Amphiphile Structures in the Solid State: Complex Cations with Lipophilic Substituents

Jack M. Harrowfield,*[a,b] George A. Koutsantonis,[a] Gareth L. Nealon,[a] Brian W. Skelton,[a] and Allan H. White[a]

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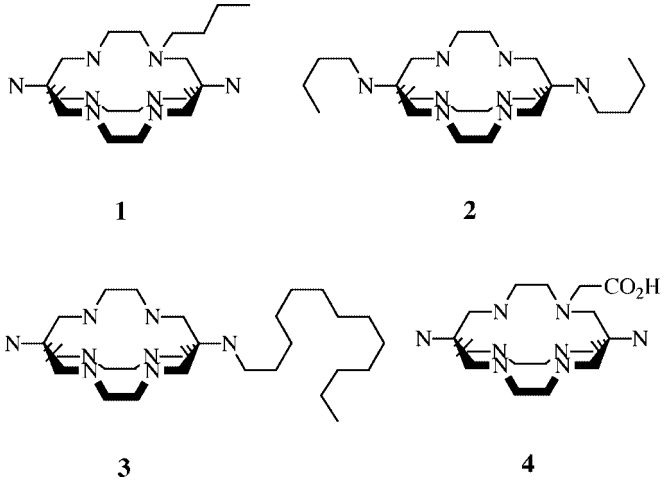
Structural characterisation of hexamine cage complexes, two containing diamagnetic Co^{III} and one containing paramagnetic Cu^{II}, to which both rather short (C_4) and relatively long (C_{13}) alkyl substituents have been attached, shows that while the longer "tail" introduces an anticipated bilayer form to the crystalline solid, even the shorter tail can be associated with a form of aggregation of lipophilic entities in the crystal. The short tail at least may also be involved in interactions with anions of a complex type. As surfactants, functionalised cage complexes contain a head group, which is a multi-site hydrogen-bonding entity, and which can thus provide a mechanism for further aggregation concomitant with that of any apolar functionality.

Introduction

As potential head groups for surfactant molecules, complex cations and anions offer the chance to introduce entities, often chiral, of unusually high charge, of variable spectroscopic and magnetic properties, and with structures that may facilitate specific forms of association of counterions with those head groups.[1] The same virtues apply, of course, in the design of metallomesogens.[2] The kinetic inertness and ease of functionality of cage amine complexes[3] render them particularly appealing for use as head groups, and it has been shown that surfactants derived from Co^{III} cage complexes can have unusual physical and biological properties.[4] In seeking to expand this field of chemistry, we have investigated alternative syntheses of amphiphiles and what might be termed "reverse" bola-amphiphiles[5,6] based on cage amine complexes of various metals and have sought to characterise these materials in detail, in the solid state, through X-ray crystallography. This report is specifically concerned with some structural results, which have uncovered both expected and unexpected properties concerning the cage amines **1**–**3**

The broad basis of the present work was an effort to develop methods for the synthesis of functionalised cage amines, which continued to exploit the advantages associated with the selective protection of nucleophilic centres by metal ion coordination,[3,4] while avoiding the commonly encountered difficulty[3f,7] of the need for extreme conditions in order to remove the new ligands from the metal centre on which they are formed. In the case of reductive alkylation reactions of amine centres as presently described, the use of a metal (Mg^{II}) easily removed[7] from the cage as an agent to protect endocyclic amine centres introduces problems in that even the mildly acidic conditions normally applied in $RCHO/NaBH_3CN$ reactions[8] cause its loss from the reactant cage. However, the value of the syntheses described herein is that they demonstrate that Mg^{II}, under weakly basic conditions, can be used to selectively protect multiple N-donor sites, while efficient reductive alkylation still occurs at unprotected centres.



1 **2** **3** **4**

Results and Discussion

Perhaps fortuitously, the use of non-acidic conditions for the reductive alkylation of "free" diaminosarcophagine by

[a] Chemistry M313, School of Biomedical and Chemical Sciences, University of Western Australia,
35 Stirling Highway, Crawley, Perth, WA 6009, Australia
[b] Current address: Laboratoire de Chimie Supramoléculaire, ISIS, Université Louis Pasteur,
8, allée Gaspard Monge, 67083 Strasbourg, France
E-mail: harrowfield@isis.u-strasbg.fr

$CH_3(CH_2)_2CHO/NaBH_3CN$ in large excess results in quite efficient monoalkylation. As in simple alkylation reactions,[3f] this monofunctionalisation appears to occur predominantly on a secondary and not a primary amine centre of the reactant, generating the ligand **1**. The reaction was studied in order to establish a model procedure for alkylations involving long-chain aldehydes, although it in fact did not prove particularly useful for this purpose. As expected for a ligand-containing tertiary nitrogen donor centres,[3c,3f,9] significant distortions of the coordination sphere of a bound metal result, this being reflected in the beautiful crimson (not yellow) colour (λ_{max} 502 nm) of the Co^{III} complex, $[Co(\mathbf{1})]^{3+}$. Given the presence of a lipophilic (albeit short) substituent on **1**, the high water-solubility of all simple salts of $[Co(\mathbf{1})]^{3+}$ was surprising and thus the crystal structure of $[Co(\mathbf{1})][Sm(dipic)_3]\cdot 15\,H_2O$ was studied in order both to characterise the Co^{III} coordination sphere and to determine what interactions with the butyl chain might be involved. The high degree of hydration of this material is typical of compounds containing $[Ln(dipic)_3]^{3-}$ species,[10,11] though it was not immediately clear that this should be the only consideration here. The discovery that $[Sm(dipic)_3]^{3-}$ in particular could be used to obtain a crystalline solid from $[Co(\mathbf{1})]^{3+}$ was purely a matter of good fortune, resulting from the availability of hydrated $Na_3[Sm(dipic)_3]$ in the laboratory, and was not a consequence of any logic other than "charge matching" of the anion and cation (Table 1).

The complex, a racemate in a non-centrosymmetric space group, crystallises with one formula unit, devoid of crystallographic symmetry, comprising the asymmetric unit of the structure. Projections of the cation, the anion, and the unit cell, viewed variously, are presented in Figure 1, with hydrogen bonding summarised in Table 2. The cation presented in part (a) of Figure 1 is very similar to that found in the complex of 3-carboxymethyl-1,8-diaminosarcophagine (**4**), in $[Co(\mathbf{4})]Cl(S_2O_6)\cdot 4.5\,H_2O$.[3f] The bond to the tertiary donor [Co–N(3b), 2.063(4) Å] is elongated compared to those to the secondary donors [1.974–2.000(4), <> 1.986(11) Å], though in the present case by only ca. 0.07 Å rather than ca. 0.09 Å. The cation again has the lel_3 configuration, with two NH units (3a,3b′) H bonding to one water molecule [O(6) ($^1/_2 - x$, $\bar{y}$, $z - {}^1/_2$)], two others (3c,3a′) H bonding to separate water molecules H-bonded to one another [O(1,4)], and the remaining NH (3c′) interacting with an uncoordinated carboxylate-*O* [O(14)] of an adjacent complex anion. Bridging of NH units by H-bond acceptors appears to be a significant feature concomitant with adoption of the lel_3 form.[3f] The primary amino groups are also involved in H bonding to both water and carboxylate groups, as part of the extended H bonding array in the heavily hydrated crystal, which resembles overall that found in other $[Ln(dipic)_3]^{3-}$ derivatives. The *N*-butyl substituent is extended and remote from water molecules, projecting towards a neighbouring complex anion, the terminal methyl group appearing to contact at least one pyridine ring, with C···ring centroid 3.76 Å (CH···π interaction?), and the adjacent methylene carbon atom [C(33b)] being 3.361(7) Å from a coordinated carboxylate-*O* [O(13)] (CH···O bonding?). The anion geometry is similar to those reported for related $[Ln(dipic)_3]^{3-}$ species,[10,11] with Sm–N 2.551–2.556(3), <> 2.554(3) Å; Sm–O 2.420–2.478(4), <> 2.45(2) Å.

