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The synthesis and lyotropic phase behaviour of some aquatetra(cyano)-dodecylaminoferrate(II) complexes

Duncan W. Bruce[a]; David A. Dunmur[a]; Peter M. Maitlis[a]; Jonathan M. Watkins[a]; Gordon J. T. Tiddy[bc]
[a] Department of Chemistry, The University, Sheffield, England [b] Unilever Research, Port Sunlight Laboratory, Bebington, Wirral, England [c] Department of Chemistry and Applied Chemistry, University of Salford, Salford, Lancashire, England

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The synthesis and lyotropic phase behaviour of some aquatetra(cyano)-dodecylaminoferrate(II) complexes

by DUNCAN W. BRUCE*, DAVID A. DUNMUR,
PETER M. MAITLIS and JONATHAN M. WATKINS
Department of Chemistry, The University,
Sheffield S3 7HF, England

and GORDON J. T. TIDDY*†
Unilever Research, Port Sunlight Laboratory,
Bebington, Wirral L63 3JW, England

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Some alkali and alkaline earth metal salts of the amphiphilic anion $[Fe(CN)_4(H_2O)(C_{12}H_{25}NH_2)]^{2-}$ have been synthesized by reaction of $[Fe(CN)_5NO]^{3-}$ with $C_{12}H_{25}NH_2$. Using optical microscopy, they have been shown to give a hexagonal (H_1) mesophase in water.

1. Introduction

Conventional surfactant molecules consist of a polar head group and a non-polar tail. These aggregate in aqueous solution first to form micelles and then, at higher concentrations, lyotropic liquid crystals. Many different chemical functionalities may be used as the head group, e.g. quaternary ammonium salts, sulphates and polyethyleneoxides, whereas the tail is usually either a long chain hydro or fluorocarbon [1].

When comparing the chemical structure of different surfactants, it is immediately apparent that metals are not utilized to a fraction of their full potential. Although metals such as sodium and potassium are commonly found as counter ions, there are very few examples where the metals are an integral part of the surfactant molecule [2–6]. The only examples of lyotropic mesophase formation of which we are aware are found with polymeric platinum group acetylides which show a nematic phase in chlorinated solvents [5], anionic copper phthalocyanines which have been reported to shown columnar mesophases [3, 4] in water and Simon's annelides [6]. In this paper we present the first results from a study directed towards the design and synthesis of lyotropic mesogens with a transition metal complex as the head group.

The advantage of using a transition metal complex is the ease with which the complex can be modified; this should prove useful in attempting to correlate molecular structure with mesomorphism. For example, head group size and charge are readily varied, so that truly multi-positive or multi-negative head groups can be accessed, something which is difficult if not impossible in all but a very few metal free systems. Finally, the length and number of alkyl chains can also be changed as required.

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* Authors for correspondence.

† Also at Department of Chemistry and Applied Chemistry, University of Salford, Salford, Lancashire M5 4WT, England.

In selecting systems for study, it is important to remember that the complex needs to be stable under the conditions found in the mesophase; for this reason, metals in substitutionally inert configurations must be chosen. The most stable configuration for octahedral systems is low spin d^6, which has the maximum crystal field stabilization energy of $-2{\cdot}4\Delta_0+2P$ and the maximum crystal field activation energy of $0{\cdot}4\,\Delta_0$. Iron(II) has a d^6 configuration and readily adopts a low spin configuration with strong field ligands such as cyanide. Thus, complexes of the general formula $M_3[Fe(CN)_5L]$ [7], were identified for study. These were of particular interest as surfactants because they give triply charged head groups where the charges are concentrated in a single moiety (see also [2 (*b*)]). Usually it is necessary to include a separate group (for example CO_2^-) for each charge.

2. Experimental

Microanalysis was performed by the University of Sheffield Microanalytical Service; low values for some nitrogen analyses were a feature of these materials. Infrared spectra were recorded on a Perkin–Elmer 1600 FT instrument between 4000 and 600 cm^{-1} as KBr discs. Optical microscopy used a Zeiss Labpol instrument equipped with a Link-Am TH 600 hot-stage, PR 600 controller and CS196 cooling accessory. All chemicals and solvents were used as supplied.

