Functionalization of Cage Amines with Pendant Aromatic and Heteroaromatic Substituents

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Structural studies have confirmed that it is possible to exploit the relatively low nucleophilicity of the "external" amino substituents on the Co^{III} complex of 1,8-diaminosarcophagine ("sarcophagine" = sar = 3,6,10,13,16,19-hexaazabicyclo[6.6.6]-icosane) in acylation and alkylation reactions leading to a variety of functionalized cage amine complexes. With the appropriate choice of solvent, all these reactions can be conducted with high efficiency, and the new complexes display properties foreshadowing the application of cage systems in, for example, electroactive polymers.

Introduction

The presence of external functional groups on the metal complexes of the very readily obtained cage amine "diaminosarcophagine" {1,8-diamino-3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane = $(NH_2)_2$sar},[1] has led to the exploration of reactions of these groups to generate derivatives offering a variety of possible applications.[2] Our interests in this area include the incorporation of $[M\{(NH_2)_2sar\}]^{n+}$ (M = metal) units into amide polymers and the use of cage complexes as electrocatalysts, and so we have been particularly interested in acylation reactions of $[M\{(NH_2)_2sar\}]^{n+}$, as well as in processes whereby potentially electroactive groups can be introduced into such complexes. A known difficulty with reactions of amino groups attached to a cationic complex ion centre is that the nucleophilicity of these groups may be strongly reduced by the proximity of the positive site.[1−6] Carboxymethylation reactions of $[Cu\{(NH_2)_2sar\}]^{2+}$, for example, proceed considerably more rapidly than those of $[Co\{(NH_2)_2sar\}]^{3+}$, although such reaction studies have also demonstrated the utility of metal ion coordination in controlling the extent and position of substitution.[6] In the present work, we explore the use of cobalt(III) complexes of cage amines in reactions that may provide models for polymer formation processes or produce materials that may be converted into polymers by electrochemical means. Thus, we have examined reactions at the external amino groups leading to the formation of amide and imide derivatives or to the attachment of groups with electropolymerizable substituents (or with substituents readily functionalized for the purpose of subsequent polymerization).

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Results and Discussion

Structural studies based on X-ray crystallography were an essential component of the present work, not only for the purpose of defining the nature of the species isolated but also to characterize the mutual influences of the core cage complex and the peripheral substituents upon one another. Certain aspects of the solid-state structures are nonetheless familiar from earlier extensive studies of simpler cage amine complexes,[1−8] so that in general we comment only briefly on the cage stereochemistry and on the interactions of counteranions with coordinated NH atoms. For convenience, the Co(sarcophagine) units in all the structures determined (Figure 1) are shown in the Δ configuration, though in fact all syntheses were conducted with racemic reactants and all crystals proved to be racemic compounds. In cases where the cage substituents were acidic or basic in nature, the localization of protons was sometimes problematic and the models presented as "best" must be regarded as tentative. It is possible, of course, that the species considered to be immobilized within the solids are not those dominant in solution, though the forms of association seen in the solids, while predictable, are nonetheless useful in considering modes that may influence solution behaviour.

The rapid electron-transfer reactions and kinetic inertness in more than one oxidation state of many cage amine complexes makes the incorporation of these entities into insoluble polymers of possible interest, for example, in constructing novel rechargeable battery systems.[9] Polyamide formation from $[M\{(NH_2)_2sar\}]^{n+}$ units would seem an

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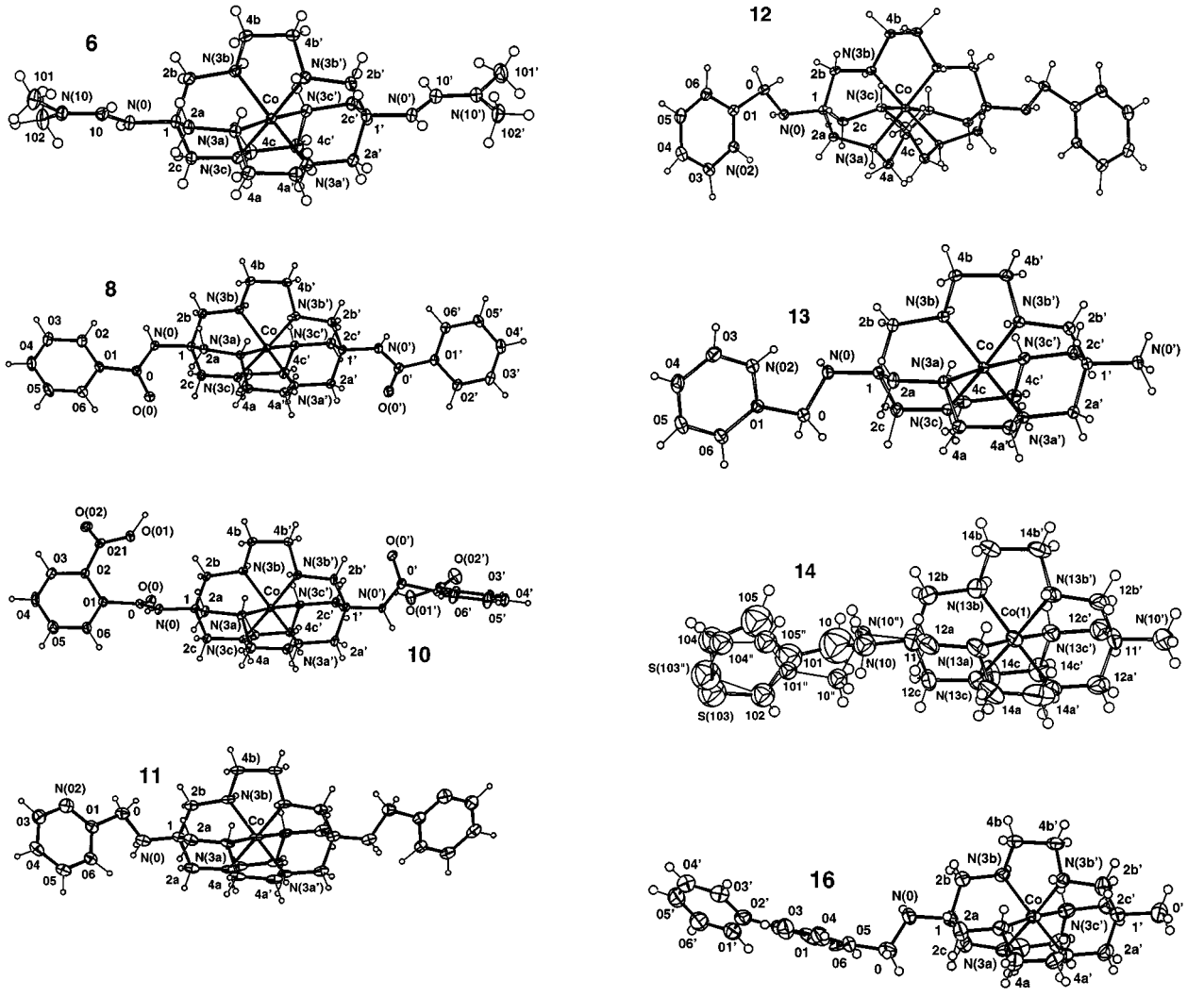

Figure 1. Projections of the cations of **6**, **8**, **10**, **11**, **12**, **13**, **14**, and **16** (cations 1 for **10**, **14**, **16**) in common orientation

obvious path to such polymers, but there is considerable flexibility in the way in which such a synthesis might be conducted. The Schotten−Baumann reaction[10] is one of the longest-known and simplest reactions for the formation of aromatic carboxamides from water-soluble amines, hence, given the fact that $[M\{(NH_2)_2sar\}]^{n+}$ complexes are typically highly water-soluble (as their chlorides, for example), this reaction was explored to see whether acceptable efficiency could be obtained even with an amine of low nucleophilicity. In the event, this was not the case, but a structure determination of the benzoylation product was of interest with regard to the possibility that the poor yields and relatively facile acid-catalysed hydrolysis might be consequences of unusual distortions of the amide resulting from its incorporation into the cage complex. The structure of hydrated $[Co\{sar(NHCOC_6H_5)_2\}]Cl_3$ (**8**, Figure 1), shows the cage Co(sar) unit to be very similar to that in the parent compound and many derivatives thereof,[1−8] with its *lel*$_3$ conformation seemingly once again stemming from the chelation of chloride counteranions by coordinated NH groups [Cl(1)···H(3a′,c) 2.49(2), 2.25(2); Cl(2)···H(3b′,a) 2.38(3), 2.29(2); Cl(3)···H(3c′,b) 2.27(3), 2.47(3) Å]. The structure is well-defined, with all hydrogens being locatable other than those in the vicinity of the partially occupied water molecule site, and both the amide NH [H(0′)···O(01) 2.22(3) Å] and O [H(01a)···O(0′) ($2 - x$, $y + 1/2$, $1\,^1/_2 - z$) 2.07(4) Å] atoms are involved in H-bonding. The amide geometry is comparable with that of benzamide itself;[11−14] benzoylation of the cage complex causes no substantial electronic distortions of the product components, though presumably the charge of the complex may facilitate attack of a polar nucleophile at the amide carbon.

A useful discovery made during efforts to use nonaqueous solvents for the acylation of $[Co\{(NH_2)_2sar\}]^{3+}$ was that the 1,8-amino groups were found to be acylated very rapidly with activated acylating agents. Thus, formation of the formamidino derivative of the cage complex appears to be complete within the time of mixing at room temperature in a benzoyl chloride/dimethylformamide medium. The presumed mechanism for this process is shown in Figure 2.

