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The Preparation, Solution and Mesophase Behaviour of Surfactant Complexes of Cobalt(III)

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The synthesis, solution and mesophase behaviour are described of some surfactant complexes of cobalt(III) containing triethylenetetramine (trien) and long-chain bipyridine ligands.

Introduction

Surfactants are ubiquitous, being components of the soaps and detergents that are used every day in a domestic setting, as well as components of our cell membranes on which we rely for our very life processes. Surfactants are a special case of amphiphiles and are generally characterised as materials having hydrophilic headgroups and hydrophobic chains. Surface adsorption accounts for their ability to lower the surface tension of water, while their assembly into micelles is an entropically driven process that leads to association colloids capable of, for example, dissolving organic-soluble materials in an aqueous system or providing discrete environments for reaction.

At much higher surfactant concentrations, these micelles can undergo a disorder-order transition to form ordered arrays of micelles – *lyotropic liquid crystal phases* – another manifestation of liquid-crystalline order. Lyotropic liquid-crystal phases are formed by DNA,[1] while the strength of natural spider silk and unnatural Kevlar originate from processing from the liquid-crystal state.

Various metal complexes can form lyotropic liquid-crystal phases.[2] Early examples were Group 10 metal polyynes, which form nematic phases in chlorinated solvents,[3] while later work showed how dirhodiumtetracarboxylates form mesophases in long-chain alkane solvents.[4] Later, Usol'tseva[5] demonstrated the mesomorphism of discotic palladium complexes in organic solvents and then in calamitic metallomesogens,[6] while we have reported on the mesomorphism of polycatenar silver(I) complexes in organic solvents.[7] Many metallophthalocyanines and metalloporphyrins are also known to form columnar lyotropic phases.[2]

Relevant to this discussion, *metallosurfactants* can be defined as surfactant molecules that contain a metal ion as part of the headgroup. As such, they will form monolayers, micelles and liquid-crystal phases in the same way that purely organic systems do, but they offer certain extra dimensions to their properties such as colour, paramagnetism, multi-charged headgroups, electron-transfer photochemistry and reactivity to name a few. The area has been covered in two reviews[8] and readers are directed to these with enthusiasm. Major contributions in this area have been reported by Fallis, Griffiths and co-workers[9] studying amphiphilic macrocycles and their metal complexes, while with Bowers, we have studied surfactant complexes of ruthenium(II) by small-angle neutron scattering[10] and by neutron reflectivity.[11] More recently, Dominguez-Gutiérrez et al. have investigated inverse structures of tetraalkylated ruthenium surfactants[12] as well as surfactant derivatives of Ni^{II} and Fe^{II}.[13] Other contributions are collected as reference.[14]

In concentrated solution, lyotropic liquid-crystal phases form and this area has also been reviewed.[2] In addition to reporting lyotropic properties of surfactant terpyridine complexes of ruthenium(II) and rhodium(III),[15] our major contribution in this area has been with surfactant bipyridine complexes of ruthenium(II)[16] (Figure 1) where we have shown that for monoalkyl complexes ($n \geq 12$, $m = 1$) I_1 cubic phases result, whereas in the dialkylated materials ($n = m \geq 12$), H_1 hexagonal phases are found.

One application of metallosurfactants is in the formation of mesoporous silicas containing metal nanoparticles, the latter derived directly from the metallosurfactant. Mesoporous oxides, in particular silica, have been widely exploited since the recognition of the so-called *liquid-crystal templating* (LCT) route,[17] in which silicas are formed in the pres-

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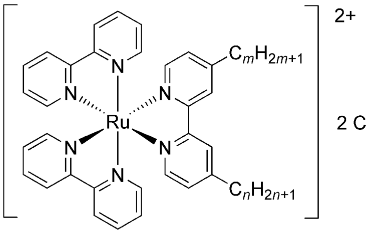


Figure 1. Surfactant ruthenium(II) complexes.

ence of surfactants at concentrations above their critical micelle concentrations yet below that necessary for mesophase formation. A significant variation on this method is *true liquid-crystal templating* (TLCT)[18] in which the surfactant mesophase is preformed and the silica is templated around it. This has the advantage that the pore morphology can be selected a priori from knowledge of the phase diagram of the surfactant.

Using approaches of this type, Dag and co-workers have shown how metal particles might be included in porous silicas,[19] while we have shown that highly active hydrogenation[20] and oxidation[21] catalysts can be prepared starting from surfactant derivatives of the *tris*(2,2′-bipyridine)ruthenium(II) cation.[22] In our work, we form the hexagonal H_1 phase of the metallosurfactant and condense $Si(OMe)_4$ around it to form a solid gel. On calcination, the pores are fixed and the metal complex decomposes to give rise to nanoparticulate RuO_2 with a fairly monodisperse particle diameter of about 2.4 nm. Seeking to expand on this general approach, it was necessary to identify other metallosurfactants that would form lyotropic mesophases that would act as suitable templates around which silica could be condensed.

