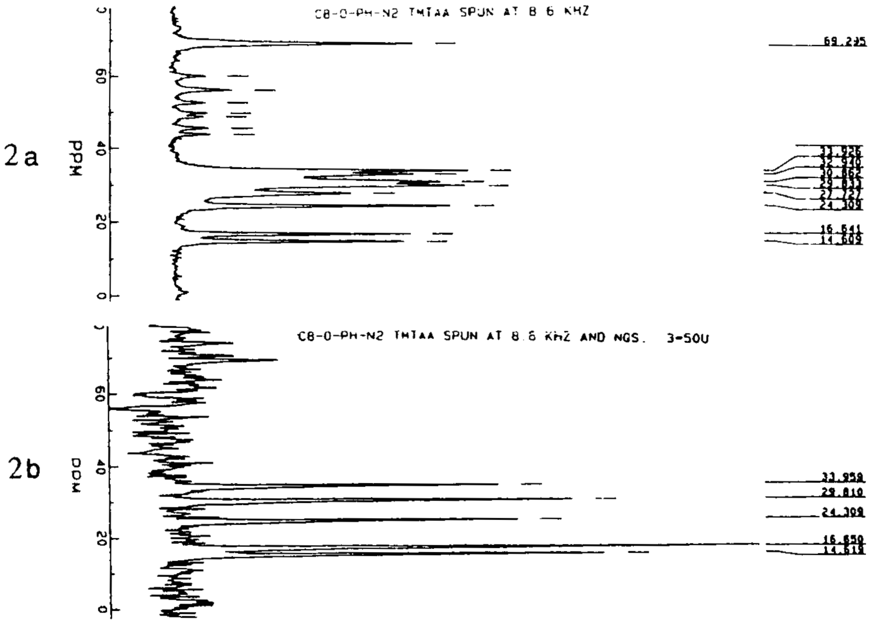


Figure 2 (a) Solid-state nmr spectrum (^{13}C CPMAS) of Ic ($M=H_2$); (b) NQS spectrum with 50μs delay time. Spectra obtained on a Bruker MSL 500 at 125.8 MHz.

THERMAL BEHAVIOUR

Differential scanning calorimetry (DSC) was used to screen the complexes for mesophase transitions (Table I).The most interesting behaviour was noted for Id (Fig.3)

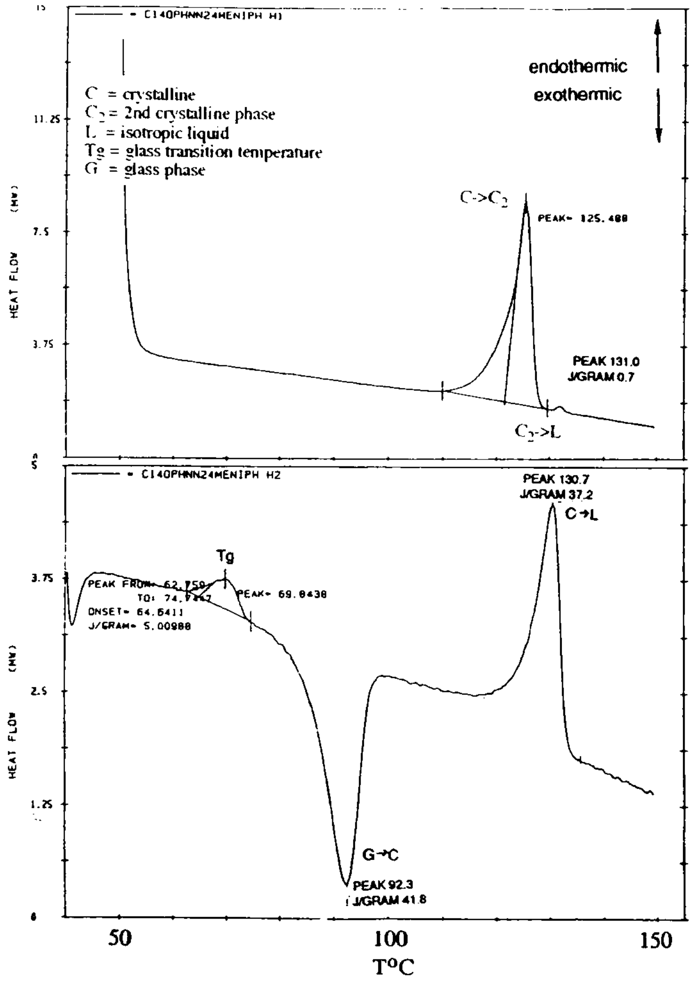


Figure 3 DSC traces for compound Id (a) first heating curve (b) second heating curve. Scan rate 10°C min^{-1}. (Perkin Elmer DSC 7).

On the first heating cycle (Figure 3a), a transition from the crystalline phase is observed at 125.5°C, with no corresponding exothermic phase transition observed on the cooling cycle, apart from a small exotherm (X) at 54.6°C which is due to the isotropic to highly viscous nematic phase (N) transition. It is only during the second heating cycle that an exothermic peak is observed at 92.3°C due to the crystallisation process (Figure 3b). This behaviour was also observed after 8 heating and cooling cycles for compound Ic (M=Ni). Amorphous and glassy states often have enhanced electron and ion transport properties compared to the crystalline state. Electronic conductivity and redox measurements of the new phases will be presented in a future publication. The glassy state was confirmed by microscopic observation of the phase transitions; the green crystals change colour to orange-red when the glassy state is formed. This state is characteristic of mesogens containing bulky central core groups.[13] Deformation of the glass by shearing the lower slip failed to produce birefringent textures seen in vitreous organic compounds.[14]

When we examined complex(II) with a narrower core consisting of ethylenediamine instead of diaminobenzene units, paradoxically we observed a higher melting point due to the greater planarity of the macrocycle (this compound has no methyl substituents around the core).