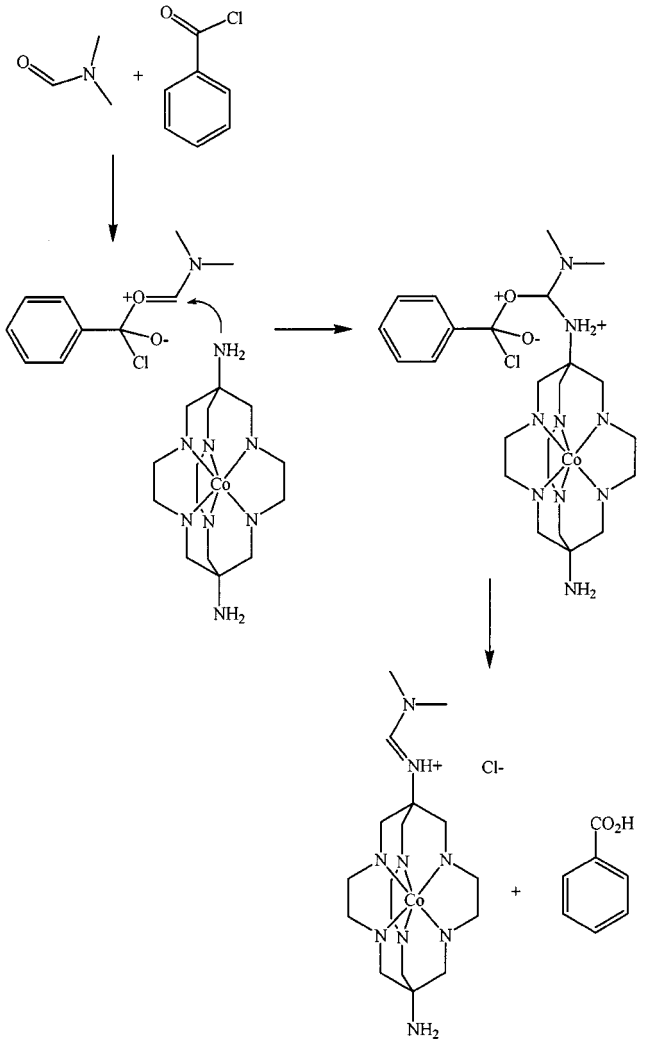

Figure 2. A possible pathway for amidine formation from dimethylformamide and $[Co\{(NH_2)_2sar\}]^{3+}$

The structure determination for $[Co\{sar[NHCHN(CH_3)_2]\}]Cl_5{\cdot}3H_2O$, **6** (Figure 1), was again sufficiently precise for hydrogen atom refinement, exemplifying yet another case of the *lel*$_3$ conformation arising from NH-bond chelation of chloride counteranions [Cl(1)···H(3c′,b) 2.34(2), 2.30(2); Cl(2)···H(3b′,a) 2.30(2), 2.29(2); Cl(3)···H(3a′,c) 2.30(2), 2.29(2) Å]. The structure confirms amidine formation, presumably as a result of the activation of DMF by acylation; both amidine groups remain sufficiently basic to be protonated in dilute HCl. Extensive H-bonding interactions are seen between the nitrogen atoms of the pendant groups and the anions and lattice water [Cl(5)···H(1) 2.31(2); O(03)···H(1′) 1.94(2) Å], and there are also direct interactions between the latter entities [Cl(3)···H(02a) 2.28(4); Cl(4)···H(02b), H(03b) ($1-x$, $-y$, $1-z$) 2.18(3), 2.33(3); Cl(5)···H(01a) (x, $y-1$, z) 2.35(3); O(2)···H(03a) (x, $y-1$, z) 1.93(3) Å]. The particular properties of dimethylformamide may be important in favouring amidine formation, as was also observed in early efforts to conduct phthaloylation reactions (see below) in this solvent; such behaviour was no longer prominent when dimethylacetamide was used as solvent. In turn, it was these observations that ultimately led to the use of dimethylacetamide in an efficient synthesis of the dibenzoylated cage complex.

As a model for reactions possibly involving the formation of a polyimide based on a cage amine and, for example, perylene dicarboximide units,[15] the formation of phthalimide derivatives of $[Co\{(NH_2)_2sar\}]^{3+}$ was examined. While the use of acetic acid as the reaction solvent appeared to result in formation of the bis(phthalimide) complex, under the conditions necessary for chromatographic purification of the reaction products ring opening to give the bis(phthalamic acid) was essentially complete. Such reactivity of the imide unit is perhaps unsurprising, given its incorporation into a highly charged cation. The use of dimethylacetamide (DMA) as a solvent for phthaloylation reactions is known[15] to favour phthalamic acid formation and, indeed, the reaction of $[Co\{(NH_2)_2sar\}]^{3+}$ with a moderate excess of phthalic anhydride in DMA led to essentially quantitative and direct formation of the "open" bis(phthalamic acid), **10**, which was structurally characterized as its chloride salt. As with the bis(benzoyl) derivative, the product did not display any anomalous structural features. The cage unit is again *lel*$_3$, once more arising from chloride anion chelation, and both the amide NH and carboxylic acid groups are involved in extended H-bonding arrays involving both water and the chloride anions. The mean bond lengths in the amide units (C−O 1.22 Å; C−N 1.35 Å) suggest some contraction of the C−O bond and elongation of the C−N bond relative to those in a simple phthalamide such as 2-phenylcarbamoylbenzoic acid,[16] although in the context of a less precise complex ion structure these differences cannot be seen as significant.

Like simpler amic acids,[15] the bis(phthalamic acid) complex could be converted into an imide form by heating in the solid state, but even under rather extreme conditions (180 °C, 5 Torr pressure, 5 h) this conversion was only ca. 20% complete. Hence, there appears to be a genuine resistance to the formation of imides, at least from $[Co\{(NH_2)_2sar\}]^{3+}$, and the hydrolytic stability seen for the bis(phthalamic acid) and, to a lesser extent, the simpler bis(benzamide) described above led us to the conclusion that the formation of polyamides should be a favourable method for the inclusion of cage units in polymers. Obviously, dimethylacetamide must currently be regarded as the solvent of choice for such reactions.

Reductive alkylations involving intermediate formation of imines between a carbonyl compound and cage amino substituents have been successfully used in the generation of a number of $[Co\{(NH_2)_2sar\}]^{3+}$ derivatives[3,5] and the work reported herein has served to extend the variety of these syntheses. We have found that the generation of imine species in reactions between aromatic aldehydes and $[Co\{(NH_2)_2sar\}]^{3+}$ in dimethyl sulfoxide can be readily monitored by ^{1}H NMR spectroscopy (most readily, through the appearance of an imine group CH resonance near $\delta = 8.5$), although in the presence of only a moderate excess of the aldehyde, conversion is slow and incomplete and, after

reduction, the product mixtures are invariably found to contain both mono- and dialkylated species. In the case of $[Co\{(CH_3)(NH_2)sar\}]^{3+}$, however, fully (mono)alkylated species are obtained more readily. In both systems, however, exhaustive chromatography of the reaction products has provided evidence of minor amounts of other (as yet, unidentified) products and the chemistry of these reactions cannot be said to be fully characterized, even though the desired products can be obtained with acceptable efficiency. Significant features of the ^1H NMR spectra of the isolated products containing groups other than 2-pyridylmethyl are summarized in Table 1. No anomalies are apparent, although it is unclear as to why the diastereotopicity of the methylene linker-group protons should be evident in some spectra (which show an AB quadruplet) and not in others.

To establish the structural influences of various cage alkylations, single-crystal structure determinations have been performed on $[Co\{(2\text{-}pyCH_2NH)_2sar\}]^{3+}$ as its monoprotonated tetranitrate **11** and its diprotonated bis(dithionate) chloride **12**, on $[Co\{(NH_2)(2\text{-}pyCH_2NH)sar\}]^{3+}$ as its diprotonated bis(dithionate) chloride **13**, and on $[Co\{(CH_3)(C_6H_5C_6H_4CH_2NH)sar\}]^{3+}$ as its mixed nitrate chloride **16** (see also the discussion of structure **14** below). The dialkylated cage structures (Figure 1) provide further examples of different conformers of a given cage complex being found in different salts;[5,6] thus, the 5+ cation of the dithionate chloride is found to be in the ob_3 form, while the 4+ cation in the tetranitrate is in the lel_3 form. This may be the only significant consequence of alkylation on the structure of the inner cage species. While there is some evidence that the preferred conformation of cages of the sarcophagine complex type may depend on the size of the 1,8-substituents,[3,5] the hydrogen atoms of the secondary N-donor atoms in the Co^{III} complexes are always involved in markedly different interactions with the counteranions and lattice solvent in the different conformers, and the availability of an H-bond acceptor capable of bridging between two NH units of different caps appears to be a significant factor favouring the lel_3 form.[3,6] Although the simple form of tris-chelation of anions as in structures **6**, **8**, and **10** does not apply for **11**, an equally elegant relative does apply (Figure 3). One of the two crystallographically independent anions is disposed with its axis (and those of its symmetry related images) approximately parallel to that of the cation, so that its three oxygen atoms interact with different cations, each O chelating two NH bonds. Thus, the relevant distances are N(3a)···O(12,13) (1/2 + x, 1/2 + y, z) 3.343(7), 3.244(6); N(3a′)···O(11,12) (1 − x, y, 1/2 − z) 3.223(6), 3.221(7); N(3b)···O(11,13) (x − 1/2, 1/2 + y, z) 3.178(7), 3.137(7) Å; from the opposite viewpoint, O(11)···N(3a′) (1 − x, y, 1/2 − z), N(3b) (1/2 + x, y − 1/2, z) 3.223(6), 3.178(7); O(12)···N(3a) (x − 1/2, y − 1/2, z), N(3a′) (1 − x, y, 1/2 − z) 3.343(7), 3.221(7); O(13)···N(3a) (x − 1/2, y − 1/2, z) 3.244(6), N(3b) (x + 1/2, y − 1/2, z) 3.137(7) Å (Figure 3).

The well-defined pendant amine hydrogen interacts with the water oxygen [H(0NA)···O(01) 2.0 (est.)], and the hydrogen of the latter is in turn coordinated by the pyridine nitrogen [N(02)···O(01) (1 − x, 1 − y, 1 − z) 2.67(1) Å]; beyond this the remainder of the structure (the other nitrate group) is disordered, with the assignment of the final hydrogen atom, as well as those of the water molecule, being dubious. The latter have four potential hydrogen-bonding interactions, two of which are presumably donor interactions [to N(02) (pyridine) (1 − x, 1 − y, 1 − z) and nitrate O(23) (disordered)], one an acceptor interaction [N(0)], and one ambiguous.

While the single proton associated with **11** appears to be bound to an amino rather than a pyridine nitrogen, in the diprotonated species **12** both protons are localized on pyridine *N* centres. Given that the acidity-enhancing effect of the adjacent Co^{III} cation should vary with distance from the metal centre,[17] it is perhaps not surprising to find a similar affinity for the two sites. In any case, protonation of the pendant groups strongly influences the nature of the H-bonding array in the solid, which in this case includes coordination of the NH units to separate H-bond acceptors [Cl···H(3b) 2.46(3), O(13)···H(3c) 2.04(4), O(22)···H(3a′) ($1\,^1/_2$ + x, y − 1/2, 1/2 − z) 2.32(4) Å] and, as in other examples of this form of H-bonding,[6] also involves the ob_3 conformation of the cage ligand. Other H-bonding interactions involve the pyridine and adjacent external amino groups [O(11)···H(0N) (x, 1 − y, z − 1/2) 2.16(5), H(02) ($1\,^1/_2$ − x, y − 1/2, −z − 1/2) 2.09(4) Å], water molecules (assumed on the basis of O···O separations, since associated protons were not located) [O(01)···O(01) (2 − x, y, 1/2 − z) 2.745(8), O(02) ($1\,^1/_2$ − x, 1/2 + y, 1/2 − z) 2.761(6); O(02)···O(03) 2.682(6); O(03)···O(03) (11/2 − x, 1/2 − y, 1 − z) 2.608(6) Å], and the dithionate anion [O(01)···O(21) 2.816(5); O(03)···O(12) (x, 1 − y, 1/2 − z) 2.744(6) Å]. The chloride environment is sparse, there being two contacts at 2.46(3) Å as above and two more to H(4cA) (x, 1 − y, 1/2 + z) (etc.) with distances of 2.74(3) Å.