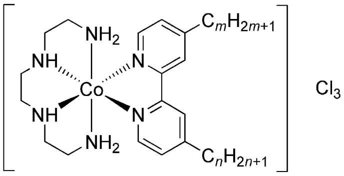
Previously,[23] we had studied surfactant cobalt(III) complexes composed of two, *cis* ethylenediamine ligands and a long-chain salicylate anion. These complexes showed H_1 hexagonal phases, but were found to be labile in aqueous solution. Other surfactant Co^{III} complexes have been described elsewhere,[24] and in particular we note (Figure 2) surfactant amine complexes prepared by Yashiro,[25] surfactant sarcophagine complexes with *anti*-nematode activity reported by Sargeson and co-workers,[26] cobalt(III) trien complexes from Arumugan and Arunachalam[27] and a series of systems from Jaeger and Bohle.[28]

To expand such an approach to other metal systems would require further examples of metallosurfactants and so in this paper, the synthesis and solution properties of some surfactants of cobalt(III) are described.

Results and Discussion

Synthesis

As target complexes, those of the tetradentate amine, triethylenetetramine (trien) in combination with an alkylated bipyridine were identified (Figure 3).



1-*n*: *m* = 1
2-*n*: *n* = *m*

Figure 3. The target cobalt(III) complex.

An issue with trien complexes is the formation of α- and β-isomers (Supporting Information), and there can be issues about obtaining isomerically pure products. However, Sargeson and Searle[29] proposed a route to the *cis*-dichloro complex that allowed ready separation of these stereoisomers in a route that proceeded via the *cis*-dinitro complex. Therefore, ice-cold aqueous solutions of trien·HCl and cobalt(II) chloride hexahydrate were mixed and added quickly to sodium nitrite, with the mixture being aerated vigorously at 0 °C leading to a yellow precipitate. Crystallisation afforded the pure product in 42% yield. The dichloro complex was then prepared by evaporating a mixture of the *cis*-α-dinitro complex and concentrated hydrochloric acid to give a crude, purple solid, from which the pure product was obtained in 60% yield after work up. The geometry of the complex was confirmed as *cis*-α by electronic spectroscopy (see Supporting Information).

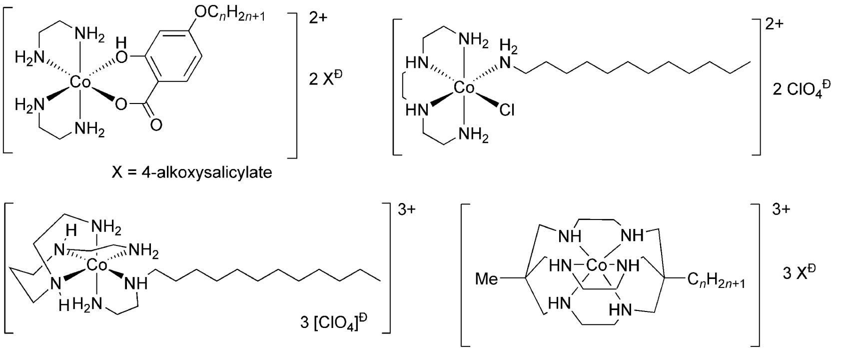


Figure 2. Surfactant Co^{III} complexes reported by: ourselves (top left), Yashiro et al. (bottom left), Arumugan and Arunachalam (top right) and Sargeson and co-workers (bottom).

cis-α-[$CoCl_2$(trien)]Cl was then heated under reflux with an alkylated bipyridine in aqueous ethanol to give a bright orange solution, which was cooled, filtered and the solvents evaporated to dryness to give a crude, orange solid, which was purified over Sephadex-LH20 to give the pure complex in up to 72% yield. The complexes were characterised by ^{1}H NMR spectroscopy, with the peaks being assigned with the aid of $^{13}C\{^1H\}$, HMQC and COSY spectra.

Eleven cobalt(III) complexes were prepared in this way; seven monoalkylated surfactants (**1**-*n*: n = 12, 13, 14, 15, 17, 18 and 19) and four dialkylated materials (**2**-*n*: n = 12, 14, 16 and 19).

Crystal and Molecular Structure of 1-18

A single crystal of **1**-18 was slowly grown from methanol. Selected crystallographic data are shown in Table 1 and the molecular structure is shown in Figure 4.