2.1. *Preparation of silver nitroprusside*—$Ag_2[Fe(CN)_5NO]$

Solutions of sodium nitroprusside (10 g, 33·6 mmol) in water (50 cm^3) and silver nitrate (11·9 g, 70·0 mmol) in water (30 cm^3) were mixed and stirred vigorously for 30 min. The product was filtered off, washed thoroughly with water and acetone, and dried at 55°C under vacuum.

Yield = quantitative. Microanalysis: expected C(13·9) N(19·5)
found C(13·7 N(18·7)

2.2. *Preparation of* $M_2[Fe(CN)_5NO].xH_2O$

Silver nitroprusside (5 g, 11·6 mmol) was added to a solution of MCl (23·1 mmol) in water (50 cm^3) and stirred vigorously for 30 min. The precipitated silver chloride was filtered off through celite and the filtrate was taken almost to dryness at 45°C under vacuum. After trituration with acetone, the product was filtered off, washed with acetone and dried at 55°C under vacuum. Yields and microanalytical data are collected in table 1.

Table 1. Yields and microanalytical data for $M_2[Fe(CN)_5NO]$.

M	Yield	Degree hydration	C calc(found)	H calc(found)	N calc(found)
Li	3·4 g	—	—	unstable	—
Na				Used as supplied	
K	2·3 g (63%)	1	19·2 (18·9)	0·5 (0·5)	26·9 (25·5)
0·5 Ca	5·5 g (97%)	3	19·4 (19·3)	2·0 (2·4)	27·1 (25.0)

2.3. *Attempted preparation of* $Na_3[Fe(CN)_5(H_2NC_{12}H_{25})]$

Sodium nitroprusside (0·5 g, 1·68 mmol) and sodium acetate (0·25 g, 3·05 mmol) were dissolved with stirring in a mixture of warm water (2 cm^3) and methanol (5 cm^3), and dodecylamine (4·0 g, 21·6 mmol) was added. The mixture was kept at 55–60°C until the nitroprusside spot test was negative. Methanol (5 cm^3) was added and the mixture was filtered hot. Ethanol (95 per cent, 50 cm^3) was added and the resulting precipitate was spun down in a centrifuge and washed three times with ethanol (95 per cent). After drying at 55°C under vacuum, the solid was crushed to a powder, rewashed and redried at 55°C under vacuum.

Other complexes were prepared in a similar fashion, except that for M = Li, the product was precipitated and washed with a mixture of acetone and methanol (95/5 v/v). Yields and microanalytical data for these complexes are collected in table 2.

Infrared data (cm^{-1}): ν_{CN} 2048 s; 2019 sh; ν_{CH} 2958 sh, 2920 s, 2851 s; ν_{NH} 3289, 3259, 3181 m; $\delta_{HOH}/\delta_{HNH}$ 1618, 1602 m, br.

Due to problems associated with the rapid decomposition of these materials in water and methanol (in which they were soluble), it was not possible to record NMR data.