That the particular choice of anions and degree of protonation are not the sole determinants of the solid-state conformation of the cage is shown by the fact that $[Co\{sar(NH_3)[NHCH_2(C_5H_4NH)]\}](S_2O_6)_2Cl\cdot 3H_2O$ (**13**), in which protonation of the pyridine nitrogen again seems preferred to that of the alkylated aliphatic nitrogen, is found in the lel_3 conformation. This is associated with a return to prominence of the tris(chelate) role of the core amine hydrogens in this compound, although with a diversity of interaction types: Cl···H(3b′,a) 2.17(4), 2.36(4) Å is conventional; H(3c′)···O(13) (x, y − 1, z), H(3b)···O(12) (x, y − 1, z) 2.31(3), 2.09(4) Å indicate a spanning of the pair of NH groups by O−S−O of one end of a dithionate anion, and in H(3a′,c)···O(03) 1.91(4), 1.95(4) Å, a water molecule oxygen is sequestered. The chloride shows a close contact to a water molecule, Cl···H(02A) 2.2 Å (est.). The terminal protonated NH_3^+ group shows contacts with a water molecule [H(0′A)···O(02) (x, y − 1, z) 1.69(7) Å] and with anionic oxygen atoms [H(0′B)···O(11) (− x, 1 − y, 1 − z) 1.88(4), H(0′c)···O(33) (x, 1/2 − y, z − 1/2) 2.09(5) Å], while at the other end the strongest interaction is found between the pyridinium hydrogen and an anionic oxygen [H(02)···O(21) 2.17(4) Å]. A limited number of the remaining anionic oxy-

Table 1. Functional group resonances in the ^{1}H NMR spectra (200 MHz, 0.1 M DCl solution) of $[Co(X)(YNH_2)sar]^{n+}$ complexes

X	Y	δ
CH_3	$C_6H_5CH_2$	CH_3 0.90 CH_2(Y) 4.13, 4.19, 4.20, 4.27 ArH 7.43
CH_3	4-$CH_3C_6H_4CH_2$	CH_3(X) 0.90 CH_3(Y) 2.31 CH_2(Y) 4.04, 4.11 (d), 4.18 ArH 7.28
CH_3	$C_6H_5CH(CH_3)CH_2$	CH_3(X) 0.89 CH_3(Y) 1.27, 1.30 ArH 7.3−7.5 (m)
CH_3	$C_6H_5C_6H_4CH_2$	CH_3 0.90 CH_2(Y) 4.10 ArH 7.41−7.53 (m), 7.66−7.73 (m)
CH_3	(4-C_5H_4N)CH_2	CH_3 0.90 CH_2(Y) 4.54, 4.59, 4.66, 4.71 ArH 8.18, 8.21 (d), 8.82, 8.86
CH_3	2-furanylCH_2	CH_3 0.85 CH_2(Y) 4.33 Furanyl-H 6.41 (m), 6.56, 6.58, 7.51 (d)
CH_3	2-thiophenylCH_2	CH_3 0.87 CH_2(Y) 4.48, 4.53, 4.56, 4.61 Thiophenyl-H 7.04, 7.05, 7.06, 7.25, 7.27, 7.50, 7.53
NH_3^+	$C_6H_5CH_2$	CH_2(Y) 3.86 ArH 7.30−7.40 (m)
NH_3^+	4-$CH_3C_6H_4CH_2$	CH_3(Y) 2.39 CH_2(Y) 3.97 ArH 7.24
NH_3^+	3-$CH_3C_6H_4CH_2$	CH_3(Y) 2.30 CH_2(Y) 4.00 ArH 7.14−7.35 (m)
NH_3^+	2-$CH_3C_6H_4CH_2$	CH_3(Y) 2.32 CH_2(Y) 4.15 ArH 7.25−7.35 (m)
NH_3^+	$C_6H_5CH(CH_3)CH_2$	CH_3 1.25, 1.28 ArH 7.29, 7.31, 7.32, 7.36, 7.39
NH_3^+	(4-C_5H_4N)CH_2	CH_2 4.58 ArH 7.16, 7.20, 8.80, 8.83
NH_3^+	2-furanylCH_2	CH_2 4.20 Furanyl H **6.4**0 (m), 6.52 (m), 7.50 (m)
NH_3^+	2-thiophenylCH_2	CH_2 4.38 Thiophenyl-H 7.00, 7.01, 7.03, 7.04, 7.17, 7.19, 7.44 (d), 7.47 (d)
NH_3^+	3-thiophenylCH_2	CH_2 4.16 Thiophenyl-H 7.02 (d), 7.35 (q), 7.44 (d)
$C_6H_5CH_2$	$C_6H_5CH_2$	CH_2 4.11, 4.17, 4.19, 4.25 ArH 7.43
4-$CH_3C_6H_4CH_2$	4-$CH_3C_6H_4CH_2$	CH_3 2.29 CH_2 4.13, 4.19, 4.21, 4.27
$C_6H_5CH(CH_3)CH_2$	$C_6H_5CH(CH_3)CH_2$	CH_3 1.28, 1.31 CH_2 **3.5**3 (br), 3.58 (br) ArH 7.31, 7.33, 7.35, 7.38, 7.41, 7.45
(4-C_5H_4N)CH_2	(4-C_5H_4N)CH_2	CH_2 4.58 ArH 7.16, 7.20, 8.80, 8.83
2-furanylCH_2	2-furanylCH_2	CH_2 4.29 Furanyl-H 6.43 (m), 6.57 (m), 7.53 (m)
3-thiophenylCH_2	3-thiophenylCH_2	CH_2 3.58 (q) Thiophenyl-H 6.88 (d), 7.10 (d), 7.24 (q)

gens are strongly hydrogen-bonded with water: O(31)···H(01A) (1 − *x*, *y* − 1/2, 1 $^1/_2$ − *z*) 1.8 (est.), O(41)···H(02B) (1 − *x*, 1/2 + *y*, 1/2 − *z*) 2.3 (est.), O(42)···H(01B), H(03B) (1 − *x*, *y* + 1/2, 1 $^1/_2$ − *z*) 2.2, 1.9 Å (est.). A strong water···water interaction [H(03A)···O(01) 1.7 (est.)] is found. In **13**, as in **12**, there is no evidence of stacking interactions of the pyridine rings, despite the fact that in **12** parallel arrays of pyridine rings from separate complex ion units may be discerned in the lattice. In **11**, however, arrays of parallel pyridine rings may be indicative of some stacking, as suggested by C···C contacts of ca. 3.7 Å.

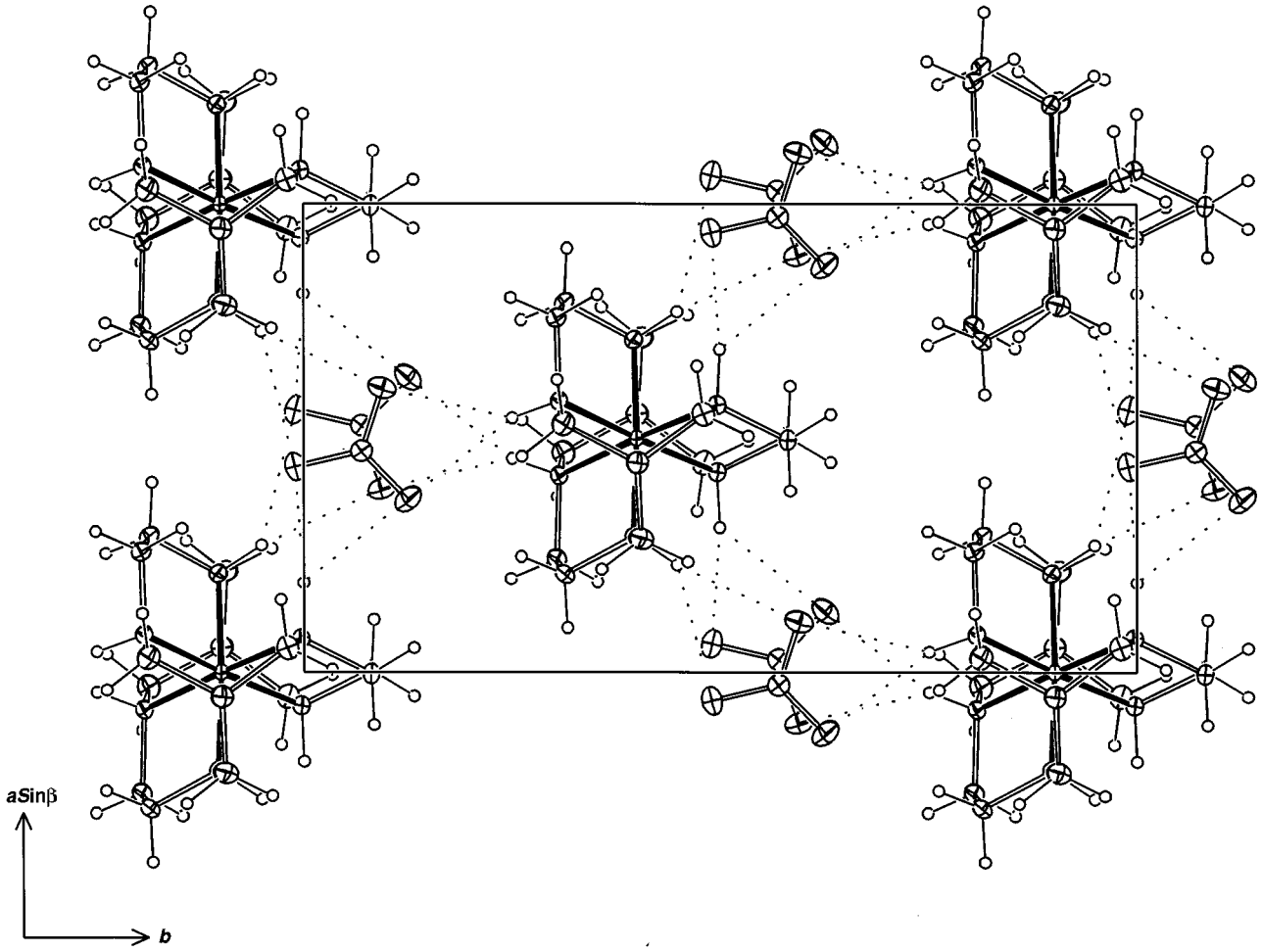

Figure 3. Section of the structure of **11**, projected down *a*, showing the cations centred at $z = 1/4$, on twofold axes, with the cage pendants being omitted so as to display the linking of cations centred on that plane by associated hydrogen-bonded nitrate ions