Table II DSC Data for Macrocycle and Complexes

Sample	Transition	T/°C	DH/kJ mol^{-1}
Ia	C -> I decomp	>240	-
Ib	C -> I decomp	>250	-
Ic (M=Ni)	C -> C_2	144.5	91.7
	C_2 -> I	183.9	15.4
on 9th heating	G -> C_2	123.5	-44.2
	C_2 -> I	188.8	42.9
Ic(M=H_2)	C -> I	151.0	35.5
Id	C -> C_2	125.5	86.6
	C_2 -> I	131.0	0.7
on 2nd heating	Tg	69.8	5.2
	G -> C_2	92.3	-43.22
	C_2 -> I	130.6	38.4
II	C -> C_2	136.5	10.7
	C_2 -> I	186.4	11.1

SOLVATOCHROMISM

The compound Ib (C_8O,M=Ni) when dissolved in $CHCl_3$ forms a green solution which rapidly turns red, accompanied by broadening of the ^1H nmr peaks suggesting that a square planar (diamagnetic) to octahedral (paramagnetic) equilibrium is set up through dimerization or oligomerization process.

ELECTROCHEMISTRY

The surface activity of the new compounds were studied by cyclic voltammetry. In order to detect monolayer coverage we used the Co complex since Co (tetraaza-annulenes) are active towards O_2 reduction in alkaline solution giving measurable catalytic currents. Figure 4(a) shows the response at a freshly polished gold electrode, with a broad O_2 reduction wave commencing at −0.3V vs SCE.

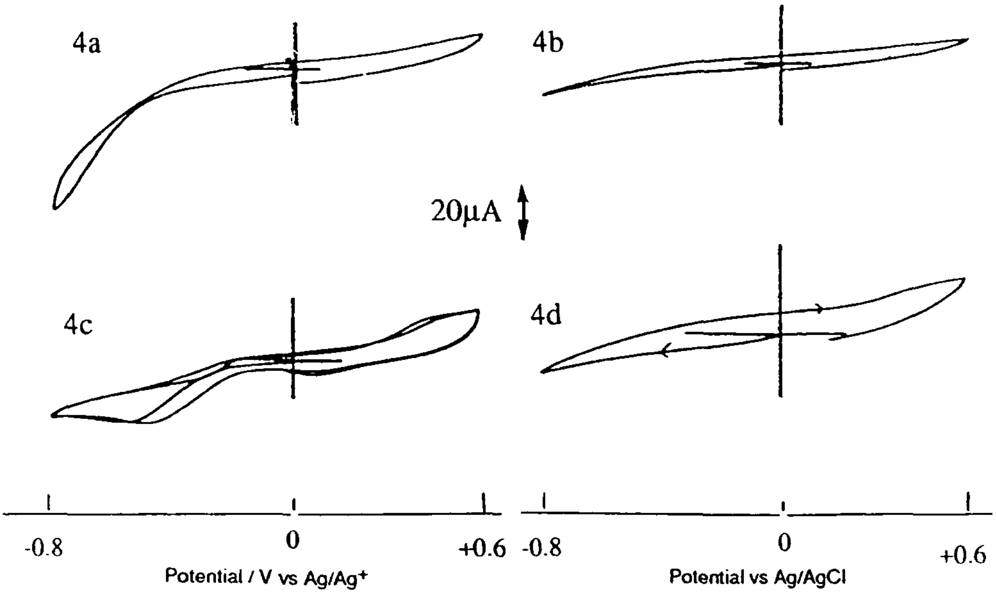


Figure 4 Cyclic voltammograms (50 mVs^{-1}) for O_2 reduction in O_2–saturated (1.2mM)/0.1M NaOH at 291K for: (a) a bare gold disk electrode (area = 0.07 cm^2); (b) electrode dipped in 10^{-4}M Co(Ic) in CH_2Cl_2 for 10 mins; (c) electrode dipped in 10^{-4} M $Me_2dixylylN_4Co$; (d) electrode coated with $C_{18}H_{37}SH$.

After coating with Co (Ic) we observe (Fig. 4b) a large decrease in capacitive current and the absence of any O_2 reduction current, in contrast to the complex without azo groups (Fig. 4c) which shows a catalytic reduction wave commencing at –0.2V. The blocking behaviour of Co (Ic) is characteristic of surface–active thiols such as $C_{18}H_{37}SH$ (Fig. 4d).[15,16] The mode of adsorption of Co(Ic) is therefore similar to the thiols in that the long alkyl chains are directed away form the surface preventing the access of O_2 and ions to the Co centre. It is interesting to compare this behaviour with that of a C_{16}–alkylated cationic Co porphyrin which remains active for O_2 reduction after adsorption on gold.[17] We attribute this difference to the greater hydration of the cationic head group.

CONCLUSIONS

The complexes Ic and Id may be readily converted to glassy states on heating. This glass recrystallizes much more readily for the longer chain derivative (Id). Liquid crystalline behaviour appears to be disfavoured by the bulky core groups of the molecule.

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