3. Results and discussion

3.1. *Synthesis*

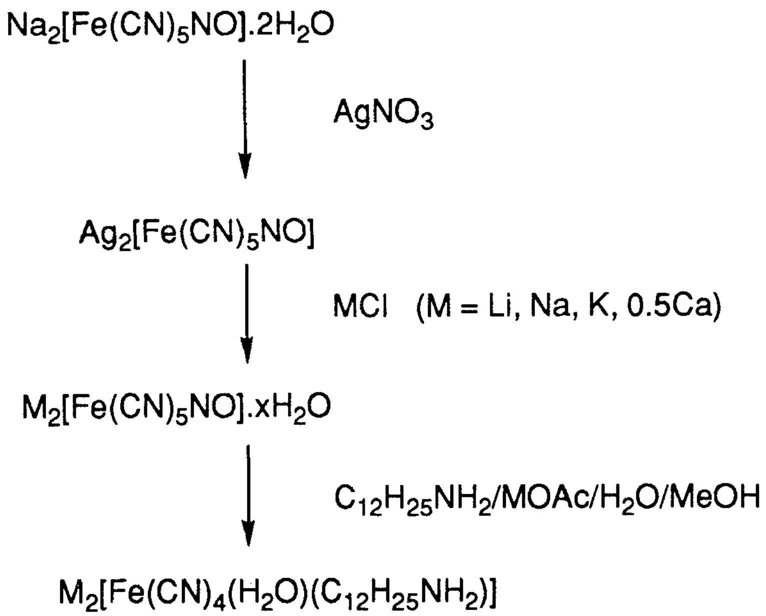
Different salts of the nitroprusside anion were obtained by metathesis using silver. Thus, reaction of silver nitroprusside (obtained from sodium nitroprusside and silver nitrate) with an alkali metal or alkaline earth metal chloride gave silver chloride and the desired nitroprusside. These salts were then reacted with dodecylamine to give the amphiphilic iron complexes as yellow powders, using the general conditions described by Kenney *et al.* [7] for $Na_3[Fe(CN)_5L]$ (see scheme). The recovered complexes can be stored in a dessicator for periods of at least 4 weeks without significant degradation, although the studies described here always used freshly prepared samples.

Consideration of the microanalytical data for these complexes quickly showed that they were not in fact the materials which it had been set out to synthesise. In fact the complexes isolated with Na^+ as the counter cation appear to be of the anion $[Fe(CN)_4(H_2O)(C_{12}H_{25}NH_2)]^{2-}$, while for Li^+, the complex appears to be the trihydrate of the same anion with one of the Li^+ ions replaced by $C_{12}H_{25}NH_3^+$. The calcium complex also analyses for the same anion and includes a methanol of crystallisation. No potassium salt of a material which could be shown (by microanalysis) to contain *only* the $[Fe(CN)_4(H_2O)(C_{12}H_{25}NH_2)]^{2-}$ anion was isolated, although the microanalytical data have a carbon content of around 37 per cent implying the presence of amine. It is believed that this is due to the fact that the potassium salts are

Table 2. Yields and microanalytical data for the amine complexes.

M	Yield	Calculated† (Found)/% C	H	N
Li	0·45 g	55·1 (55·3)	10·4 (9·7)	13·8 (13·8)
Na	0·61 g (83%)	46·9 (46·9)	7·1 (7·2)	17·6 (17·6)
0·5 Ca	0·46 g (66%)	46·9 (47·7)	7·6 (8·1)	16·1 (15·7)

† Calculated values correspond to: $Li(C_{12}H_{25}NH_3)[Fe(CN)_4(H_2O)(C_{12}H_{25}NH_2)].3H_2O$ $Na_2[Fe(CN)_4(H_2O)(C_{12}H_{25}NH_2)]$, $Ca[Fe(CN)_4(H_2O)(C_{12}H_{25}NH_2)].MeOH$.



Scheme. Synthesis of the iron complexes.

readily hydrolysed to $[Fe(CN)_4(H_2O)_2]^{2-}$, making isolation of pure $K_2[Fe(CN)_4(H_2O)(C_{12}H_{25}NH_2)]$ very difficult. This agrees with the observed trend in reactivity for the group 1 metal salts of this anion as we were not able to isolate any Rb or Cs salts containing amine. This was shown by the microanalytical data (carbon around 10 per cent) which corresponded to materials with no carbon other than that from the cyanide ligands. Further, no ν_{N-H} or ν_{C-H} vibrations could be seen in the infrared spectra. Nevertheless, the lyotropic phase behaviour of the potassium derivative did not reflect an impure material, suggesting that the sample contained predominantly the $[Fe(CN)_4(H_2O)(C_{12}H_{25}NH_2]^{2-}$ anion.

It is known that the free amine itself has a lamellar ($L\alpha$) phase in water [8] and given the hydrolytic instability of these complexes, this made phase identification difficult (see later). However, the mesomorphism of the amine would not interfere with the mesomorphism of the iron complexes and hence the observations and particularly the conclusions derived later are held to be valid. That the complexes were hydrolytically unstable was at first surprising. However, $[Fe(CN)_5(H_2O)]^{3-}$ [9] exchanges co-ordinated cyanide rather than coordinated water in the presence of free cyanide [10] implying that the Fe–H_2O interactions are quite inert. Thus, we assume that $[Fe(CN)_4(H_2O)(C_{12}H_{25}NH_2)]^{2-}$ hydrolyses to give $[Fe(CN)_4(H_2O)_2]^{2-}$ which is also inert. Further support for the hydrolytic instability of $[Fe(CN)_5L]^{3-}$ is provided by the lack of success in synthesising pure trialkylphosphite complexes of $[Fe(CN)_5]^{3-}$ [11].