When a neutral aromatic unit is introduced as a substituent, as is the case with the biphenylmethyl unit in **16**, diminished charge repulsions appear to allow more significant stacking interactions, as indicated by the "herringbone" array of the biphenyl groups evident in this solid (in the projection down *a*). The cage unit adopts an lel_3 conformation, once again attributable to NH chelation of the anions, though the interactions are somewhat complicated to describe in this mixed anion species. Those of cation 1 involve the halide and a pair of nitrate groups: Cl···H(13b′,a) 2.5, 2.1; O(21)···H(13b,c′) 1.9, 2.2; O(13)···H(13a′,c) (x, 2 − y, z + 1/2) 2.2, 2.2 (est.) [also involving O(12)···H(13a′) (x, 2 − y, z + 1/2) 2.2 Å]. For cation 2, one chelate involves a water oxygen, O(06)···H(23b′,a) (x, y + 1, z) 2.3, 2.0, while the other two involve nitrate oxygens, O(41)···H(23c′,b) (x, 1 − y, z + 1/2) 2.1, 2.0; O(52,52′)···H(23c′,a) (x, y + 1, z) 2.2, 2.1; 2.30, −; O(53,53′)···H(23a′) (x, y + 1, z) 2.2, 2.3 Å (est.). Other H-bonds are formed to the pendant amino group nitrogen atom: H(10N)···O(12) 1.9, H(20N)···O(53) (x, 2 − y, z − 1/2) 2.0 Å (est.).

The introduction of aromatic substituents on cage amine complexes through the present and other means[18] is facile and is of interest in that the stability of these complexes in strongly acidic media allows functionalization of the aromatic units under simple, conventional conditions for electrophilic substitution. Such further functionalization could endow the complexes with new properties, for example, the introduction of vinyl substituents may possibly offer another route to polymer-immobilized cage complexes. As in the acylation and alkylation reactions of amino groups attached to the cages, some retardation of electrophilic attack, in this case on a pendant aromatic unit, was to be expected as a result of the cationic charge on the complex. At least in the case of $[Co\{(C_6H_5CH_2NH_2)_2sar\}]^{5+}$, however, this did not appear to be an important effect. Reaction of the complex in H_2SO_4/HNO_3 at room temperature for 5 min resulted in predominant symmetrical disubstitution at the 3-positions of the ring, with a small amount of mono-3-substituted material also being present. Reductions of these nitro compounds and reactions of the resulting aromatic amine derivatives are currently under investigation.[19]

A more direct pathway to the formation of polymers incorporating cage complex substituents is offered by complex derivatives containing electropolymerizable groups

such as furan, pyrrole, and thiophene.[20] Although reductive alkylation of $[Co\{(NH_2)_2sar\}]^{3+}$ with 2-pyrrolecarbaldehyde appeared to be successful, the product underwent acid-catalysed conversion into a "pyrrole black",[21] which was irreversibly absorbed on Dowex 50 cation-exchange resin; as yet we have not succeeded in obtaining the simple pyrrolylmethyl cage derivatives in a pure form. The furan and thiophene analogues, however, are readily obtained. As derivatives of 2-substituted heterocycles, these are not expected[20,21] to readily undergo oxidative polymerization, but they can at least be taken as putative models for the behaviour at the metal centre in a polymerized derivative. Encouragingly, electrochemical measurements have shown that the substituted Co^{III} cage complexes exhibit a quasi-reversible Co^{III}/Co^{II} couple at potentials essentially identical to those of their unsubstituted analogues. For both the thiophene and furan derivatives, a highly irreversible oxidation wave near +1.4 V may be consistent with an oxidation process at the ring, but no real evidence has been obtained for any resulting polymerization (for example, ion-exchange chromatography after extensive electrolysis or vigorous chemical oxidation only showed the presence of materials with similar elution characteristics to those of the reactants). The heterocycle oxidation wave alone has been taken as evidence for the occurrence of polymerization processes in closely related systems,[22] but in the present case measurements were made in aqueous solution and water is known to strongly inhibit oxidative polymer formation.[20]

More interesting redox properties were expected of the 3-substituted thiophene derivative, and to characterize fully the nature of the 3-thiophenyl substituent attached to a cage, the structure of $[Co\{[3\text{-}(C_4H_3S)CH_2NH_2](NH_3)sar\}]Cl_5\cdot 3H_2O$ (**14**) was determined by single-crystal X-ray crystallography. This confirmed the anticipated nature of the complex, with the cation adopting the familiar lel_3 conformation and the substituent lying in an extended position such that the cobalt cage unit clearly does not congest regions near the 2- (and 4-) positions of the thiophene ring. The cage again chelates chloride anions [(cation 1) Cl(1,1′)···H(13c′) 2.4, 2.7; Cl(1,1′)···H(13b) 2.2, 2.0; Cl(7)···H(13a′,c) (x, 1 − y, z − 1/2) 2.2, 2.1; Cl(8)···H(13b′,a) (x, 1 − y, z − 1/2) 2.3 (×2); (cation 2) Cl(6)···H(23c′,b) (1/2 + x, 1/2 + y, z) 2.3, 2.2; Cl(5)···H(23b′,a) (1 + x, y, z) 2.3, 2.1; Cl(3)···H(23a′,c) (1 + x, y, z) 2.1, 2.3 Å (all est.)], albeit with some disorder, and while the thiophene rings can be seen to form a herringbone array, there are no close inter-ring contacts. Cyclic voltammetry of the complex (in aqueous media) showed characteristics similar to those of the 2-thiophenyl analogue in that an irreversible oxidation wave near +1.4 V was apparent, but vigorous chemical oxidation in concentrated nitric acid gave contrasting results in that the product did show some properties of a large molecule. Thus, the product was of very low solubility in water and the bulk of it was irreversibly retained on both Sephadex and Dowex cation-exchange resins (it appeared possible to elute some material initially, but, on standing, even this small fraction became impossible to elute). Furthermore, the solid was a bright-yellow colour and in aqueous solution showed an absorption spectrum with an intense maximum near 420 nm, quite atypical of Co^{III} cage amine complexes, but typical of polythienyls.[20] All "solutions" were in fact perceptibly cloudy to the eye, again consistent with the solid containing high molecular weight species. The most prominent feature of the cyclic voltammogram of the solution was a strong oxidation wave near 1.4 V, with evidence for interconversion of a Co^{III}/Co^{II} couple near −0.3 V being retained. This material is currently being subjected to a more detailed investigation, one of the possible complications arising from its method of synthesis being that of nitrosation,[1,6,7] although it may be noted that simple dissolution of the dialkylated reactant complex in concentrated HNO_3 alone gives only species having the characteristics of mononuclear Co^{III} cage amine complexes.

A more conventional approach to oxidative polymerization of thiophene derivatives is to use electrochemical methods in nonaqueous solvents. Although the choice of solvent is restricted by the nature of the cage amine complex, it is possible to examine the triflate salt of the mono(3-thiophenyl) derivative in acetonitrile. Representative cyclic voltammograms for a series of measurements using a Pt working electrode and sodium triflate as the electrolyte are shown in Figure 4.

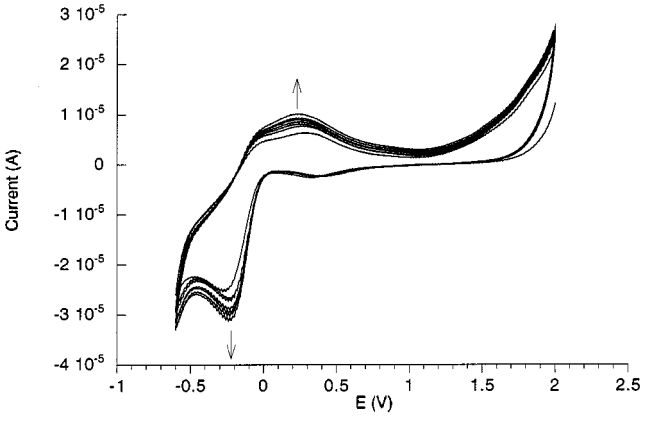

Figure 4. Electropolymerization of Co-cage thiophene conjugate

Although simple chemical experiments show the Co^{III}/Co^{II} interconversion to be reversible, it is apparently not electrochemically reversible, seemingly because of adsorption of the Co^{II} species in the present case.[23] Nevertheless, repeated scanning shows the current to increase with each consecutive scan, consistent with the deposition of a conductive material on the electrode surface. After such a series of measurements, the electrode was removed, washed well with water to remove any adhering monomeric complex, dried, and then placed in a simple acetonitrile solution of sodium triflate. Cyclic voltammograms subsequently obtained are shown in Figure 5.

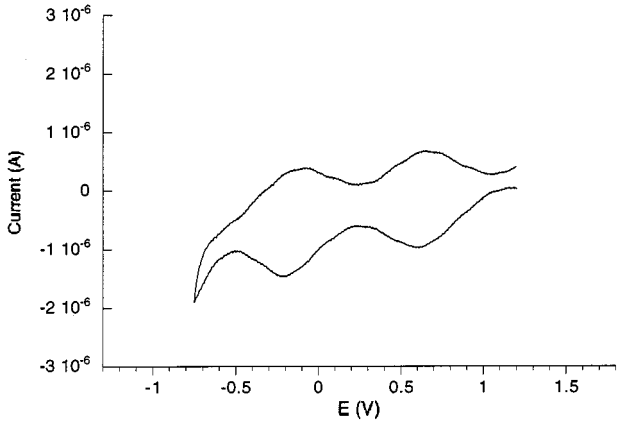

Figure 5. Cyclic voltammogram of modified electrode

Clearly, a conductive and electroactive material had been deposited on the electrode surface, and we tentatively ascribe the two waves with very small anodic/cathodic peak separations to polymer-pendant Co^{III}/Co^{II} (near −0.2 V) and polythiophene (near +0.6 V) centred processes. Obviously, there are interesting prospects here with regard to use of chiral Co^{III} monomers as sources of possible asymmetric electrocatalysts[24] and with regard to varying the electrochemical properties of the polymer by substituting the Co by other transition metals.