When viewed down *a* and *b* [part (b) of Figure 1], the lattice of $[Co(\mathbf{1})][Sm(dipic)_3]\cdot 15\,H_2O$ appears to contain separate columns of the two metals, Co and Sm, running parallel to *a*. Two Sm columns nearly superimpose and may be considered as one column gently undulating about *a*. Along *c*, these columns are separated by double columns of Co atoms which can also be considered as in a markedly zig-zagged array of a single column down *a*. The alternations in both these "columns" are associated with the fact

Table 1. Crystal data, details of data collection and structure refinement.

Complex	$[Co(\mathbf{1})][Sm(dipic)_3]\cdot 15\,H_2O$	$[Co(\mathbf{2}H_2)]Cl_5\cdot 6\,H_2O$	$[Cu(\mathbf{3}H)][Cu(\mathbf{3}H_2)](ClO_4)_7\cdot 6\,H_2O$
Formula	$C_{39}H_{81}CoN_{11}O_{27}Sm$	$C_{22}H_{64}Cl_5CoN_8O_6$	$C_{54}H_{135}Cl_7Cu_2N_{16}O_{34}$
M	1345.4	773.0	1928.0
Crystal system	orthorhombic	monoclinic	triclinic
Space group	$Pca2_1$	C2/*m*	*P*-1
a [Å]	18.890(3)	14.0970(7)	8.664(2)
b [Å]	10.439(2)	24.911(1)	8.727(2)
c [Å]	28.014(5)	12.1088(6)	32.942(7)
α [°]			93.318(4)
β [°]		116.495(1)	93.178(4)
γ [°]			119.555(4)
V [Å^3]	5524	3777	2153
D_c [g cm^{-3}]	1.61_7	1.35_9	1.48_6
Z	4	4	2
Size [mm]	0.50 × 0.45 × 0.40	0.32 × 0.18 × 0.14	0.50 × 0.28 × 0.12
μ_{Mo} [cm^{-1}]	14.5	8.5	8.0
Transmission (min./max.)	0.77	0.82	0.63
$2\theta_{max}$ [°]	75	75	50
N_t	114531	39324	20637
N (R_{int})	14810 (0.059)	10071 (0.022)	7540 (0.063)
N_o	11393	8184	5916
R	0.037	0.044	0.10
R_w (n_w)	0.048 (2)	0.069 (2)	0.13 (0.4)

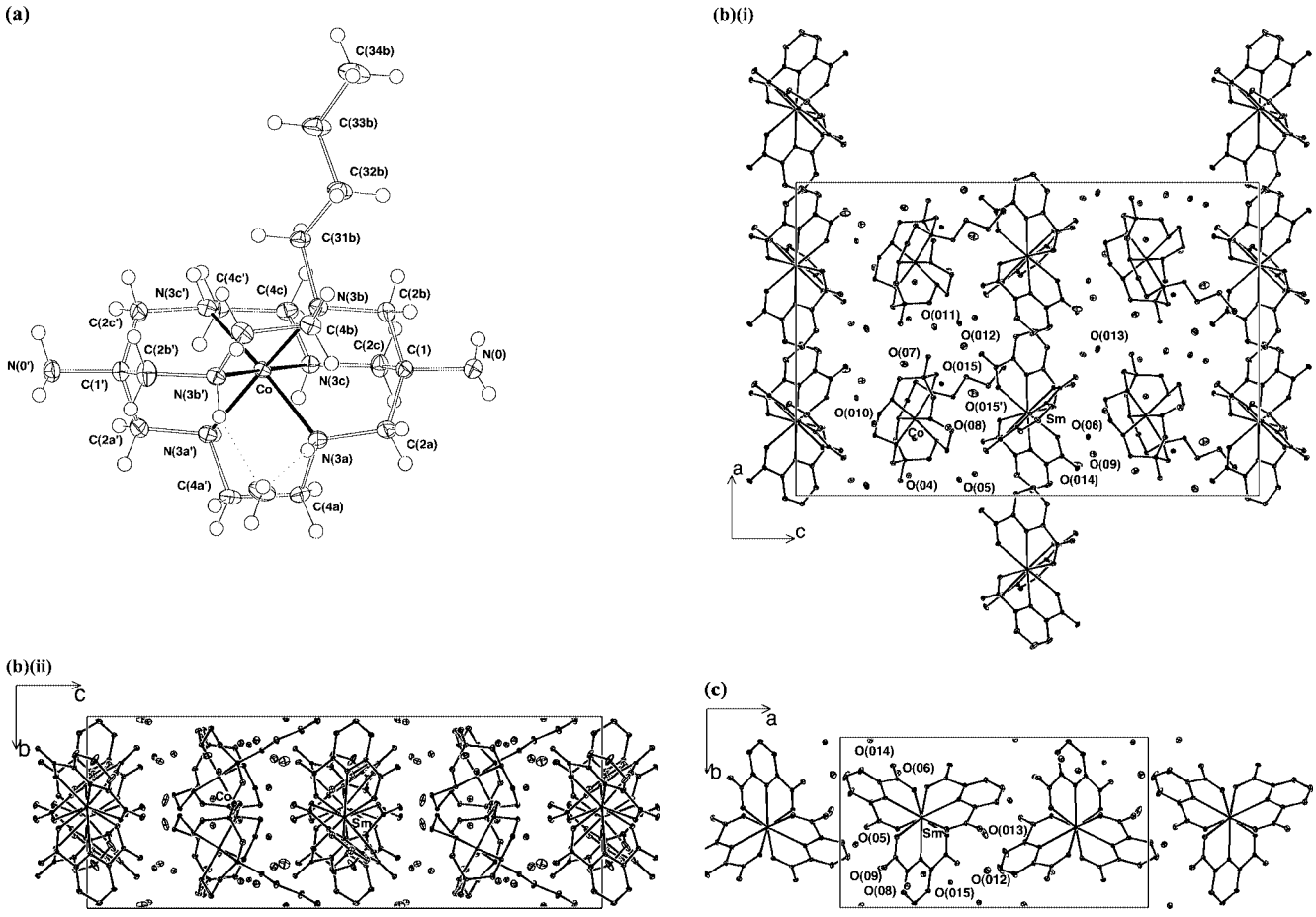


Figure 1. (a) Projection of the $[Co(\mathbf{1})]^{3+}$ cation, showing the lel_3 ligand conformation and the "chelated" associated water molecule. (b) Unit cell contents of $[Co(\mathbf{1})][Sm(dipic)_3]\cdot 15\,H_2O$ projected down (i) *b*, (ii) *a*. (c) The layer of anions about $z = 0.5$.