Table 1. Crystallographic data for **1**-18.

Empirical formula	$C_{36}H_{68}Cl_3CoN_6O$	
Formula weight	766.24 g mol^{-1}	
Temperature	120(2) K	
Crystal system	triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 7.5684(3) Å	α = 92.9300(10)°
	b = 9.7666(4) Å	β = 90.7060(10)°
	c = 28.6250(16) Å	γ = 92.557(2)°
Volume	2110.79(17) Å^3	
Final R indices [$F^2 > 2\sigma(F^2)$]	R_1 = 0.0619, wR_2 = 0.1094	
R indices (all data)	R_1 = 0.1471, wR_2 = 0.1309	

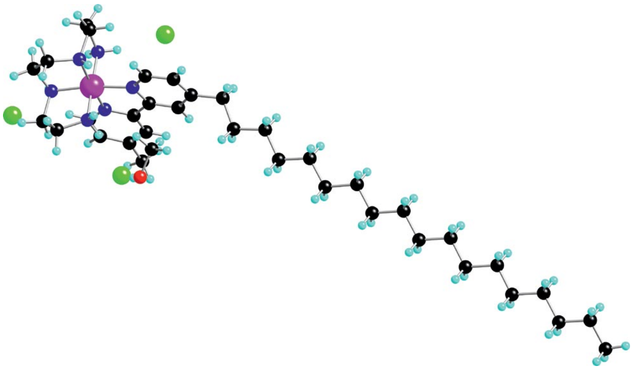


Figure 4. Crystal structure of **1**-18.

The structure shows that the stereochemistry of the complex is as expected, with triethylenetetramine coordinated in a *cis*-α fashion around the distorted octahedral cobalt(III) centre. The average Co–N bond length is 1.960 Å for the amine nitrogens and 1.947 Å for the bipyridine nitrogens, in agreement with that reported by Yamamoto et al. for related *cis*-α-salicylato(trien)cobalt(III) complexes.[30] The only significant deviation was N2–Co (1.985 Å). It should be noted that the complex crystallised with one molecule of methanol.

Some selected bond lengths and angles are given in the Supporting Information and it is noted that the chelate rings of the trien and bipyridine distort the octahedral environment around the metal centre, with the rings consistently having N–Co–N bond angles below 90°, compensated by the corresponding bond angles that are not chelating being consistently above 90°.

The packing diagram (Figure 5) indicates that the complex packs into a lamellar structure in the solid state, where the chains are interdigitated. Arulsamy et al.[31] also found that their double-chained amphiphilic cobalt(III) surfactants packed into a lamellar structure in the solid state, although the orientation of the alkyl chains determined whether the chains were interdigitated or end-to-end.

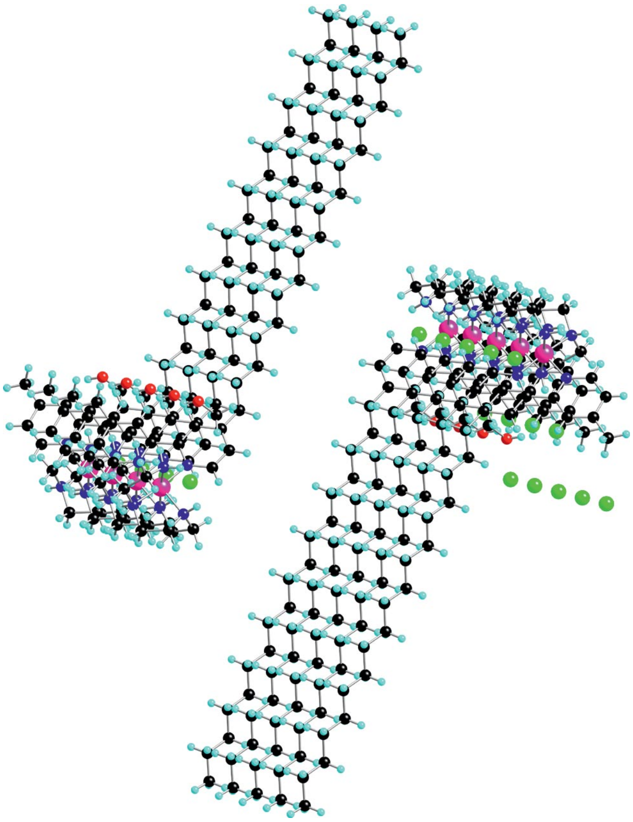


Figure 5. The packing diagram of **1**-18 in the solid state.