3.2. *Mesomorphism*

The mesophase behaviour was determined by performing standard penetration experiments on a hot stage polarising microscope fitted with a cooling unit [12, 13]. All of the complexes showed a hexagonal (H_1) phase with a non-geometric texture when viewed through crossed polars. The penetration temperatures shown in table 3 (T_{pen}) [8] represent the lowest temperature at which the mesophase was observed in the

Table 3. Transition temperatures for the amphiphilic complexes.

M	T_{pen}/°C	Upper limit/°C
Li	9	100
Na	22	100
K	35	75†
0·5 Ca	21	100

† Compound is unstable at high temperatures; 75°C is the temperature at which hydrolysis is complete.

penetration experiment. The upper limit represents the point at which measurements could no longer be made because of water loss. At first sight, we might have expected that the lithium derivative, having two paraffin chains of which one is cationic, would give a lamellar rather than a hexagonal phase. However, the anion has a very large head group and a larger degree of micellar surface roughness might be expected which would favour a hexagonal phase over a lamellar.

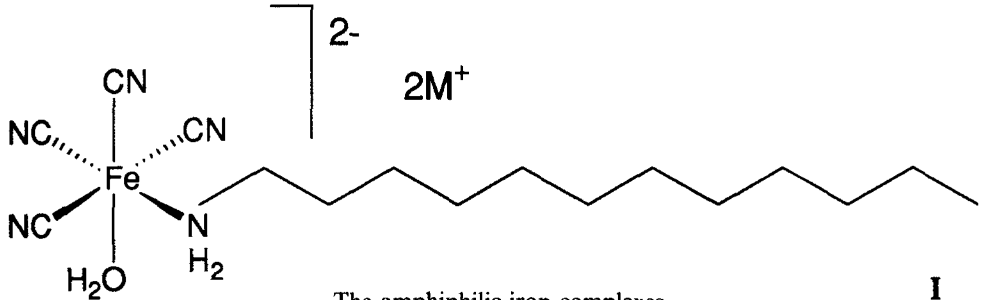
That only the H_1 phase is observed is unexpected. Following the packing constraint idea of Israelachvili *et al.* [14], the key parameter for determining micelle and mesophase type is the area per chain (A) at the micelle surface. Briefly, we expect [1, 14]:

$\mathrm{A} \geqslant 70\,\text{Å}^2$—spherical micelles/cubic (I_1) phase.

$70\,\text{Å}^2 > A \geqslant 47\,\text{Å}^2$—rod micelles/hexagonal (H_1) phase.

$47\,\text{Å}^2 > A$—disc micelles/lamellar (L_α) or reversed phases.

Treatment of the complex (**I**) as a conventional surfactant with head group and alkyl chain gives an estimated head group radius of about 4 Å [15] (note that while the aqua ligand is drawn *cis* to the amine, there is no spectroscopic evidence (for example from infrared) to rule out a *trans* arrangement). The cross sectional area of the head group is then *c.* 50 Å^2. Thus, the non-hydrated head group is just about large enough for H_1. If a single layer of water is included (head group radius *c.* 6 Å) then $A \approx 110\,\text{Å}^2$, i.e. an I_1 phase is expected. This is reinforced if we include electrostatic effects, especially those of a doubly anionic group, (recall that even the tiny CO_2^- head group has $A \approx 55\,\text{Å}^2$, forming an H_1 phase due to strong head group electrostatic repulsions [16]).



The amphiphilic iron complexes.