that the metals are the centres of chiral entities (cationic for Co, anionic for Sm), such that the undulation/zig-zag can be described as ···Δ–Λ–Δ–Λ–Δ–Λ–Δ–Λ··· in both cases. Columnar arrays, more often homochiral {as in the closely-related $[Co(sar)][Eu(dipic)_3]\cdot 13\,H_2O$;[10] and see below} than heterochiral as here, are very commonly seen in structures of $[Ln(dipic)_3]^{3-}$ derivatives,[10,11] interactions (stacking and edge-to-face[12]) of the heteroaromatic ligands, as seen in many similar helical complexes,[13] possibly being one factor favouring their presence. Given its persistence, it is perhaps appropriate to regard this array as a kind of "molecular register" which, in the present case, determines the associated array of chiral cations. Along *c*, the necessarily polar cation array is such that the butyl substituents of both Δ and Λ species are oriented to the one side of each zig-zag column, creating two different "sides" to the undulating Sm complex columns (perpendicular to the undulation plane). For a given Sm centre, its nearest Co neighbour [at 7.027(1) Å] to one side is from a complex unit of the same chirality for which the butyl substituent approaches the dipicolinate ligand atoms on the Sm. To the other side, a slightly more remote Co [at 7.392(1) Å] is the centre of a complex cation of the opposite chirality. Interactions here occur through a pair of H-bonded water molecules which is H-bonded to a cation NH and an uncoordinated carboxylate-*O* of the anion.

A possibly simpler analysis of the lattice is provided in the view down *b*, from which it appears that the two metals can also be considered to form true columns parallel to *b*. The complexes in these columns are all of the same chirality, species contacts within the columns all seemingly the result of H bonding involving lattice water, so that the (homochiral) Sm···Sm distance, *b* [10.439(2) Å], is longer than the (heterochiral) separation, *a*/2 [= 18.890(2)/2 Å], associated with aromatic/aromatic interactions in the undulating column parallel to *a*. Homo- and hetero-chiral Co···Co separations, *b* and 10.235(2) Å, respectively, differ much less, perhaps reflecting the fact that H bonding (via water) is the common cause of contact.

A feature lacking in the lattice of $[Co(\mathbf{1})][Sm(dipic)_3]\cdot 15\,H_2O$ is any sign of close contact between the butyl substituents of the cations. This is consistent with the lack of any evidence for surfactant properties of $[Co(\mathbf{1})]^{3+}$ or the related dibutylated complex $[Co(\mathbf{2})]^{3+}$ in aqueous solution, and with the expectation that a butyl chain would be too short to induce such properties in a cage complex.[4] Though the difficulty of obtaining adequate crystals means that relatively limited structural data are available for true

Table 2. Hydrogen-bonding in [Co(**1**)][Sm(dipic)$_3$]·15 H_2O(N,O···H est.).

Atoms	Distance [Å]	Atoms	Distance [Å]
(a) To the terminal NH_2 groups			
O(04),H(04B)···N(0^{i})	2.052(6), 2.1	O(07),H(07A)···N(0′^{ii})	2.808(6), 2.1
(b) From the other (NH) amine groups			
N(0),H(0A)···O(07)	3.053(6), 2.3	N(0′),H(0A′)···O(02^{iii})	3.143(6), 2.3
N(0),H(0B)···O(24)	3.194(6), 2.4	N(0′),H(0B′)···O(011^{iv})	3.017(6), 2.1
N(3a),H(3a)···O(06^{iii})	2.879(5), 2.0	N(3a′),H(3a′)···O(04)	2.919(5), 2.1
		N(3b′),H(3b′)···O(06^{iii})	2.922(5), 2.1
N(3c),H(3c)···O(01)	2.902(5), 2.1	N(3c′),H(3c′)···O(14)	2.925(5), 2.4
(c) To the (uncoordinated) anion oxygen atoms			
O(09),H(09A)···O(12)	2.832(6), 2.1	O(03),H(03A)···O(14)	2.717(6), 2.0
O(013),H(013A)···O(12)	2.742(7), 2.2		
O(02),H(02A)···O(22)	2.753(5), 2.0	O(05^{ii}),H(05B^{ii})···O(24)	2.863(6), 2.0
		O(012),H(012A)···O(24)	2.801(7), 2.1
O(02^{v}),H(02B^{v})···O(32)	2.832(5), 2.0	O(03^{v}),H(03B^{v})···O(34)	2.815(6), 1.9
		O(05),H(05A)···O(34)	2.760(6), 2.1
		O(08),H(08B)···O(34)	2.915(6), 2.1
[O(06),H(06A)···O(21)	2.904(5), 2.2]		
(d) Between water molecules			
O(01),H(01A)···O(08)	2.738(6), 1.8	O(04),H(04A)···O(013^{iii})	2.632(6), 2.0
O(01),H(01B)···O(04)	2.703(5), 2.0	O(06),H(06B)···O(014)	2.708(7), 2.0
O(07),H(07B)···O(09^{iii})	2.775(6), 1.9	O(08),H(08A)···O(015)	2.692(8), 2.0
O(09),H(09B)···O(07^{vi})	2.775(6), 2.2	O(08),H(08A)···O(015′)	2.80(2), 2.0
O(010),H(010A)···O(09^{iii})	2.750(6), 2.7	O(011),H(011A)···O(05^{ii})	2.864(6), 2.0
O(010),H(010B)···O(01)	2.777(6), 2.1	O(011),H(011B)···O(03^{vii})	2.843(6), 2.1
O(014),H(014A)···O(09^{viii})	2.837(7), 2.1	O(012),H(012B)···O(015)	2.733(8), 1.9
O(014),H(014B)···O(02^{iv})	2.808(7), 2.7	O(013),H(013B)···O(04^{vi})	2.632(6), 2.7
O(014),H(014B)···O(06)	2.708(7), 2.7		

Transformations of the asymmetric unit: i: $x - {}^1/_2$, $1 - y$, z. ii : $x + {}^1/_2$, $1 - y$, z. iii: ${}^1/_2 - x$, $\bar{y}$, $z - {}^1/_2$. iv: $x - {}^1/_2$, $\bar{y}$, z. v: x, $1 + y$, z. vi: ${}^1/_2 - x$, y, ${}^1/_2 + z$. vii: ${}^1/_2 + x$, y, z. viii: x, $y - 1$, z.