Conclusion

From the present and related works,[2,3,5,6] a substantial array of usefully 1,8-functionalized derivatives of the cage complex $[Co(sar)]^{3+}$ is now available. It would appear to be generally true that substitution at the 1,8-positions of this complex does not significantly modify the properties of the central unit. Correspondingly, the properties of the pendant groups do not appear to be critically modified by the presence of the nearby cationic centre. The Co^{III} should be replaceable by numerous other metals,[2,6] so that there may be many pathways to truly practical applications of cage amine complexes, such as in radiopharmaceutical agents based on Cu^{II}, for example.[25]

Experimental Section

General Remarks: NMR spectra were acquired from samples in D_2O solution on Varian Gemini 200 (^1H at 200 MHz and ^{13}C at 50.3 MHz) or Bruker ARX 500 (^1H at 500.13 MHz and ^{13}C at 125.8 MHz) spectrometers. Chemical shifts are expressed in ppm relative to an internal standard of acetone ($\delta = 2.04$ for ^1H NMR spectra and $\delta = 29.4$ for ^{13}C NMR, relative to TMS). − Ion-exchange chromatography was performed under gravity flow using Dowex 50W × 2 (H^+ form, 200−400 mesh) or SP Sephadex C25 (Na^+ form, 200−400 mesh) cation-exchange resins. All evaporations were performed at reduced pressure (ca. 20 Torr) using a Büchi rotary evaporator and a water aspirator. The Schlenk technique using high purity argon or high purity nitrogen was employed wherever it was necessary to exclude oxygen from preparative mixtures. − UV/Vis absorption spectra (200−800 nm) were recorded on a Hewlett−Packard 8452A diode-array spectrophotometer. − Cyclic voltammograms were recorded with a MacLab$\curlyvee$ potentiostat controlled by a Macintosh SE computer employing AD Instruments Echem software, using a platinum working electrode, a platinum counterelectrode, and a silver/silver chloride reference electrode. All solutions had a composition of 1−5 mM analyte in 0.1 M $NaClO_4$ solution. Water was purified using a Milli-Q ultra-pure water system. All solutions were purged with argon and were analysed at ambient temperatures. − Microanalyses for carbon, hydrogen, and nitrogen were carried out by the Australian National University Microanalytical Service. All samples were thoroughly dried in vacuo (0.1 Torr) at 50 °C for 4 h prior to their analysis.

$[Co\{(NH_3)_2sar\}]Cl_5\cdot H_2O$ was prepared as described previously.[7] Solvents from Fluka (pyridine, acetonitrile, dimethyl sulfoxide, dimethylformamide) and Eastman (dimethylacetamide) were used as received, as were reagents (phthalic anhydride, triethylamine) from Aldrich. Benzoyl chloride (Aldrich) was distilled prior to use. Aldehydes (2-pyridinecarbaldehyde, 4-pyridinecarbaldehyde, benzaldehyde, 3- and 4-methylbenzaldehyde, 2-phenylpropanal (hydratropaldehyde), biphenyl-4-carboxaldehyde, furancarbaldehyde, 2-thiophenecarbaldehyde, and 3-thiophenecarbaldehyde) from Aldrich were used as received. Various solids containing the $[Co\{(NH_2)_2sar\}]^{3+}$ cation were used as sources of this unprotonated cage complex (although equivalent results were often obtained simply by adding a base such as triethylamine to a solution of a protonated complex salt). $[Co\{(NH_2)_2sar\}]Cl_3\cdot nH_2O$ was prepared by heating (80 °C) a mixture of $[Co\{(NH_3)_2sar\}]Cl_5\cdot H_2O$ (5.7 g) and Li_2CO_3 (0.74 g) in water (5 mL) until effervescence had ceased. The deep brown-yellow solution was filtered, cooled, and gradually diluted with ethanol (50 mL) to precipitate a yellow, crystalline solid (4.5 g, 92%). − **$[Co\{(NH_2)_2sar\}]Cl_3\cdot 1.5H_2O$ (1):** calcd. C 33.18, H 7.36, N 22.11; found C 33.4, H 7.4, N 22.2. The analogous acetate salt was obtained by passing a solution of $[Co\{(NH_3)_2sar\}]Cl_5\cdot H_2O$ (5.70 g) in water (5 mL) through a column containing a tenfold excess of acetate-form Dowex 1 × 8 anion-exchange resin. The complex was washed from the column with water, the eluate was concentrated to a viscous, orange oil under reduced pressure, the residue was almost dried by twofold co-evaporation of ethanol, and finally it was crystallized from ethanol by the addition of diethyl ether. (Note that without the repeated evaporations, the solid retained some excess acetic acid.) Yield: 3.50 g, 52%. − **$[Co\{(NH_2)_2sar\}](CH_3CO_2)_3\cdot 6.5H_2O$ (2):** calcd. C 35.98, H 8.45, N 16.78; found C 35.9, H 8.5, N 16.8. To obtain the triperchlorate, perchloric acid (70%, 1 mL; CAUTION!) was added to a solution of the acetate (0.99 g) in ethanol (10 mL) to give initially a yellow, crystalline precipitate (1.13 g, 81%) of the pentaperchlorate. This was collected by filtration and washed first with ethanol/diethyl ether and then with diethyl ether. The solid rapidly underwent a colour change to red-orange on exposure to air, presumably as a result of hydration, although it did not deliquesce. − **$[Co\{(NH_3)_2sar\}](ClO_4)_5\cdot 4H_2O$ (3):** calcd. C 17.80, H 4.69, N 11.86; found C 17.9, H 5.1, N 11.9. (Note that as a possibly safer procedure, the pentaperchlorate may also be isolated from water as orange needles, although the yield is poor due to the high solubility of the compound.) The pentaperchlorate (1.40 g) and NaOH (0.11 g; one pellet) were dissolved in water (1 mL). The resulting solution took on a dark-yellow colour before copious precipitation of yellow-brown crystals commenced. Ethanol (10 mL) was then added and the mixture was cooled in ice to maximize precipitation of the solid (0.92 g, 88%), which was collected and washed with ethanol and

diethyl ether. − **[Co{$(NH_2)_2$sar}]$(ClO_4)_3$·2H_2O (4):** calcd. C 23.76, H 5.41, N 15.83; found C 23.9, H 5.7, N 15.8. Despite the apparently low solubility in water of the triperchlorate, attempts to isolate it directly from the more convenient starting material [Co{$(NH_3)_2$sar}]$Cl(ClO_4)_4$·2H_2O[6] invariably resulted in the chloride-perchlorate. Thus, [Co{$(NH_3)_2$sar}]$Cl(ClO_4)_4$·2H_2O (2.3 g) and NaOH (0.25 g) were dissolved in water (2.5 mL) to give a dark-brown solution; $NaClO_4$·H_2O (2.00 g) was added and the solution was diluted with ethanol (50 mL) to give a yellow precipitate, which was then recrystallized from hot water (5 mL) containing concentrated aqueous ammonia (2 drops) by the addition of ethanol (50 mL). Yield: 1.65 g, 100%. − **[Co{$(NH_2)_2$sar}]$Cl_2(ClO_4)$·H_2O (5):** calcd. C 29.93, H 6.46, N 19.95; found C 30.3, H 6.7, N 19.9.

Reactions of [Co{$(NH_2)_2$sar}]$^{3+}$ under Benzoylation Conditions: Attempts to react aqueous solutions of [Co{$(NH_3)_2$sar}]Cl_5·H_2O (containing sufficient base to both deprotonate the complex and neutralize the acid produced in acylation) with benzoyl chloride resulted in very low yields of (mono- and di-) benzoylated complexes, even when highly concentrated solutions (ca. 1−5 M) of the very soluble complex were used. For example, from the reaction of [Co{$(NH_3)_2$sar}]Cl_5H_2O (5.70 g, 10 mmol) in water (10 mL) with a fourfold excess of benzoyl chloride (5.60 g) in the presence of triethylamine (6.10 g), cation-exchange chromatography (SP Sephadex, 0.5 M NaCl/0.5 M $NaClO_4$ as eluent) enabled the isolation of ca. 200 mg of the monobenzoylated and ca. 20 mg of the dibenzoylated complexes. Absorption on Dowex 50W × 2 cation-exchange resin and re-elution with HCl to recover the complexes from the Sephadex column eluates led to partial hydrolysis of the benzoyl compounds, so these yields are lower estimates but not dramatically so. Attempts to use other solvents (acetonitrile, dimethyl sulfoxide, pyridine) as the reaction medium were even less successful, except in the cases of dimethylformamide and dimethylacetamide. In dimethylformamide, benzoylated products could be observed in moderate yields along with formamidino derivatives of the cage, and by varying the reaction conditions both products could be obtained quite readily.

[Co{[$(CH_3)_2$NCHNH]$_2$sar}]Cl_5·3H_2O (6): Triethylamine (0.5 mL) was added to a solution of [Co{$(NH_3)_2$sar}]$Cl(ClO_4)_4$·H_2O (0.50 g) in dimethylformamide (5 mL), which led to an appreciable darkening of the yellow solution. Under vigorous stirring, benzoyl chloride (0.70 g) was rapidly added, resulting in a lightening of the colour of the solution, followed, almost immediately, by the deposition of a yellow precipitate. After 5 min, the mixture was poured into water (50 mL) containing concentrated HCl (2 mL) and the precipitated benzoic acid was extracted into dichloromethane. The aqueous phase was passed through a column of H^+ form Dowex 50W × 2 cation-exchange resin to absorb the complex cation(s). The column was washed with water, then eluted with 1 M HCl to remove $[HN(C_2H_5)_3]^+$, and finally the yellow complex band was eluted with 3 M HCl. Although no separation was observed, ^{1}H NMR spectra of the residues obtained upon evaporation of the solvent from sequential eluate fractions indicated that at least two materials were present; resonances near δ = 7.5 and 7.9 showed a significant variation in their relative intensities through the sequence. The combined eluates were concentrated to dryness under reduced pressure and the yellow residue was redissolved in water (2 mL). Addition of ethanol (50 mL) led to precipitation of a yellow solid, which was recrystallized in a similar manner to furnish a material (0.20 g, 44%) showing only the lower field of the aforementioned two resonances in its ^{1}H NMR spectrum. A further recrystallization from water by vapour diffusion of ethanol provided clear yellow tablets suitable for X-ray crystallography. − ^{1}H NMR: δ = 2.62−2.85 (m, cage amine CH_2, 12 H), 2.92, 3.18 (two s, formamidino methyl groups, 12 H), 3.30−3.40 (m, cage amine CH_2, 12 H), 7.85 (br. s, formyl H, 2 H). − ^{13}C NMR: δ = 39.1, 46.6 (formamidino methyl), 55.5, 57.6 (cage methylene), 62.5 (cage quaternary), 156.3 (formyl). − For elemental analysis, the complex was recrystallized from 1 M HCl by the addition of ethanol; the results indicated that the complex formed as a "hydrochloride" under these conditions. − $[CoC_{20}H_{46}N_{10}]Cl_5HCl$·4$H_2O$ = $C_{20}H_{55}Cl_6CoN_{10}O_4$: calcd. C 31.14, H 7.19, N 18.16; found C 31.1, H 6.4, N 17.7.