Solution Behaviour

Critical Micelle Concentration

The critical micelle concentration (cmc) of the cobalt(III) surfactants **1**-*n* was measured using *surface tensiometry* employing the *Du Noüy ring method*. Data for **2**-*n* were not recorded as in each case the Krafft point was above room temperature and the tensiometer was designed to work at ambient temperature. Difficulties were encountered in collecting these data for some chain lengths as it became apparent that in some cases the complexes were not stable under the conditions employed. Thus, complexes **1**-12 to **1**-15 were found to throw down a colourless deposit on standing in water, which we attribute to the dissociation of the free ligand. Thus, while the data obtained for **1**-17, **1**-18 and **1**-19 are good (Figure 6), those for the shorter-chain homologues are not (Supporting Information). Measured surface tensions are constant at just below 50 mN m^{-1}. Further, the measured cmc for **1**-17 to **1**-19 (Table 2, Figure 7) show the expected decrease with increasing chain length, while the cmc values obtained for **1**-12 to **1**-15 appear to be lower (these are included in Figure 7 for the purposes of illustration). Given that Co^{III} in these systems is low-spin d^6, this lability is at first sight unexpected. However, as a 3+ cation, it is a much poorer π-donor than analogous d^6 complexes of Group 8 metals and, as a consequence, the π-accepting bipyridine ligand is less strongly bound.

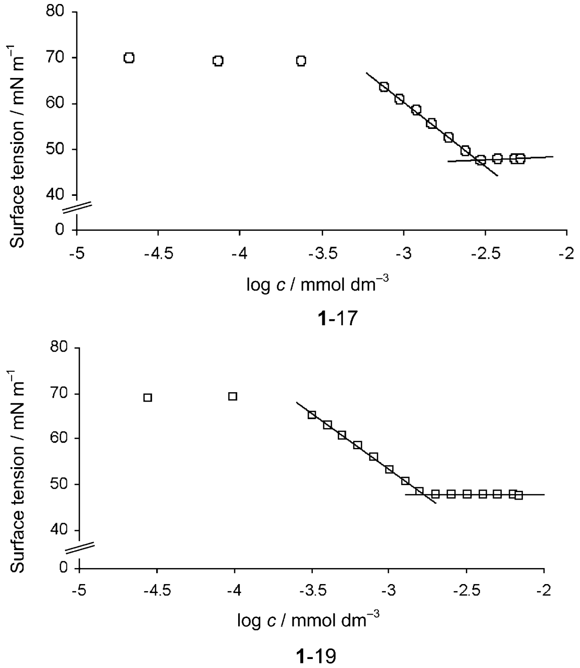


Figure 6. Surface tension isotherms measured for **1**-17 and **1**-19 at 25 °C.

Table 2. cmc values obtained for **1**-n surfactants, obtained by surface tension measurements.

n	cmc [mmol dm^{-3}]
17	3.02
18	2.29
19	1.81

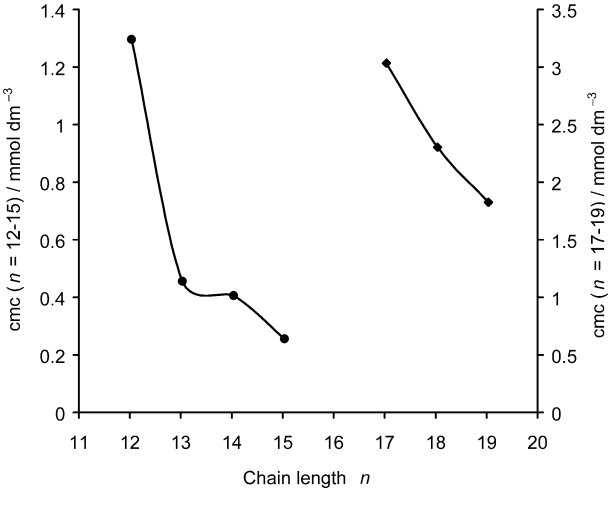


Figure 7. Graph showing the variation of cmc with chain length of **1**-n. *Note:* the data for n = 12 to 15 are unreliable (see text) and are included for the purposes of illustration.