surfactant complexes,[1,14] these do show prominent aggregation of the lipophilic moieties in the lattice. It is somewhat surprising, therefore, that the crystal structure of [Co(**2**H_2)]Cl_5·6H_2O does provide evidence for association of the butyl substituents. In this complex, one half of the formula unit comprises the asymmetric unit of the structure. The cation present in this compound [part (a) of Figure 2], disposed with the central Co on a crystallographic *2*-axis, adopts the relatively uncommon but still quite familiar *ob*$_3$ conformation,[3b–3f] but has properties otherwise completely unexceptional for a Co^{III} complex of a cage amine. The *ob*$_3$ conformation, as in other cases, appears to result from the abundance of H-bond acceptors within the lattice, this leading in particular to the absence of any bridging interactions involving the secondary NH entities of a given complex unit. Such bridging "chelation" of chloride anions by *lel*$_3$ cations formally results, in several instances,[3] in the presence of D_3-symmetric {Co(L)Cl_3} ion quartets, but here the coordinated NH centres of the cation separately hydrogen-bond to chloride ions [N,H(3a)···Cl(1) 3.149(2), 2.3; N,H(3b)···Cl(1) (${}^1/_2 + x$, ${}^1/_2 - y$, z) 3.202(1), 2.3$_5$; N,H(3c)···Cl(2) 3.144(1), 2.3 Å], while the terminal ammonio groups contact both Cl [N(0),H(0a)···Cl(3) 3.058(2), 2.2 Å] and water molecule oxygen [N(0),H(0b)···O(01) 2.791(2), 1.9 Å], displacement amplitudes of all non-hydrogen atoms in this cation/anion/solvent system being small ($U_{eq} \leq 0.031$ Å^2), the cation "tail" excepted. Amplitudes in the latter increase markedly towards its periphery [parts (b) and (c) in Figures 2] and are high, as are those of the remaining anion, Cl(4), (which, located on a "special position" of the lattice, may be susceptible to unresolved disorder) and the remaining water molecules, many of these modelled as disordered fragments and forming a much less well-defined segment of the array. Cl(1–3), in fact, all have bridging functions, Cl(1) bridging a pair of cations as indicated above, while Cl(2,3), both located on symmetry elements – a mirror plane and a *2*-axis, respectively – link the symmetry images, via NH···Cl interactions. Other close contacts to the chlorides are sparse (Table 3), involving for Cl(1,3) a further pair of water molecules (or fragments), symmetry-related for Cl(3).

The lattice of [Co(**2**H_2)]Cl_5·6H_2O can be regarded as built up from alternating sheets parallel to the [–2,0,1] plane, one sheet containing complex cations and some chloride anions, the other water molecules and chloride ions. Viewed down *b*, the sheets are seen edge-on, with the cations extended in the *ac* plane. Within the cation sheets, there are regions where all polar entities, including chloride, are excluded and the butyl chains aggregate. These "greasespot" regions (Figure 3) are defined by laterally compressed hexagonal clusters of essentially coplanar cation units, which alternate in chirality Δ–Λ–Δ–Λ–Δ–Λ around the hexagon. The arrays in adjacent cation planes are displaced such that each greasespot contacts carbon atoms of ethylene links of the complex cations, two sets thereof in each plane above and below, creating thus a "greaseball". Closest C···C contacts within this greaseball range from 3.7–4.3 Å, very similar to analogous contacts in structures of true surfactants,[1] with the shortest present contact being 3.743(4) Å between the 3-carbon atoms of adjacent butyl chains. Though the greaseball structure may be a conse-

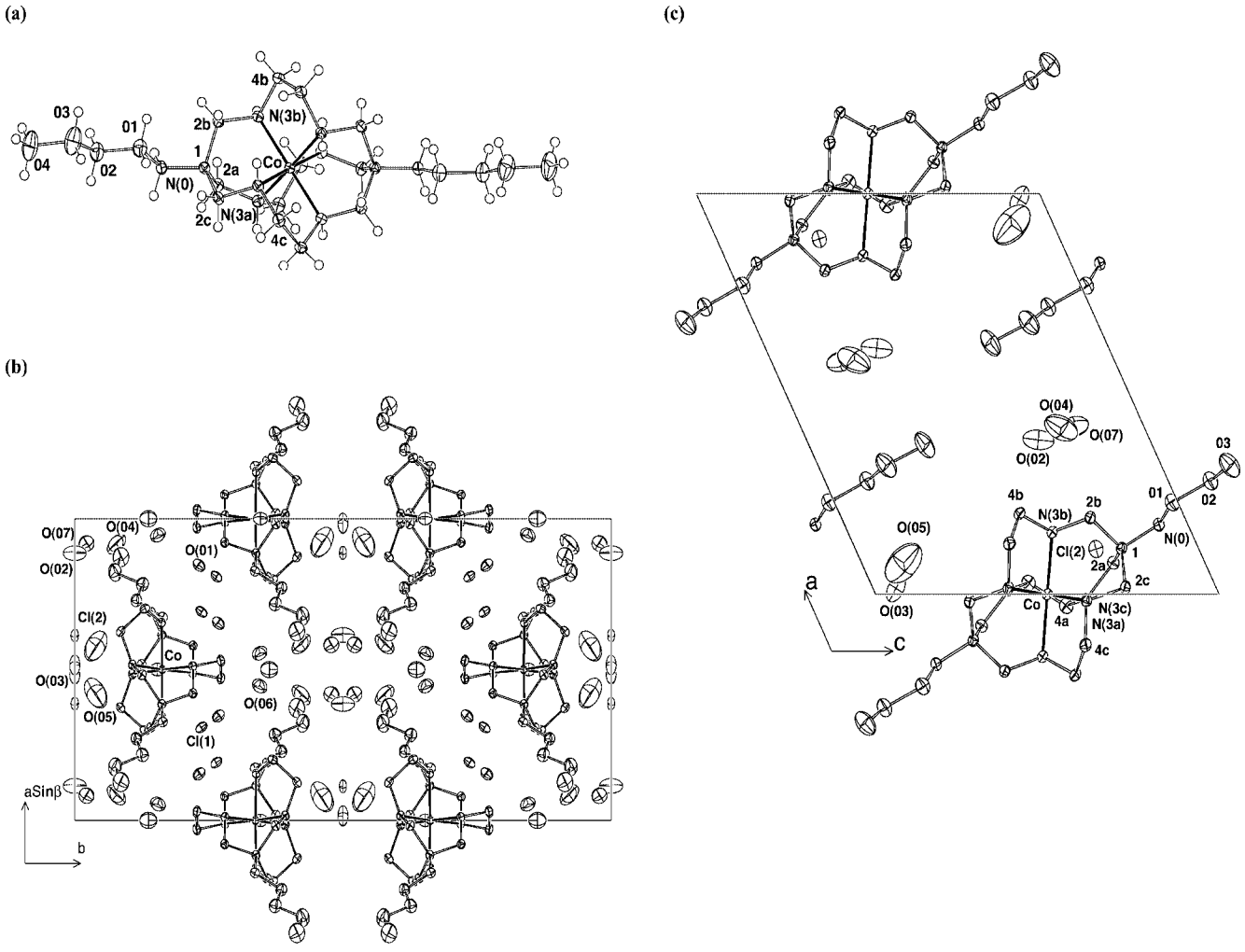


Figure 2. (a) The $[Co(\mathbf{2}H_2)]^{5+}$ cation, which lies disposed on a crystallographic *2*-axis passing through the mid-point of the ligand string "a", showing the ob_3 ligand conformation. (b) Unit cell contents of $[Co(\mathbf{2}H_2)]Cl_5{\cdot}6H_2O$, projected down *c*. (c) A slice of the cell, about $y = 0.5$, projected down *b*.