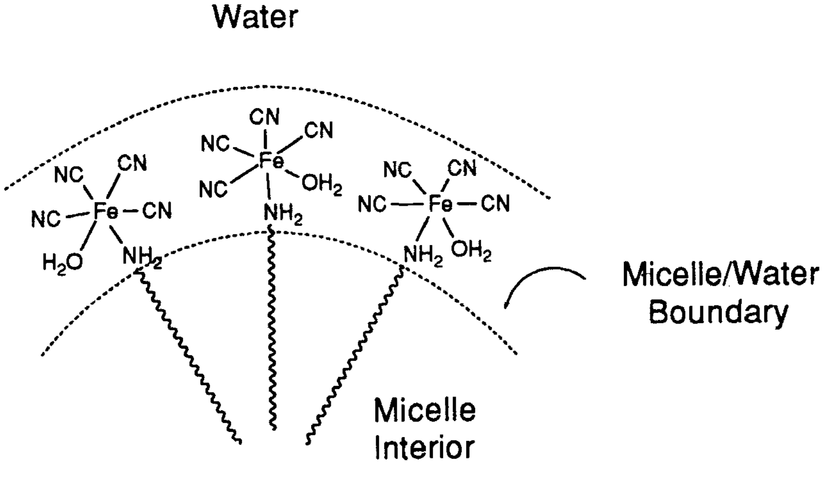
I

Hence the absence of I_1 is surprising. It is very likely due to strong counterion binding which would be expected in this type of complex [17], although the instability of the complexes prevents proper spectroscopic confirmation. However, in the absence of this evidence, a higher than expected critical micelle concentration (cmc) giving high electrolyte levels cannot be ruled out. The latter could arise from a rough micelle surface due to the bulky head groups and the multiple counterions. (Di and trivalent ionic head groups give much higher cmc values than monovalent ionic surfactants [18]. Both of these effects would reduce electrostatic repulsions. Also, it is possible that the head group is not strongly hydrated. We are unable to investigate these further because of the chemical instability of the surfactants.

The T_{pen} values are closely related to the Krafft temperature for the surfactant (the temperature below which the sufactant is insufficiently soluble for micelle formation). While the variation of T_{pen} shown for the derivatives with monovalent counterions is unremarkable, the close similarity of T_{pen} for the Ca and Na complexes is unusual. Calcium salts of anionic surfactants are usually insoluble, but here we expect the calcium salt to form micellar solutions. Unfortunately again, the chemical stability of the complex precludes further study.

The mesophase determinations were severely complicated by the fact that these complexes were unstable to water, being readily hydrolysed to give the aqua complex, $[Fe(CN)_4(H_2O)_2]^{2-}$ and the free amine, the latter of which is known to exhibit an L_α phase. This is also the reason why no upper temperature limit is quoted for the potassium complex as its hydrolysis was too rapid. Moreover, the same effect explains why we were unable to obtain the related complexes of rubidium and caesium as it appears that for the group 1 elements, the rate of hydrolysis of $[Fe(CN)_4(H_2O)(C_{12}H_{25}NH_2)]^{2-}$ increases as the atomic radius of M^+ increases; thus, $M_2[Fe(CN)_4(H_2O)(C_{12}H_{25}NH_2)]$ (M = Rb, Cs) hydrolyse as soon as they are formed. It was also apparent that hydrolysis was much more rapid in the L_1 phase than the H_1 phase. The rate of hydrolysis is likely to be related to the accessibility of the amine to water (see figure). This will be higher in the micellar phase both because of the larger fluctuations at the micelle surface and the larger proportion of surfactant present as monomer.

Some complexes of octyl- and decyl-amine were also prepared with sodium counter ions and preliminary studies on samples contaminated with a little free amine showed the octylamine derivative to be non-mesomorphic, while the decylamine derivative had an H_1 phase at around ambient temperature. However, given the instability of the system in general, these were not pursued further.



Schematic representation of the micelle/water boundary region.

4. Conclusions

Despite the choice of an inert metal fragment, these complexes proved too unstable for detailed study under the conditions required for mesophase formation. These amine complexes do, however, succeed in demonstrating that it is possible to use a transition metal fragment as the head group of a lyotropic liquid crystal. Therefore, metal complex stability is identified as the major obstacle to be overcome before systematic studies become possible.

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