Lyotropic Liquid-Crystal Behaviour

Monoalkylated Complexes

The phase behaviour for the longer-chain monoalkylated complexes is shown in Table 3. These data were obtained using the Lawrence penetration method,[32] which creates a concentration gradient allowing a snapshot of the phase diagram to be seen. The temperatures given are indicative of where changes in the mesomorphism were observed. (Data for the shorter-chain homologues are given in the Supporting Information. They are not included here as the complexes descompose slowly in water, although we do not believe that this affects the qualitative results significantly)

Table 3. Variation of mesophase behaviour of **1**-n with chain length; phases observed shown (left to right) as increasing in concentration.

n	T [°C]	Phases observed
17	0	L_1·I_1·I_1'·H_1·S
	114	I_1'·H_1·S
	116	H_1·S
18	0	L_1·I_1·I_1'·H_1·S
	104	I_1'·H_1·S
	105	H_1·S
19	0	L_1·I_1·I_1'·H_1·S
	106	I_1'·H_1·S
	108	H_1·S

Thus, for each of the surfactants, two non-birefringent phases were found between the micellar solution, L_1, and the normal H_1 hexagonal mesophase (Figure 8). These phases also showed air bubbles that were non-spherical in nature, indicating a high viscosity not associated with that of micellar solutions. As such, they are assigned as two I_1 cubic phases (I_1 and I_1') owing to their location between the L_1 and H_1 phases. As the headgroup of these Co^{III} surfactant is smaller than that of tris(bipyridine)ruthenium(II) surfactants, which also show I_1 cubic phases,[22] then the dominance of the cubic phase in these systems is consistent with the Israelachvili packing constraint idea.

A feature of these materials is the existence of a mesophase at $T > 100$ °C and indeed Figure 8 (C) shows the hexagonal phase at 100 °C. However, at 125 °C, the phase destabilised to give a non-birefringent solid, which cracked on further heating. On reaching 160 °C, the solid then appeared to decompose to give, in part, a purple solid; perhaps that of the [CoCl$_2$(trien)]$^+$ precursor to the complexes.

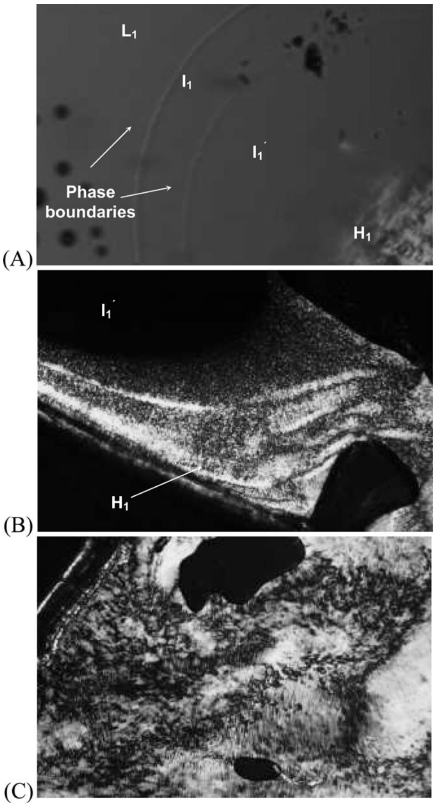


Figure 8. (A) Upper: Typical photograph of a Lawrence penetration experiment (ca. 40 °C) showing increasing concentration from top left to bottom right. Faint lines show the boundaries between micellar solution (L_1, top left), two cubic phases (indicated by arrows) and the hexagonal phase (very bottom right); (B) Lower: sample at 90 °C with increasing concentration from top left to bottom right, showing the cubic I_1' phase and the non-geometric texture of the hexagonal H_1 phase; (C) hexagonal H_1 phase at 110 °C.

Such a proposal is consistent with the suggestion, made earlier in this chapter, that the lability of these complexes arises from loss of the bipyridine ligand.

Dialkylated Complexes

The phase behaviour for the dialkylated complexes **2**-*n* is shown below in Table 4. It should be noted that the Krafft point for these materials is above room temperature, which is reflected in the lower temperatures at which mesophases are seen in each case. Furthermore, despite some evidence with **2**-12 of the presence of free ligand, these dialkylated materials appeared generally more inert than their mono-chained analogues.

The surfactants, $n = 14$, 16 and 19, show similar mesophase behaviour, with the hexagonal H_1 phase (Figure 9), a non-birefringent phase, and lamellar L_α phase (Figure 9) all being observed.

The assignment of the viscous, non-birefringent phase was based on its position between the hexagonal and lamellar phases; therefore, it was assigned as the bicontinuous V_1 cubic phase. Furthermore, the lamellar phase was distinguished from the hexagonal phase on the basis of its characteristic texture.