Table 3. Hydrogen-bonding in $[Co(\mathbf{2})]Cl_5{\cdot}6H_2O$.

Atoms	Distance [Å]	Atoms	Distance [Å]
(a) From the terminal nBuNH$_2^+$ group			
N(0),H(0A)···Cl(3)	3.058(2), 2.2	N(0),H(0B)···O(01)	2.791(2), 1.9
(b) From the other (NH) amino groups			
N(3a),H(3a)···Cl(1)	3.149(2), 2.3	N(3b),H(3b)···Cl(1^{i})	3.202(1), 2.4
N(3c),H(3c)···Cl(2)	3.144(1), 2.3		
(c) Other components of the chloride environments (Cl···O < 3.4 Å)			
Cl(1)···O(01^{ii})	3.223(2)	Cl(3)···O(05)	3.175(9)
Cl(1)···O(06)	3.230(8)		
Transformations of the asymmetric unit: i, ii $x \pm {}^1/_2$, ${}^1/_2 - y$, z.			

quence of the multitudinous interactions occurring in the solid state, it is unlike that of a conventional micelle and may indicate that rather particular forms of aggregation are possible for metal complex surfactants in solution.

Some further particularities of complex ions as surfactant headgroups are apparent in the crystal structure of the Cu^{II} complex of the ligand **3**, a complex which, unlike those of **1** and **2**, displays typical surfactant properties, readily forming aqueous emulsions and foams. The synthesis of **3**,

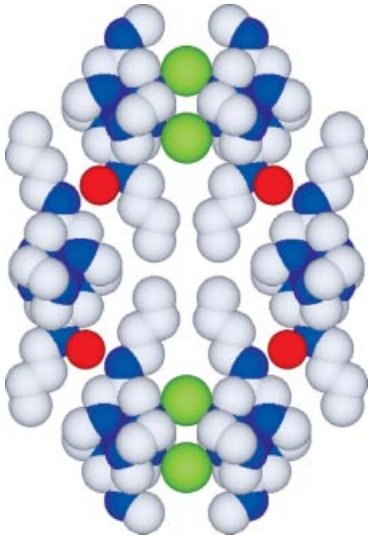


Figure 3. A simplified, space-filling representation of the "grease-spot region" of the lattice of $[Co(\mathbf{2}H_2)]Cl_5{\cdot}6H_2O$, showing the segregation of polar and apolar entities. Atom code: C = white; Cl = green; Co = dark blue; N = blue; O = red.

based on the use of Mg^{II} to protect the secondary amino group nitrogen atoms of the reactant, illustrates a problem presumably due to association in the preparative medium. Thus, dialkylation predominates even in media where the reactant ratio is 1:1, a result which may be explicable if initially-formed mono-alkylated complex associates with unreacted aldehyde and so favours its attack on the other primary amino group of the same complex entity. (Note that the dialkylated product is the symmetrical 1,8 isomer.) The complex as crystallised, modelled as $[Cu(\mathbf{3}H)][Cu(\mathbf{3}H_2)](ClO_4)_7{\cdot}6H_2O$, contains formally a 1:1 mixture of diprotonated and monoprotonated cations [part (a) of Figure 4], a circumstance encountered in various unfunctionalised cage complexes[15] and, presumably, another indication of the important influence of H bonding on the form of the lattices, since the "additional" proton is taken to be shared between pairs of monoprotonated complex cations. The lattice, as viewed down *c*, for example, [part (b) in Figure 4] shows multiple layering, one aspect of which is the double layer of cage units formed by the (amino) head-to-head H-bonded array of complex cations. Consistent with related known structures[3c,3f,15,16] and the susceptibility of Cu^{II} to Jahn–Teller distortions, the CuN_6 environment (Table 4) in the cage is not only irregular, but disordered with the chiral, *lel*$_3$ complex cations distributed equally as Δ and Λ species over the available sites. The cores of the cations are disposed about copper atoms lying at (approximately) $z = {}^1/_3, {}^2/_3$, forming layers encompassing perchlorates 1,3 which lie close and equidistant to either side [*z*(Cl(1,3)) 0.27, 0.40], the "inwardly" directed oxygen atoms O(11–13;31–33) interacting directly with the cation or a translation image within the layer by way of hydrogen bonds with the core NH centres, and in such a way that the interaction is with one or other of the disordered components. Thus, O(11) contacts H(3a,3cB), O(12) contacts H(3b,3aB) ($x - 1$, $y - 1$, z) and O(13) contacts H(3c,2bB) (where "B" atoms belong to the Λ form of the cation, otherwise Δ) among the unprimed $(NH)_{3(2/2)}$ triad, while O(31) contacts H(3a′,3b′B) ($x - 1$, $y - 1$, z), O(32) H(3b′,3c′B) ($x - 1$, $y - 1$, z), and O(33) H(3c′,3a′B) among the primed, all at distances of 2.1–2.4 Å. No disorder is resolvable in these two perchlorates, U_{eq} among the hydrogen-bonded oxygens all ≤ 0.08 Å^2, excepting O(31) (0.13). Displacement amplitudes on perchlorate 2 are also ≤ 0.1 Å^2, presumably in consequence of its proximity to water molecules 1,2 [O(21)···O(02); O(23)···O(01) both 2.96(1) Å, hydrogen atoms not located] but anion **4** is modelled with half-occupancy, presumed disordered in concert with O(03,04) (water) about $z = 0.5$, this plane also imaging the $NH_2{\cdots}H{\cdots}H_2N$ cation components.