[Co{$(C_6H_5CONH)(NH_3)$sar}]$(NO_3)_4HNO_3$·2H_2O (7): Triethylamine (0.41 g) was added to a solution of [Co{$(NH_2)_2$sar}]$(ClO_4)_3$·2H_2O (0.68 g) in dimethylformamide (1 mL), which led to a colour change from yellow-orange to dark brown. The resulting solution was cooled in ice, and then benzoyl chloride (0.56 g) was added under vigorous stirring. A yellow precipitate formed immediately and, after 5 min, precipitation was completed by the addition of ethanol (20 mL) and diethyl ether (10 mL). The solid was collected by filtration and redissolved in water (2 mL). Addition of ethanol (50 mL) precipitated a yellow powder (largely composed of the formamidino compound described above), which was filtered off, and then the filtrate was concentrated to dryness under reduced pressure. The deliquescent residue was redissolved in water (2 mL) and the yellow solution was cooled in ice. Dilute nitric acid (4 M, 2 mL) was added and the mixture was kept in the ice-bath as a crystalline precipitate formed. After 5 min, this was collected, washed with methanol and diethyl ether, and dried, giving 0.35 g (44%) of the complex. Analysis for $[CoC_{21}H_{39}N_8O](NO_3)_4$·$HNO_3$·2$H_2O$ ≡ $C_{21}H_{44}CoN_{13}O_{18}$: calcd. C 30.55, H 5.37, N 22.06; found C 30.8, H 5.3, N 22.3. − ^{1}H NMR: δ = 2.80−3.05 (m, cage amine CH_2, 12 H), 3.33−3.51 (m, cage amine CH_2, 12 H), 7.35 (m, ArH, 2 H), 7.46 (m, ArH, 1 H), 7.53 (m, ArH, 2 H). Additional very weak signals in this spectrum were possibly indicative of the presence of some mixed formamidino-benzoyl cage complex. The most efficient preparation of the dibenzoyl complex was that conducted in dimethylacetamide, after which chromatography indicated no more than trace amounts of any other product. Thus, triethylamine (0.41 g) was added to a solution of [Co{$(NH_2)_2$sar}]$(ClO_4)_3$ (0.68 g) in dimethylacetamide (1 mL), which led to a colour change from yellow-orange to dark brown. The resulting solution was cooled in ice, and then benzoyl chloride (0.56 g) was added under vigorous stirring. The colour of the solution rapidly became lighter and a yellow precipitate began to form within 10 s. After 5 min, ethanol (5 mL) was added to ensure hydrolysis of any remaining benzoyl chloride, and then diethyl ether (50 mL) was added to complete precipitation of the yellow solid. This was collected and redissolved in water (10 mL); the yellow solution was filtered and the filtrate was treated with conc. HCl (1 mL). Some precipitate formed but redissolved upon addition of ethanol (50 mL). Diethyl ether (ca. 400 mL) was then added to the point of permanent turbidity and the mixture was left to stand for 30 min to allow precipitation of fine, yellow crystals (0.37 g, 41%). Despite the intent to obtain the complex as its chloride, this procedure seemed to result in retention of the original perchlorate anion. − [Co{$(C_6H_5CONH)_2$sar}]$(ClO_4)_3$·4H_2O (**8**) ≡ $C_{28}H_{50}Cl_3CoN_8O_{18}$: calcd. C 35.32, H 5.29, N 11.77; found C 35.0, H 5.0, N 11.7. To ensure conversion into the chloride, **9**, this solid was shaken with an aqueous slurry of chloride-form Dowex 1 × 8 anion-exchange resin and the solution obtained was concentrated to dryness under reduced pressure. Crystals suitable for X-ray diffraction analysis were grown by redissolving the residual solid in hot (80 °C) water and allowing the solution to cool slowly to room temperature. − ^{1}H NMR: δ = 2.93−2.99 (br. d, cage amine CH_2,

6 H), 3.18, 3.24 (d, cage amine CH_2, 6 H), 3.57−3.67 (m, cage amine CH_2, 12 H), 7.55 (m, ArH, 2 H), 7.66 (m, ArH, 1 H), 7.73 (d, ArH, 2 H). − ^{13}C NMR: δ = 54.2, 55.5 (cage methylene), 60.6 (cage quaternary C), 129.8, 131.2, 135.1, 135.7 (ArC), 173.9 (carbonyl C).

Phthaloylation of $[Co\{(NH_2)_2sar\}]^{3+}$. − Method 1: A mixture of $[Co\{(NH_2)_2sar\}]Cl_3\cdot 2H_2O$ (1.00 g, 1.94 mmol) and phthalic anhydride (1.44 g, 9.73 mmol) in glacial acetic acid (80 mL) was heated under reflux for 2 h, in the course of which the initially orange solution darkened appreciably. The solvent was then removed under reduced pressure, the residue was extracted with water (50 mL), and the insoluble (white) material was filtered off. The filtrate was concentrated to leave an orange residue (1.10 g), which was redissolved in water (200 mL) and applied to a column (30 cm × 4 cm) of Na^+-form SP Sephadex C25 cation-exchange resin. The column was eluted with 0.5 M NaCl solution to separate four components, from which the complexes present were individually isolated by absorbing the eluate fractions on H^+-form Dowex 50W × 2 cation-exchange resin, washing the resin with water (100 mL) and 1 M HCl (100 mL), eluting the orange material with 3 M HCl, and concentrating the eluate to dryness under reduced pressure. Fraction 1 (ca. 0.20 g, 12%): ^{1}H NMR: δ = 2.50−3.95 (m, cage amine CH_2, 24 H), 7.41−8.06 (m, ArH, 8 H). − ^{13}C NMR: δ = 52.8, 55.0, 59.6, 128.7, 129.4, 131.7, 131.9, 134.3, 137.7, 171.0, 174.4. This was identified as the bis(phthalamic acid) derivative. Fraction 2 (ca. 0.60 g, 36%), as isolated, gave identical spectra to Fraction 1 except for the presence of a sharp singlet at δ = 7.84 in the ^{1}H spectrum, consistent with the presence of ca. 5% of an imide species. Fractions 3 and 4 were not well-separated and provided residues with identical spectroscopic properties, consistent with those of a mono(phthalamic acid): ^{1}H NMR: δ = 2.76−3.74 (m, cage amine CH_2, 24 H), 7.40−8.04 (m, ArH, 4 H). − ^{13}C NMR: δ = 52.6, 55.5 (cage methylene), 60.0 (cage quaternary C), 128.6, 128.8, 131.7, 131.9, 134.4, 137.8 (ArC), 170.5, 174.2 (carbonyl C).

Method 2: A mixture of $[Co\{(NH_2)_2sar\}]Cl_3\cdot 2H_2O$ (1.00 g, 1.94 mmol) and phthalic anhydride (1.44 g, 9.73 mmol) in dimethylacetamide (DMA; 70 mL) was heated at 90 °C for 17 h. After cooling the orange solution, it was diluted with diethyl ether (400 mL) and placed in a refrigerator (4 °C), whereupon orange needles slowly precipitated. The crystals were collected, washed with diethyl ether, and then redissolved in water (500 mL) to allow absorption of the complex(es) on a column (30 cm × 4 cm) of Na^+-form SP Sephadex C25 cation-exchange resin. Elution with 0.5 M NaCl produced a single band, from which the complex (1.30 g, 77%) was recovered as described above. The ^{1}H and ^{13}C NMR spectra of the residue were identical to those summarized above for the bis(phthalamic acid). The complex was recrystallized from hot water by cooling in ice to furnish orange needles. − $[CoC_{30}H_{42}N_8O_6]Cl_3\cdot 5H_2O$ (**10**) = $C_{30}H_{52}Cl_3CoN_8O_{11}$: calcd. C 41.60, H 6.05, N 12.94; found C 41.6, H 5.1, N 12.9.

Reductive Alkylation of $[Co\{(NH_2)_2sar\}]^{3+}$ and $[Co\{(CH_3)(NH_2)sar\}]^{3+}$

The following procedures, described for reactions involving 2-pyridinecarbaldehyde, were also carried out using 4-pyridinecarbaldehyde, benzaldehyde, 4-methylbenzaldehyde (*p*-tolualdehyde), 3-methylbenzaldehyde, 2-phenylpropanal (hydratropaldehyde), 4-biphenyl-4-carboxaldehyde (the product from reaction with $[Co\{(CH_3)(NH_2)sar\}]^{3+}$ ultimately being characterized by a crystal structure determination as the nitrate-chloride, **16**), furancarbaldehyde and 2-thiophenecarbaldehyde. In most cases, the relevant products were obtained in acceptable yields, though the syntheses were not optimized in each individual case and as a result some reactions of $[Co\{(NH_2)_2sar\}]^{3+}$ provided only the monoalkylation product. An efficient alternative synthesis of the product of the reaction of $[Co\{(CH_3)(NH_2)sar\}]^{3+}$ with 4-pyridinecarbaldehyde has been described in the literature.[3]