Table 4. Variation of mesophase behaviour of **2**-*n* with chain length, phases observed shown (left to right) as increasing in concentration.

n	*T* [°C]	Phases observed
12	41	$L_1 \cdot X \cdot V_1 \cdot S$
	89	$L_1 \cdot X \cdot V_1 \cdot L_a \cdot S$
	104	$L_a \cdot S$
14	53	$L_1 \cdot H_1 \cdot S$
	57	$L_1 \cdot H_1 \cdot V_1 \cdot L_a \cdot S$
	101	$L_a \cdot S$
16	55	$L_1 \cdot H_1 \cdot S$
	60	$L_1 \cdot H_1 \cdot V_1 \cdot S$
	66	$L_1 \cdot H_1 \cdot V_1 \cdot L_a \cdot S$
	106	$L_a \cdot S$
19	66	$L_1 \cdot H_1 \cdot S$
	77	$L_1 \cdot H_1 \cdot V_1 \cdot L_a \cdot S$
	107	$L_a \cdot S$

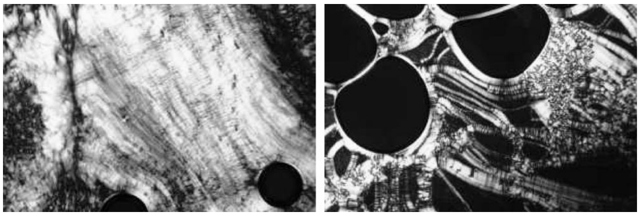


Figure 9. Photomicrograph of (left) **2**-14 at 53 °C showing the non-geometric texture of the hexagonal H_1 phase and (right) at 78 °C showing the oily-streaky texture of the lamellar phase.

The phase behaviour of **2**-12 was slightly more difficult to assign. Firstly, it should be noted that this phase appeared to contain some unreacted ligand, although this was not identified in the ^{1}H NMR spectrum of the complex or by elemental analysis. More than that, it does not show any lyotropic behaviour, although it could act as co-surfactant and influence mesomorphism. The lamellar phase was assigned on the basis of its optical texture and the identity of the cubic phase as V_1 was by analogy with the other complexes studied. However, it is not clear that the hexagonal phase was observed. Rather there was a non-birefringent phase (denoted X) that appeared at concentrations between the micellar solution and the bicontinuous cubic phase, having a viscosity intermediate between both of these phases. The phase appeared to become birefringent when disrupted mechanically, although it became optically isotropic immediately afterwards. It should be noted that the bicontinuous phase was not birefringent on mechanical disruption and that the X phase did not appear to be biphasic. It is not impossible that X could be a homeotropically aligned hexagonal H_1 phase, although in our experience, such a strong prference for homeotropic alignment is uncommon. Mesophase, X remains, therefore, uncharacterised.

The temperatures of the phase changes in the surfactant series show a chain-length dependence, with all the temperatures increasing with increasing chain length as longer chains show lower solubility in water. Conversely, the destabilisation of all phases, except the lamellar phase, occurs at similar temperatures. This is due to the loss of water from the system above 100 °C.

Comparison of Mono- and Di-alkylated Complexes

There are two main differences between the two series of surfactants. Firstly, the temperature at which the first mesophases are seen is vastly different. Thus, mesophases of the monoalkylated complexes form below room temperature and are stable down to 0 °C, even at extended chain lengths, such as $n = 19$. Conversely, mesophases of the dialkylated surfactants do not form until 41 °C for the shortest-chain length surfactant ($n = 12$). This indicates mesophase formation is a function of the molecular weight of the complex, where the Krafft point of a dialkylated complex would be expected to be higher than that of its monoalkylated analogue.

In comparison to their monoalkylated derivatives, the dialkylated surfactants have double the alkyl chain volume; this accounts not only for the higher temperatures at which mesophases form, but also the types of mesophase observed. Israelachvili's ratio[33] suggests that an increase in alkyl chain volume decreases the surface curvature of the micelles that are present at the cmc. For the cobalt surfactants reported here, the cross-sectional area of the headgroup, a_0, was calculated as 75.4 Å^2 from a headgroup radius of 9.8 Å, whilst the chain length, l, of a dodecyl group calculated to be 15.0 Å as 90% of the all-*trans* configuration. If the volume of a methyl group is assumed to be 54 Å^3 and that of a methylene to be 27 Å^3 then the volume, v, of the dodecyl chain would then be 351 Å^3. Therefore, **1**-12 has a packing parameter (v/a_0l) of 0.31, indicating the presence of spherical micelles, whilst that for **2**-12 is 0.62, indicating the presence of disk-like micelles. Whilst this theory does not extend to high surfactant concentrations, one might expect that mesophases of reduced surface curvature might exist for the dialkylated surfactants. This is apparent here, where the mono-alkylated surfactants form only micellar cubic and hexagonal phases, whilst the di-alkylated surfactants show hexagonal, bicontinuous cubic and lamellar phases.