Between the polar layers just described, the tridecyl chains aggregate to form a lipophilic layer about 13 Å thick, the extended, *transoid* chains being bent away from the *pseudo-C$_3$* axis of the head group complexes so as to lie, with their neighbours down *a*, in sheets which confront similar, parallel sheets arising from the next layer of complex units. As in some[14,17] but not all[1] related complex structures, there is no interdigitation of the chains, and closest

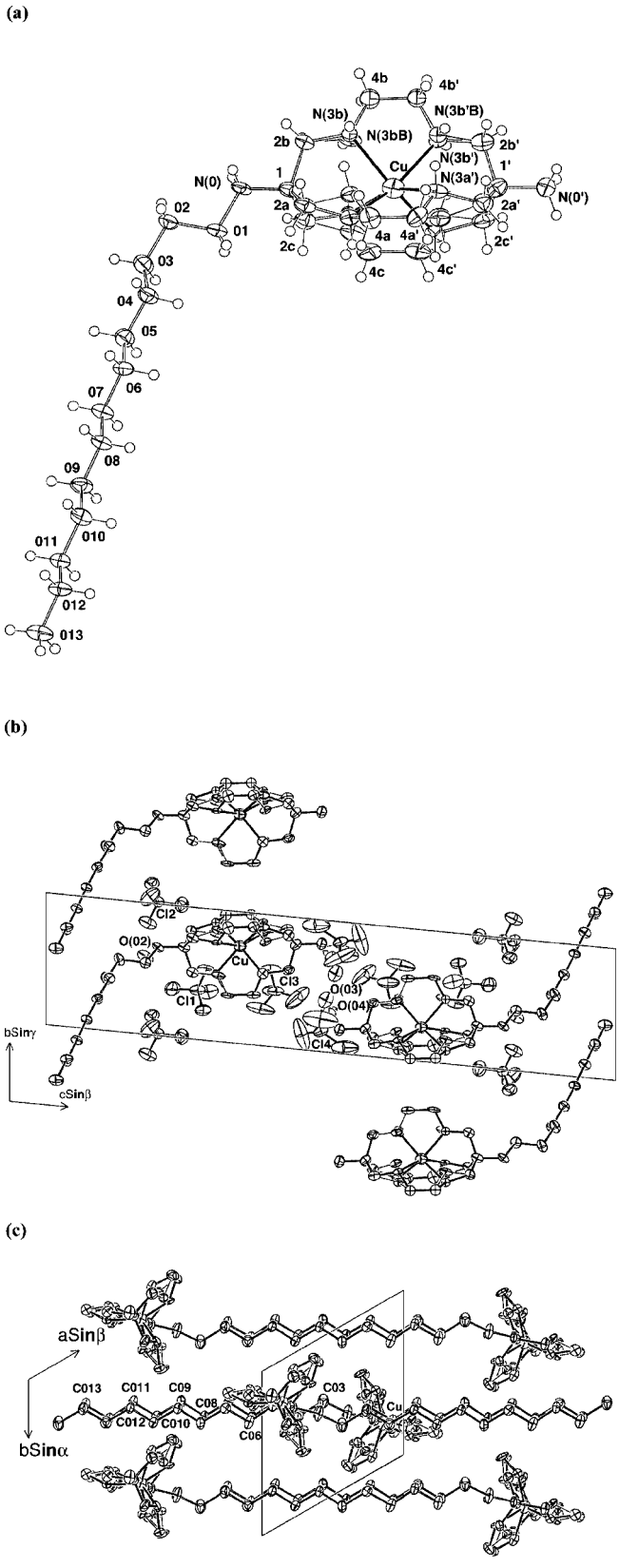


Figure 4. (a) The [Cu(**3**)] species, shown as the tetrapositive cation. (b) Unit cell contents of $[Cu(\mathbf{3})]_2H(ClO_4)_7{\cdot}6H_2O$, projected down *a*. (c) A slice of the cell about $y = 0$, projected down *c*.

Table 4. Selected bond lengths and bond angles for [Cu(**3**H)][Cu(**3**H_2)]$(ClO_4)_7$·6H_2O.

Atoms	Bond lengths [Å]	Atoms	Bond angles [°]
Cu–N(3a)	2.17(1)	N(3a)–Cu–N(3a′)	79.4(5)
Cu–N(3aB)	2.16(1)	N(3aB)–Cu–N(3a′B)	80.8(5)
Cu–N(3a′)	2.24(2)	N(3b)–Cu–N(3b′)	83.2(4)
Cu–N(3a′B)	2.27(1)	N(3bB)–Cu–N(3b′B)	82.3(4)
Cu–N(3b)	2.16(1)	N(3c)–Cu–N(3c′)	82.9(4)
Cu–N(3bB)	2.15(1)	N(3cB)–Cu–N(3c′B)	80.7(5)
Cu–N(3b′)	2.15(1)		
Cu–N(3b′B)	2.151(9)		
Cu–N(3c)	2.21(1)		
Cu–N(3cB)	2.10(1)		
Cu–N(3c′)	2.07(1)		
Cu–N(3c′B)	2.18(1)		

C···C within and between chain layers lie in the range ca. 4.1–4.3 Å, presumably indicative of extensive but rather weak dispersion interactions (as found in other systems, interdigitated or not). For a given H-bonded pair of complex cations bridging a layer the tails are oppositely oriented, so as to make a centrosymmetric entity.

Conclusions

The high aqueous solution solubility of simple salts of [Co(**1**)]$^{3+}$ is presumably indicative of a low lattice energy for the solids, since substitution of N(butyl) for NH in the cation would, again presumably, not enhance its hydration energy. A low lattice energy could result from the particular regioisomeric form being such as to inhibit association between butyl entities and other components present (e.g. water, chloride) not being capable of significant interactions with butyl, so that the apparent CH_3-π and CH···O interactions of the butyl group observed in [Co(**1**)][Sm(dipic)$_3$]·15H_2O may be important determinants of its insolubility. Although yet to be quantified, such effects are of potential interest for the systematic construction of crystalline solids, in particular for the use of a "molecular register" defined by columnar arrays of $\{[Ln(dipic)_3]^{3-}\}_n$.[18] The structure of [Co(**2**H_2)]Cl_5·6H_2O shows that a butyl substituent upon a cage complex is not too short to be involved in lipophilic aggregation processes and indicates that there may be novel ways for such "reverse bola-amphiphile" complexes to aggregate in solution, possibly more readily exploited in systems with alkyl-functionalised chelate arms. Association of relatively water-soluble cage complexes in solution may be a more useful means of creating a multi-electron redox catalyst than that of linking cage units through kinetically inert scaffolds.[19] The structure of the true surfactant species [Cu(**3**H)][Cu(**3**H_2)]$(ClO_4)_7$·6H_2O shows both that introduction of a sufficiently long alkyl-chain substituent gives rise to solid state aggregation of a familiar form, and that, when considered with the other structures presently described, a cage complex head group is not a simple cationic centre and may be involved in a variety of interactions which could provide mechanisms for the control of solution aggregation processes.

Experimental Section

Instrumentation and Procedures: ^1H and ^{13}C NMR spectra were recorded with a Bruker ARX 500 instrument (^1H at 500.13 MHz, ^{13}C at 75.5 MHz) using solvent resonances [CH_3OH (^1H: 3.34 ppm, ^{13}C: 49.50 ppm); $(CH_3)_2CO$ (^1H: 2.22 ppm, ^{13}C: 215.94, 30.89)] as internal references. Tridecanal was freed of contaminant acid by washing its dichloromethane solution with aqueous $NaHCO_3$. Cation exchange chromatography was conducted under gravity flow in glass columns using either Na^+-form SP Sephadex C25 or H^+-form Dowex 50Wx2 resins.