$[Co\{(2\text{-}pyCH_2NH)_2sar\}]^{3+}$ and $[Co\{(2\text{-}pyCH_2NH)(NH_2)sar\}]^{3+}$: $[Co\{(NH_3)_2sar\}]Cl_5\cdot H_2O$ (1.8 g, 3 mmol) was converted into its acetate salt by dissolution in water, passage through a column of acetate-form Dowex 1 × 8 anion-exchange resin, concentration of the eluate to a viscous oil, and crystallization of the latter by precipitation from methanol by the addition of diethyl ether. Although conversion was quantitative, the acetate prepared in this way invariably appeared to have a composition intermediate between those of $[Co\{(NH_3)(NH_2)sar\}](O_2CCH_3)_4$ and $[Co\{(NH_2)_2sar\}](O_2CCH_3)_3$, hence a base was added in the following step of the synthesis. Thus, the acetate was dissolved in dimethyl sulfoxide (30 mL) containing triethylamine (1 mL). 2-Pyridinecarbaldehyde (0.96 g, 9 mmol) was added and the resulting mixture was heated at 90 °C for 12 h under a nitrogen atmosphere. After cooling the solution to room temperature, sodium borohydride (0.50 g) was added and the mixture was stirred vigorously for 1 h. The excess borohydride was then destroyed by the slow addition of 3 M HCl (20 mL), and the solution was diluted with water (1 L) containing hydrogen peroxide (30%, 1 mL) to ensure complete conversion of Co^{II} back to Co^{III}. The orange solution thus obtained was absorbed on a column (4 × 50 cm) of H^+-form Dowex 50W × 2 cation-exchange resin and, after washing the column with water (2 L) and 0.5 M HCl (1 L), the remaining orange complexes were eluted with 3 M HCl. Three components were observed; the individual eluates were concentrated under reduced pressure and then the complexes were precipitated by the addition of ethanol. The first band contained unchanged starting material, the second (F2) contained the monosubstituted complex, and the third (F3) contained the disubstituted complex. Yield from F2: 1.13 g, 56%. − $C_{20}H_{41}Cl_5CoN_9\cdot 1.5H_2O$: calcd. C 35.81, H 6.61, N 18.79; found C 35.8, H 6.6, N 19.0. − UV/Vis (0.1 M HCl): λ_{max} = 472 nm, ε_{max} = 115 M^{-1} cm^{-1}. − ^{1}H NMR: δ = 2.76−3.60 (complex multiplet, 24 H, cage methylene), 4.41 (s, 2 H, CH_2py), 8.00, 8.02, 8.04, 8.06, 8.54, 8.58, 8.59, 8.74, 8.77 (m, 4 H, ArH). − Yield from F3: 1.18 g 53%. − $C_{26}H_{45}Cl_4CoN_{10}\cdot 2H_2O$: calcd. C 42.52, H 6.72, N 19.07; found C 42.5, H 6.3, N 19.1. − UV/Vis (0.1 M HCl): λ_{max} = 470 nm, ε_{max} = 95.4 M^{-1} cm^{-1}. − ^{1}H NMR: δ = 2.61, 2.67, 2.69 and 3.16, 3.22, 3.26 (ill-resolved multiplets, 24 H, cage methylene), 4.23 (s, 4 H, CH_2py), 7.1 (br. s, 6 H, NH), 7.73, 7.76, 7.80, 7.86, 8.30, 8.35, 8.38, 8.50, 8.54 (m, 8 H, ArH). − In seeking to obtain crystals from F3 suitable for X-ray crystallography, aqueous solutions of the chloride were treated with dilute HNO_3 and $Li_2S_2O_6$, giving, on slow evaporation of the solvent from the product solutions at room temperature, materials that were established by subsequent structure determinations (see below) to be the differently protonated species $[Co\{(2\text{-}pyCH_2NH)(2\text{-}pyCH_2NH_2)sar\}](NO_3)_4\cdot 2H_2O$ (**11**) and $[Co\{(2\text{-}pyCH_2NH_2)_2sar\}](S_2O_6)_2Cl\cdot 6H_2O$ (**12**), respectively. F2 was subsequently also crystallized by the use of dithionate to give the diprotonated dithionate-chloride $[Co\{sar(NH_3)[NHCH_2(C_5H_4NH)]\}](S_2O_6)_2Cl\cdot 3H_2O$ (**13**).

$[Co\{(2\text{-}pyCH_2NH)(CH_3)sar\}]^{3+}$: $[Co\{(CH_3)(NH_3)sar\}]Cl_4\cdot 0.5H_2O$ (1.05 g, 2 mmol) was converted into the acetate following the procedure described above. This was dissolved in dimethyl sulfoxide (30 mL) containing triethylamine (0.20 g), after which 2-pyridinecarbaldehyde (0.32 g, 3 mmol) was added and the mixture was heated at 90 °C for 10 h. Reduction with borohydride, re-oxidation of the metal, and chromatographic workup of the product mixture

were conducted as described above. In this case, only two bands were observed, the first corresponding to the reactant and the second being the desired product. Yield (F2): 1.10 g, 88%. − $C_{21}H_{41}Cl_4CoN_8{\cdot}H_2O$: calcd. C 40.40, H 6.94, N 17.95; found C 40.4, H 6.9, N 18.0. − UV/Vis (0.1 M HCl): λ_{max} = 472 nm, ε_{max} = 129 M^{-1} cm^{-1}. − ^{1}H NMR: δ = 0.98 (s, 3 H, CH_3), 2.45, 2.52, 2.71, 2.78. 2.82, 2.86, 3.06, 3.10, 3.13, 3.35, 3.39 (m, 24 H, cage methylene), 4.31 (s, 2 H, CH_2py), 7.00, 7.15 (br. s, 6 H, NH), 7.98, 8.01, 8.03, 8.05, 8.54, 8.58, 8.62, 8.75, 8.79 (m, 4 H, ArH).

Apparent Polymerization Processes

When the procedure described above for the reactions of $[Co\{(NH_3)_2sar\}]Cl_5{\cdot}H_2O$ was followed using 2-pyrrolecarbaldehyde as the substrate, all proceeded as expected until attempts were made to elute the crude reaction product from H^+-form Dowex 50W × 2 resin using 3 M HCl. The orange eluate rapidly began to darken and within a few hours appeared black. Dilution and reabsorption of the solution on the resin gave a black deposit, which could not be removed even by the use of concentrated HCl as eluent.

In the case of the product obtained from the reaction with 3-thiophenecarbaldehyde, isolation of the alkylated cage complexes was straightforward, but under strongly oxidative conditions some evidence of polymerization was obtained. Thus, 3-thiophenecarbaldehyde (0.35 g) was added to a solution of $[Co\{(NH_2)_2sar\}](ClO_4)_3$ (1.00 g) in dimethylacetamide (2 mL) and the mixture was heated on a steam bath for 20 min. Excess $NaBH_4$ (0.10 g) was added to the cooled orange solution, which led to an immediate colour change to an intense violet (presumably due to the *N*-deprotonated cage complex[7]). After 5 min, this solution was poured into 1 M HCl (50 mL) and, when the effervescence due to decomposition of the excess $[BH_4]^-$ had subsided, the orange solution was left to stand at room temperature for 12 h, in the course of which the bulk of the dialkylated product complex precipitated as fine, yellow needles. This solid (0.30 g, 26%) was filtered off, washed with ethanol, and the combined filtrate and washings were passed through a column of H^+-form Dowex 50W × 2 resin to absorb the residual soluble complexes as an orange band. The column was washed with 1 M HCl to remove Na^+, then eluted with a gradient of 3 M → 7 M HCl to reveal three orange components. The first proved to be a trace of reactant, the second consisted of the monoalkylated complex (0.26 g, 26%), and the third consisted of additional dialkylated complex (0.17 g, 14%). Note that in a similar experiment using only 0.18 g of 3-thiophenecarbaldehyde in the hope of obtaining largely the monoalkylated complex, a mixture of the same three species was obtained, although the monoalkylated complex (0.36 g, 37%) did predominate over the dialkylated (0.18 g, 15%). Analysis for the monoalkylated complex $C_{19}H_{40}Cl_5CoN_8S{\cdot}3H_2O$: calcd. C 32.47, H 6.60, N 15.94, S 4.56; found C 33.0, H 7.3, N 15.4, S 4.3; for the dialkylated complex $C_{24}H_{44}Cl_5CoN_8S_2{\cdot}5H_2O$: calcd. C 34.52, H 6.52, N 13.42, S 7.68; found C 34.8, H 6.8, N 13.5, S 7.4. − UV/Vis: monoalkylated complex (0.1 M HCl): λ_{max} = 472 nm, ε_{max} = 108 M^{-1} cm^{-1}; dialkylated complex (water): λ_{max} = 471 nm, ε_{max} = 152 M^{-1} cm^{-1}. Monoalkylated complex: ^{1}H NMR: δ = 2.80 (m), 3.42 (m, ethylene bridge AA′BB′ system), 2.91 (d), 3.32 (d, cap methylene AB systems), 4.16 (s, substituent methylene), 7.02 (d), 7.35 (q), 7.44 (d, thiophene CH). − ^{13}C NMR: δ = 40.1, 49.1, 50.3, 53.17, 53.21 (CH_2), 55.0, 60.0 (quaternary C), 126.9, 127.0, 127.1 (thiophene ArCH), 129.7 (thiophene ArC); dialkylated complex: ^{1}H NMR: δ = 2.40 (d), 3.02 (d, cap methylene AB system), 2.56 (m), 3.10 (m, ethylene bridge AA′BB′ system), 3.58 (q, substituent methylene), 6.88 (d), 7.10 (d), 7.24 (q, thiophene CH). − ^{13}C NMR: δ = 40.2, 48.1, 52.4 (CH_2), 59.7 (quaternary C), 127.0, 127.2, 127.5 (thiophene ArCH), 128.6 (thiophene ArC). Note that, as for all cage complexes with basic external substituents, chemical shift values and the overall appearance of the spectra are generally very dependent on both the concentration and pH of the solutions.[7] Crystals of the monoalkylated complex (as its pentachloride, **14**) suitable for X-ray diffraction analysis were obtained by adding ethanol to a solution of the complex in water to the point of turbidity and then allowing the mixture to stand at room temperature for 24 h. Of various attempts made to achieve chemically oxidative oligomerization of the thiophene-substituted complexes, only the following provided some evidence of success. The dialkylated complex (chloride, **15**; 100 mg) was dissolved in concentrated HNO_3 (2 mL) and this orange solution was mixed with a slurry of $[NH_4]_2[Ce(NO_3)_6]$ (80 mg) in concentrated HNO_3 (1 mL). Agitation of the mixture resulted in the rapid dissolution of all solids and a colour change of the solution to deep yellow-orange. After 5 min, water (10 mL) was added, which led to the deposition of a yellow-orange solid. The mixture was cooled in ice for 5 min and then the precipitate was collected, washed with water (2 mL), ethanol, and diethyl ether, and dried in air (74 mg). The cloudy filtrate and washings were pale-yellow in colour.

Structure Determinations

Diffraction data were acquired in a number of modes, at the specified temperature, using monochromatic Mo-K_α radiation, λ = 0.71073 Å, on all instruments. Using a single counter instrument in 2θ/θ scan mode, *N* unique reflections were measured within the specified $2\theta_{max}$ limit, N_o with $I > 3\sigma(I)$ being considered "observed", gaussian absorption corrections being applied. Data were also measured using a Bruker AXS CCD instrument ($2\theta_{max}$ = 58°), the total number of reflections, N_t, within a full sphere being merged to *N* unique, R_{int} as specified after "empirical"/multiscan absorption correction within the proprietary/preprocessing software; the "observed" criterion applied was $F > 4\sigma(F)$. Anisotropic thermal parameter forms were refined in a full-matrix context for non-hydrogen atoms, $(x, y, z, U_{iso})_H$ being constrained at estimated values. Conventional residuals *R*, R_w (statistical weights) on |*F*| are quoted at convergence. Neutral atom complex scattering factors were employed within the Xtal 3.4 program system.[24] Pertinent results are given in the Figures and below; individual variations in procedure/difficulties/idiosyncrasies are cited as "*variata*". Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-151305−151312. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge, CB2 1EZ, U.K. [Fax: (internat.) +44 (0)1223/336033; E-mail: deposit@ccdc.cam.ac.uk]. Cation projections are shown in Figure 1; common *ad hoc* crystallographic numbering is shown, carbon atoms being denoted by number only. Non-hydrogen atoms are shown with 20% (room temperature) or 50% (low temperature) probability displacement ellipsoids. Bond lengths and angles are generally as expected throughout the array and are not addressed further, the interest lying in the isomeric and conformational variations discussed in the text above and shown in the Figures.