Possible Use in Mesoporous Templating

We have shown previously how the H_1 mesophase of Ru^{II} surfactants in water may be used to template the formation of mesoporous silicas with hexagonal pore distribution and that during the preparation, nanoparticulate RuO_2 is deposited which is either active itself in oxidation catalysis or is active in hydrogenation following reduction. Given the occurrence of H_1 mesophases in the present materials, the same approach was attempted. Thus, $Si(OMe)_4$ is added to the mesophase at pH 2 and a sol-gel condensation is allowed to proceed before the solid gel is calcined. However, in the case of these materials, addition of the $Si(OMe)_4$ leads to precipitation of the Co surfactant and subsequent destruction of the mesophase. This was confirmed by the absence of any porosity (BET) or order (XRD) in calcined samples.

Conclusions

Heteroleptic surfactant complexes of cobalt(III), with a tetradentate amine ligand (triethylenetetramine) and an alkylated bipyridine, have been prepared successfully. The monoalkylated complexes were soluble in water and found to be surface active, the critical micelle concentration of the complexes being determined by surface tensiometry. The surfactants with $n = 17$ to 19 gave good quality surface tension isotherms and showed the expected decrease in cmc as chain length increased, while for surfactants $n = 12$ to 15 the data were unreliable, something attributed to the lability of the complexes in water on account of their higher solubility. The cmc of the dialkylated surfactants was not measured owing to their Krafft point being below room temperature.

The lyotropic liquid-crystal behaviour of the monoalkylated complexes in water showed micellar cubic and hexagonal phases up to 100 °C, whilst the dialkylated surfactants showed a preference to form mesophases of less positive surface curvature.

Attempts to use these surfactants in the true liquid-crystal templating of mesoporous silicas were unsuccessful.

Experimental Section

General: All solvents were used as received except for tetrahydrofuran (THF), which was dried by distillation over sodium and benzophenone, and methanol, which was dried by distillation over methyl iodide and magnesium immediately prior to use. For surface-tension measurements, purified water was passed through a mixed-bed ion-exchange column and particulate filter immediately prior to use, giving water with a surface tension of between 70 and 72 mN m^{-1}.

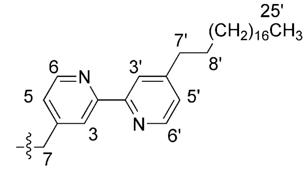
Sephadex LH-20 was prepared by soaking in a saturated solution of sodium chloride for 7 d followed by thorough washing with water. The Sephadex was reactivated by washing thoroughly with warm mixture of 2-propanol and water.

NMR spectra were recorded with either an Avance Bruker DRX400 spectrometer or a Bruker ACF-300 spectrometer running at 400 MHz and 300 MHz, respectively.

Elemental analyses were performed by the microanalysis service at the Department of Chemistry, University of Exeter, and UV/Vis spectra were recorded with a UNICAM UV4 spectrometer. Surface tension measurements were performed with a KSV Sigma 70 automated tensiometer using the Du Noüy ring method.

Unless otherwise stated, all reactions were performed under nitrogen, at atmospheric pressure using degassed solvents.

NMR Labelling Scheme: The ligands and complexes have been labelled in the following way for NMR spectra:



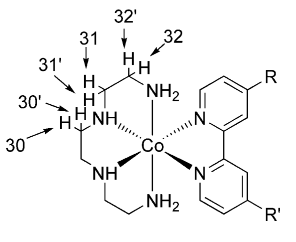


Table 5. Yield and elemental analysis data for the mono- and di-alkylated ligands.

Complex	% Yield	Waters of hydration	Elemental analysis data, % found (expected)		
			C	H	N
1-12	71	2.5	50.2 (50.1)	8.3 (8.3)	12.4 (12.1)
1-13	70	1	53.1 (52.8)	8.3 (8.7)	11.4 (12.3)
1-14	72	3	51.0 (50.9)	8.6 (8.5)	11.6 (11.5)
1-15	62	2	53.1 (52.9)	8.8 (8.6)	11.4 (11.6)
1-17	61	2	53.7 (54.1)	9.0 (8.8)	11.3 (11.1)
1-18	67	2	55.1 (54.6)	9.1 (8.9)	10.7 (10.9)
1-19	68	2.5	54.5 (54.5)	9.4 (9.9)	10.6 (10.6)
2-12	61	2	57.8 (57.8)	9.6 (9.6)	9.8 (9.8)
2-14	55	2	59.0 (59.0)	10.2 (9.7)	9.2 (9.4)
2-16	54	2	60.1 (60.5)	10.4 (10.0)	8.6 (8.8)
2-19	61	2	62.6 (62.6)	10.8 (10.3)	7.7 (8.1)