Synthesis: 1,8-Diamino-3-butylsarcophagine (**1**), and its Co^{III} Complex, [Co(1)][Sm(dipic)$_3$]·15H_2O (dipic = pyridine-2,6-dicarboxylate, dipicolinate). $(NH_2)_2$sar[7] (0.53 g) and large excesses of butanal (3.0 mL) and $NaBH_3CN$ (0.25 g) were dissolved in absolute ethanol (50 mL) and the mixture heated at reflux under Ar for 24 h. The solvent was then removed under reduced pressure and the oily brown residue acidified with concentrated HCl. The resulting mixture of a clear brown solution and a small amount of brown oil was again taken to dryness and *cis*-[$CoCl_2(OH_2)_4$]·2H_2O (0.44 g) in water (20 mL) added, followed by sufficient ethanol to give a homogeneous solution. After aerating and heating (steam bath) the mixture for 30 min, the deep pink-red supernatant solution was decanted from some residual brown oil, diluted with water (500 mL) and passed through a column of Na^+ form SP Sephadex C25 cation exchange resin. The absorbed complexes were then eluted with 0.1 mol L^{-1} Na_2HPO_4. A small amount of Co^{II} was rapidly eluted first, followed by a trace amount of a pink species which was not further characterised beyond recording its ^1H NMR spectrum, which indicated that it did contain (probably mono-) alkylated cage ligand. The bulk of the product was in the third eluted fraction, from which the complex was recovered as its chloride by H^+ form Dowex 50Wx2/HCl chromatography. This material proved to be extremely soluble in water and no efficient way of precipitating the cation from solution was found other than to crystallise it as its $[Sm(dipic)_3]^{3-}$ derivative. Thus, the residue obtained by evaporating a 3 mol L^{-1} HCl solution of the complex to dryness was dissolved in water and an excess of $Na_3[Sm(dipic)_3]$[10] added. The precipitate which formed immediately (due to acid decomposition of the Sm complex), was dissolved by the dropwise addition of aqueous NH_3 (2 mol L^{-1}) and the deep pink solution formed was allowed stand overnight as small, pink tablet-like crystals, as used for the X-ray work, deposited. Sample drying prior to analysis appeared to cause some loss of water relative to the composition found from the crystal structure determination: [Co(1)][Sm(dipic)$_3$]·8H_2O = $C_{39}H_{67}CoN_{11}O_{20}Sm$ (1219.3): calcd. C 38.42, H 5.54, N 12.64; found C 38.3, H 5.4, N 12.4. NMR spectra were recorded on the residue obtained by evaporating a solution of the chloride salt after it had been re-evaporated (twice) from D_2O. ^1H NMR (D_2O): δ = 0.96 (t, 3 H), 1.42 (m, 2 H), 1.75–2.00 (m, 2 H), 2.85–3.70 (m, 26 H) ppm. $^{13}C\{^1H\}$ NMR (D_2O): δ = 13.66, 20.37, 24.82, 51.22, 51.51, 52.46, 53.02, 53.29, 53.83, 54.09 (br. s, possibly two unresolved resonances), 54.93, 55.07, 55.68, 56.60, 60.27, 61.22, 61.38 ppm.

1,8-Di(butylamino)sarcophagine (2) and its Co^{III} Complex [Co(2H_2)]Cl_5·*n*H_2O: [Co{$(NH_2)_2$sar}]$(OAc)_3$·6.5H_2O[3b] (626 mg), a large excess of butanal (20 mL) and an excess of $NaBH_3CN$ (170 mg) were dissolved in absolute EtOH (50 mL) and the reaction mixture heated at reflux under Ar for 24 h. The mixture was dried, treated with concentrated HCl (ca. 50 mL), and then dried again before adding water (ca. 100 mL). The brown mixture was then extracted with CH_2Cl_2 (4 × 150 mL), and after discarding the organic extracts, the aqueous layer was applied to a column of Na^+ SP

Sephadex cation exchange resin. Elution with 0.1 M Na_2HPO_4 solution removed a very broad orange band, in which dialkylated product appeared to lead monalkylated but with imperfect separation, so that the leading third of the band was taken to obtain an eluate of predominantly the dialkylated species. Purification by absorption on H^+ Dowex 50Wx2 resin, elution with 5 M HCl, evaporation to dryness and crystallisation (twice) from the minimum quantity of hot water by addition of EtOH, gave a fine yellow powder of $[Co(\mathbf{2}H_2)]Cl_5{\cdot}nH_2O$ (50 mg; the total yield of mixed species was 270 mg) in a form which, after vacuum desiccation, appeared to be a trihydrate of the fully protonated complex. $C_{22}H_{52}Cl_5CoN_8{\cdot}3H_2O$ (719.0): calcd. C 36.75, H 8.13, N 15.59; found C 37.1 , H 7.1, N 15.5. ^{1}H NMR (D_2O): δ = 0.87 (t, 6 H), 1.35 (m, 2 H), 1.53 (m, 2 H), 2.85–3.20 (m, 16 H), 3.40–3.75 (m, 16 H) ppm. $^{13}C\{^1H\}$ NMR (D_2O): δ = 15.04 (CH_3), 21.43 (CH_2), 30.46 (CH_2), 45.05 (CH_2), 52.18 (CH_2), 55.52 (CH_2), 62.65 (4 C) ppm. Crystals for the structure determination were obtained by vapour diffusion of ethanol into a concentrated solution of the complex in 1 mol L^{-1} HCl, the structure solution being consistent with the tentative formulation of the crystalline material as an ethanol sesquisolvate trihydrate, $[Co(\mathbf{2}H_2)]Cl_5{\cdot}3H_2O{\cdot}1.5CH_3CH_2OH$. An inadvertent discovery appreciated only after completion of further structural work was that it would appear possible to separate the mono- and dialkylated complexes by fractional crystallisation of their chlorides. Thus, in an attempt to obtain crystals of the monoalkylated complex, vapour diffusion of ethanol into an aqueous solution of the residue from the trailing third of the SP Sephadex/Na_2HPO_4 chromatography band (indicated by ^{1}H NMR to be at least 90% monoalkylated complex) gave crystals subsequently shown, by means of the structure recorded herein, to be essentially those of the dialkylated species as its pentachloride hexahydrate.

Tridecylation of Diaminosarcophagine to give 1-Alkylated and 1,8-Dialkylated Derivatives 3 and 4, respectively: $(NH_2)_2$sar (1.02 g), $Mg(OAc)_2$ (1.89 g), tridecanal (0.990 mL) and $NaBH_3CN$ (215 mg) were dissolved in absolute EtOH (50 mL) and the reaction mixture heated at reflux for 24 h under argon. The white precipitate of magnesium acetate hydroxide was filtered off, the solution dried, and the oily white residue treated with concentrated HCl (ca. 10 mL). The mixture was again dried, and the white solid extracted with $CHCl_3$ (3 × 50 mL; discarded) and 1 mol L^{-1} HCl (3 × 10 mL), leaving a residue of dialkylated ligand hydrochloride. This was recrystallised from boiling methanol to give a white, waxy solid (762 mg). $(C_{13}H_{27}NH)_2$sar·4 HCl·3 H_2O = $[\mathbf{4}H_4]Cl_4{\cdot}3H_2O$ = $C_{40}H_{96}Cl_4N_8O_3$ (879.1): calcd. C54.65, H 11.01, Cl 16.13, N12.75; found 54.7, H 9.3, Cl 16.1, N 12.7. ^{1}H NMR (CD_3OD): δ = 0.90 (t, 6 H), 1.29 (m, br., 36 H), 1.39 (m, 4 H), 1.66 (m, 4 H), 2.75–3.50 (m, 28 H), 4.50 (m., br., NH) ppm. $^{13}C\{^1H\}$ NMR (CD_3OD): δ = 14.44, 23.73, 27.55, 28.00, 30.20, 30.47, 30.50, 30.62, 30.74, 30.77, 33.06, 42.88, 49.88, 53.19, 58.2 ppm. To isolate the pure monoalkylated ligand (as its Cu^{II} complex), the 1 mol L^{-1} HCl extracts of the bulk product were dried, the residue dissolved in water (ca. 30 mL) and excess $Cu(OAc)_2$ added. Concentrated ammonia (ca. 1 mL) was added and the blue solution was heated to boiling, producing a green precipitate of copper acetate hydroxide. After filtration, concentrated $HClO_4$ (ca. 1 mL) was added to the filtrate, producing a blue precipitate of the monoalkylated ligand complex. Yield: 144 mg. [Cu{(1-tridecylammonio)(8-ammonio)sar}][Cu{(1-tridecylammonio)(8-amino)sar}]$(ClO_4)_7{\cdot}6H_2O$ = $[Cu(\mathbf{3}H)][Cu(\mathbf{3}H_2)](ClO_4)_7{\cdot}6H_2O$ = $C_{54}H_{135}Cl_7Cu_2N_{16}O_{34}$ (1928.0): calcd. 33.64, H 7.06, Cl 12.87, N 11.62; found C 34.1, H 6.9, Cl, 13.7, N 11.6. ESMS: *m*/*z* (658.7) = $[Cu(\mathbf{3})(ClO_4)]^+$; *m*/*z* (320.8) = $[Cu(\mathbf{3})(CH_3CN)_2]^{2+}$; *m*/*z* (300.4) = $[Cu(\mathbf{3})(CH_3CN)]^{2+}$. The filtrate from the bulk of the rather insoluble Cu^{II} complex was allowed to evaporate slowly, producing blue crystals as used for the X-ray work. In order to obtain NMR spectra for the (coordinated) ligand, the complex was dissolved in hot water and converted into the zinc complex by addition of Zn powder. After heating and stirring the mixture for 15 minutes on the steam bath, the solid was filtered off and the clear filtrate was dried. The white solid obtained was only slightly soluble in D_2O, so the solution was acidified with a few drops of concentrated DCl, causing the solid to dissolve rapidly. ^{1}H NMR (D_2O/DCl): δ = 0.82 (t, 3 H), 1.25 (br. 20 H), 1.67 (br., 2 H), 2.50–3.70 (m, br. 26 H), 4.28 (br., ≈ 5 H, NH) ppm. $^{13}C\{^1H\}$ NMR (D_2O): 14.36, 23.11, 26.90, 27.12, 29.70, 29.99, 30.04, 30.30, 30.32, 30.37, 30.43, 32.44, 42.55, 49.20, 51.70, 53.12, 54.81, 56.49 ppm. It again appears that two methylene-C signals may superimpose but the important aspect of this $^{13}C\{^1H\}$ NMR spectrum is the appearance of two distinct quaternary carbons at δ = 51.70 and 56.49.

Structure Determinations: Full spheres of "low"-temperature CCD area-detector diffractometer data were recorded (Bruker AXS instrument, ω-scans; monochromatic Mo-K_α radiation, λ = 0.7107$_3$ Å; *T* ca. 153 K) yielding $N_{t(otal)}$ reflections, merging to *N* unique (R_{int} cited) after "empirical"/multiscan absorption correction (proprietary software), N_o with $F > 4\sigma(F)$ considered "observed" and used in the full-matrix least-squares refinements, refining anisotropic displacement parameter forms for the non-hydrogen atoms, $(x, y, z, U_{iso})_H$ (where defined) constrained at estimates. Conventional residuals *R*, R_w on |*F*| are cited at convergence {weights: $[\sigma^2(F_o) + 10^{-3}n_w F_o^2]^{-1}$}. Neutral atom complex scattering factors were employed within the Xtal 3.7 program system.[20] Pertinent results are given below and in the Tables and Figures, the latter showing 50% probability amplitude displacement envelopes, hydrogen atoms having arbitrary radii of 0.1 Å. Individual diversities in procedure are noted below (variata).

Variata: $[Co(\mathbf{1})][Sm(dipic)_3]{\cdot}15H_2O$. The residue assigned as water molecule oxygen 15 was modelled as disordered over a pair of sites of equal occupancy separated by 2.17(2) Å, associated hydrogen atoms not being located. Hydrogen atoms were located in association with all other water molecule oxygen atoms. "Friedel" data being retained distinct, x_{abs} refined to 0.062(8).

Variata: $[Co(\mathbf{2}H_2)]Cl_5{\cdot}6H_2O$ (crystallised from a solution containing largely the monoalkylated complex). Difference map residues were refined as (disordered) water molecule oxygen atom fragments. The O(01) site was fully occupied, with associated hydrogen atoms resolvable; for the remainder, no credible hydrogen atom complement could be resolved, occupancies being set at 0.5 [O(02–05)] or 0.25 [O(06–07)], after trial refinement. The possibility that the lattice contained both mono- and dialkylated species was a cause of some concern, the site occupancies of the "tail" components having little impact on the refinement for a range between 85 and 100%, though being finally set at the latter. As noted above, material more confidently assigned as fully dialkylated was also studied, being formulated in the refinement as an ("isomorphous") mixed ethanol/water solvate. Displacement parameters on the solvent component were very high, however, and the overall precision of the determination appreciably lower, so that the "hexahydrate" determination was ultimately preferred and presented, there being otherwise no non-trivial differences in cation model and geometries.

Variata: $[Cu(\mathbf{3}H)][Cu(\mathbf{3}H_2)](ClO_4)_7{\cdot}6H_2O$. The coordinated nitrogen atoms were modelled as disordered over pairs of sites, occupancies set at 0.5 after trial refinement. Perchlorate **4** was modelled over two sets of sites, occupancies set at 0.5, as also for water molecule oxygen residues O(03,04). Hydrogen atoms were not located in association with water molecule oxygen atoms; the stoichiometry

of the compound is rationalised in terms of the proximity of the amine cap N(0′) lying in the vicinity of an inversion image, distance 2.86(1) Å, postulating the array as $–NH_2\cdots H\cdots H_2N–$ or derivative.

For the latter two compounds, attempted refinement in lower symmetry was (inherently) unfruitful, the bulk of the structure (including the major species) being generally well-behaved in refinement except as detailed.

CCDC-194249, -194250 and -261886 contain 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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