Synthesis

***cis*-α-Dinitro(triethylenetetramine)cobalt(III) Chloride Monohydrate:** Ice-cold solutions of triethylenetetramine (5 cm^3, 4.85 g, 0.033 mol) in HCl (2.9 cm^3, 0.034 mol, 11.6 M) and cobalt(II) chloride hexahydrate (7.93 g, 0.033 mol) in water (6.7 cm^3) were mixed and added quickly to sodium nitrite (4.84 g, 0.070 mol). The mixture was aerated vigorously for 1.5 h at 0 °C and the yellow solid filtered, washed with ice-cold HCl (1 M), ethanol (absolute) and acetone and air dried. The crude product was crystallised from hot water to give a yellow solid (4.85 g, 0.014 mol) in 42% yield. $C_6H_{20}ClCoN_6O_5$ (350.65): calcd. C 20.6, H 5.8, N 24.0; found C 20.2, H 5.6, N 23.9.

***cis*-α-Dichloro(triethylenetetramine)cobalt(III) Chloride:** HCl (2.2 cm^3, 0.026 mol, 11.6 M) was added to a solution of *cis*-α-dinitro(triethylenetetramine)cobalt(III) chloride monohydrate (3 g, 0.0086 mol) in water (3.1 cm^3) and the solvents evaporated from the mixture on a steam bath. The crude purple solid was ground in ethanol (5 cm^3, absolute), filtered, washed with ethanol (absolute) and acetone and air dried. The solid was crystallised from hot HCl (25 cm^3, 3 M) to give a purple solid (1.65 g, 0.0052 mol) in 60% yield. UV/Vis (CF_3SO_3H): λ_{max} (logε) = 380 (2.07), 536 (2.31), 624 (1.91, shoulder) nm. $C_6H_{18}Cl_3CoN_4$ (311.53): calcd. C 23.1, H 5.8, N 18.0; found C 22.7, H 6.0, N 17.9.

***cis*-α-(4,4′-Didodecyl-2,2′-bipyridine)(triethylenetetramine)cobalt(III) Chloride:** *cis*-α-Dichloro(triethylenetetramine)cobalt(III) chloride (0.16 g, 0. 51 mmol) was added to a stirring suspension of 4,4′-didodecyl-2,2′-bipyridine (0.25 g, 0.00051 mol) in ethanol (60 cm^3) and water (6 cm^3) and the mixture heated at reflux for 16 h. The orange solution was cooled to room temperature and the solvents evaporated to dryness under reduced pressure. The crude product was dissolved in methanol and purified by gel chromatography over Sephadex LH-20 (eluant MeOH). The orange band was collected and the solvents evaporated to dryness to give an orange solid (0.25 g, 0.00031 mol) in 61% yield. ^{1}H NMR (CD_3OD): δ = 0.90 (t, $^3J_{HH}$ = 6.9 Hz, 6 H, H18,18′), 1.29 (m, 36 H, H9–17,9′-17′), 1.82 (m, 4 H, H8,8′), 2.72 (m, 2 H, H32′), 2.99 (t, $^3J_{HH}$ = 7.9 Hz, 4 H, H7,7′), 3.05 (m, 2 H, H31), 3.07 (m, 2 H, H30), 3.18 (m, 2 H, H32′), 3.57 (m, 2 H, H31′), 3.88 (m, 2 H, H30′), 7.83 (dd, $^3J_{HH}$ = 6.1, $^4J_{HH}$ = 1.6 Hz, 2 H, H5,5′), 8.70 (d, $^4J_{HH}$ = 1.6 Hz, 2 H, H3,3′), 8.56 (d, $^3J_{HH}$ = 6.1 Hz, 2 H, H6,6′) ppm. ^{13}C NMR (CD_3OD): δ = 13.05 ($2\times CH_3$, C18,18′), 22.32–31.67 ($9\times CH_2$, C9–17,9′-17′), 29.96 ($2\times CH_2$, C8,8′), 34.86 ($2\times CH_2$, H7,7′), 42.92 ($2\times CH_2$, H32,32′), 55.33 ($2\times CH_2$, H30,30′), 56.85 ($2\times CH_2$, H31,31′), 125.00 ($2\times CH$, C3,3′), 128.84 ($2\times CH$, C5,5′), 152.64 ($2\times CH$, C6,6′), 157.05 ($2\times C$, C4,4′), 160.04 ($2\times C$, H2,2′) ppm.

All mono- and dialkylated analogues were prepared similarly and the analytical data are shown in Table 5.

Supporting Information (see also the footnote on the first page of this article): Structures of the α- and β-forms of the Co^{III} precursor; an electronic spectrum to show the formation of the desired isomer; table of selected bond lengths and angles from the structure of **1**-18; mesomorphism of **1**-*n*.

CCDC-217997 (for **1**-18) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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