Crystal/Refinement Data

6. $[Co\{sar[NHCHN(CH_3)_2]\}]Cl_5{\cdot}3H_2O$ ≡ $C_{20}H_{52}Cl_5CoN_{10}O_3$, $M \approx 716.9$. CCD-instrument, $T \approx 153$ K. Triclinic, space group $P\bar{1}$ (C_i^1, No.2), a = 8.902(1), b = 12.105(2), c = 16.378(2) Å, α = 70.584(2), β = 76.662(2), γ = 82.194(2)°, V = 1616.1 Å^3. $D_{calcd.}$ (Z = 2) = 1.473 g cm^{-3}. μ_{Mo} = 9.9 cm^{-1}; specimen: 0.35 × 0.20 × 0.08 mm; $T'_{min.,max}$ = 0.68, 0.89. N_t = 18312, N = 7724 (R_{int} =

0.022), $N_o = 6978$; $R = 0.027$, $R_w = 0.038$. $|\Delta\rho_{max}| = 0.51(2)$ e Å^{-3}.

Variata: $(x, y, z, U_{iso})_{HHH}$ were refined throughout.

8. [Co{sar(NHCOC$_6$H$_5$)$_2$}]Cl$_3$·1.63H$_2$O ≡ $C_{28}H_{45.26}Cl_3CoN_8O_{3.63}$, $M \approx 717.4$. Single-counter instrument, $T \approx 295$ K. Monoclinic, space group $P2_1/c$ (C_{2h}^5, No.14), $a = 16.242(8)$, $b = 13.810(4)$, $c = 16.714(16)$ Å, $\beta = 115.93(5)°$, $V = 3372$ Å^3. $D_{calcd.}$ ($Z = 4$) = 1.426 g cm^{-3}. $\mu_{Mo} = 7.9$ cm^{-1}; specimen: 0.22 × 0.65 × 0.60 mm; $T_{min.,max} = 0.62, 0.93$. $2\theta_{max} = 60°$; $N = 7728$, $N_o = 5795$; $R = 0.035$, $R_w = 0.039$. $|\Delta\rho_{max}| = 0.44$ e Å^{-3}.

Variata: Site occupancy of O(2) refined to 0.630(6); no associated hydrogen atoms were located. For all other hydrogen atoms, (x, y, z, U_{iso}) were refined.

10. [Co{sar[NHCO(*o*-C$_6$H$_4$CO$_2$H)]$_2$}]Cl$_3$·6^3/$_4$H$_2$O ≡ $C_{30}H_{55.5}Cl_3CoN_8O_{12.75}$, $M \approx 897.6$. CCD instrument, $T \approx 300$ K. Triclinic, space group $P\bar{1}$, $a = 13.433(1)$, $b = 17.434(2)$, $c = 18.997(2)$ Å, $\alpha = 97.181(2)$, $\beta = 99.057(2)$, $\gamma = 108.238(2)°$, $V = 4100$ Å^3. $D_{calcd.}$ ($Z = 4$) = 1.454 g cm^{-3}. $\mu_{Mo} = 6.8$ cm^{-1}; specimen: 0.45 × 0.35 × 0.15 mm; $'T'_{min.,max} = 0.74, 0.87$. $N_t = 47686$; $N = 19991$ ($R_{int} = 0.032$), $N_o = 7593$; $R = 0.055$, $R_w = 0.058$. $|\Delta\rho_{max}| = 0.84$ e Å^{-3}.

Variata: High "thermal motion" was evident in relation to a number of residues modelled as water molecule oxygen atoms; refinement of site occupancies suggested only that of O(14) to be seriously deviant from unity, disposed over a pair of sites 1.79(2) Å apart, its occupancies refining to ca. 0.5 and being constrained thus. Hydrogen atoms were located in difference maps as being associated with O(1)−O(7).

11. [Co{sar(NH$_2$CH$_2$C$_5$H$_4$N)(NHCH$_2$C$_5$H$_4$N)}](NO$_3$)$_4$·2H$_2$O ≡ $C_{26}H_{49}CoN_{14}O_{14}$, $M = 840.7$. Single-counter instrument, $T \approx 295$ K. Monoclinic, space group $C2/c$ (C_{2h}^6, No. 15), $a = 8.416(2)$, $b = 14.877(3)$, $c = 27.405(4)$ Å, $\beta = 95.39(1)°$, $V = 3461$ Å^3. $D_{calcd.}$ ($Z = 4$) = 1.634 g cm^{-3}. $\mu_{Mo} = 5.9$ cm^{-1}; specimen: 0.40 × 0.25 × 0.30 mm; $T_{min.,max} = 0.84, 0.96$. $2\theta_{max} = 50°$; N_t (hemisphere to 50°; sphere to 40°) = 8648, $N = 3009$ ($R_{int} = 0.079$), $N_o = 1947$; $R = 0.060$, $R_w = 0.062$. $|\Delta\rho_{max}| = 1.00$ e Å^{-3}.

Variata: Protonation as indicated is incompatible with $Z = 4$ in the centrosymmetric space group; difference map considerations suggested protonation of the "diamsar" nitrogen atoms and the proton was located thus, occupancy 0.5; other disorder, notably among one of the nitrate groups, also modelled as disposed over two sets of sites, occupancies 0.5, may be concerted with that of the protonation. Attempted refinement in a lower symmetry was (inherently) unfruitful (it has not escaped our notice that in later determinations in the series, the pyridine moiety is definitively described as protonated, rather than the NH group).

12. [Co{sar[NHCH$_2$(C$_5$H$_4$NH)]$_2$}](S$_2$O$_6$)$_2$Cl·6H$_2$O ≡ $C_{26}H_{58}ClCoN_{10}O_{18}S_4$, $M = 1021.5$. Single-counter instrument, $T \approx 295$ K. Monoclinic, space group $C2/c$, $a = 16.353(3)$, $b = 14.783(3)$, $c = 17.510(3)$ Å, $\beta = 98.38(2)°$, $V = 4188$ Å^3. $D_{calcd.}$ ($Z = 4$) = 1.620 g cm^{-3}. $\mu_{Mo} = 7.6$ cm^{-1}; specimen: 0.55 × 0.50 × 0.26 mm; $T_{min.,max} = 0.72, 0.83$. $2\theta_{max} = 55°$; N_t (hemisphere) = 7753, $N = 4813$ ($R_{int} = 0.029$), $N_o = 3694$; $R = 0.050$, $R_w = 0.066$. $|\Delta\rho_{max}| = 0.91$ e Å^{-3}.

Variata: Hydrogen atoms were not located as being associated with "water molecule oxygen atoms" O(2,3), these having apparent occupancies of unity based on refinement behaviour; (x, y, z, U_{iso}) (all other H) were refined.

13. [Co{sar(NH$_3$)[NHCH$_2$(C$_5$H$_4$NH)]}](S$_2$O$_6$)$_2$Cl·3H$_2$O ≡ $C_{20}H_{47}ClCoN_9O_{15}S_4$, $M = 876.3$. CCD instrument, $T \approx 300$ K. Monoclinic, space group $P2_1/c$ (C_{2h}^5, No. 14), $a = 14.457(1)$, $b = 9.8567(8)$, $c = 24.562(2)$ Å, $\beta = 96.990(2)°$, $V = 3474$ Å^3. $D_{calcd.}$ ($Z = 4$) = 1.675 g cm^{-3}. $\mu_{Mo} = 8.9$ cm^{-1}; specimen: 0.24 × 0.16 × 0.10 mm; $'T'_{min.,max} = 0.66, 0.93$. $N_t = 38653$, $N = 8676$ ($R_{int} = 0.038$), $N_o = 5464$; $R = 0.045$, $R_w = 0.052$. $|\Delta\rho_{max}| = 0.78$ e Å^{-3}.

Variata: (x, y, z, U_{iso}) were refined for all hydrogen atoms except those associated with the water molecules, which were located from difference maps.

14. [Co{sar(NH$_3$)(NH$_2$CH$_2$C$_4$H$_3$S)}]Cl$_5$·3H$_2$O ≡ $C_{19}H_{46}Cl_5CoN_8O_3S$, $M = 702.9$. CCD instrument, $T \approx 153$ K. Monoclinic, space group Cc (C_s^4, No. 9), $a = 19.321(3)$, $b = 19.624(3)$, $c = 16.989(2)$ Å, $\beta = 91.255(2)°$, $V = 6440$ Å^3. $D_{calcd.}$ ($Z = 8$) = 1.450 g cm^{-3}. $\mu_{Mo} = 10.5$ cm^{-1}; specimen: 0.65 × 0.17 × 0.15 mm; $'T'_{min.,max} = 0.54, 0.88$. $N_t = 17751$, $N = 4560$ ($R_{int} = 0.050$), $N_o = 4167$ ("Friedel pairs" preserved distinct); $R = 0.060$, $R_w = 0.073$; $x_{abs} = 0.06(4)$. $|\Delta\rho_{max}| = 0.70(3)$ e Å^{-3}.

Variata: The pendant residue on molecule 1 of the two independent molecules in the asymmetric unit was modelled as being disordered over two sets of sites; occupancies were set at 0.5 each after trial refinement and coalesced with a more extensive mass of disordered fragments modelled as water molecule oxygen atoms; site occupancies 0.5. Cl(1,2) were also modelled as being disordered over pairs of sites, with separations of 0.80(3), 1.49(4) Å, and occupancies refining to 0.74(2), 0.72(2); under unit totality constraint after trial refinement, these complemented the smaller fragments of the Cl; those of the other disordered non-hydrogen atoms were refined with isotropic thermal parameter forms.

16. [Co{sar(CH$_3$)(NHCH$_2$C$_6$H$_4$C$_6$H$_5$)}](NO$_3$)$_{2.5}$Cl$_{0.5}$ca. 4^1/$_8$H$_2$O ≡ $C_{28}H_{53.25}Cl_{0.5}CoN_{9.5}O_{11.625}$, $M \approx 785.7$. CCD instrument, $T \approx 153$ K. Monoclinic, space group $C2/c$, $a = 60.926(5)$, $b = 15.353(1)$, $c = 15.365(1)$ Å, $\beta = 92.410(2)°$, $V = 14360$ Å^3. $D_{calcd.}$ ($Z = 16$) = 1.454 g cm^{-3}. $\mu_{Mo} = 5.9$ cm^{-1}; specimen: 0.80 × 0.35 × 0.10 mm; $'T'_{min.,max} = 0.52, 0.86$. $N_t = 79381$, $N = 12608$ ($R_{int} = 0.10$), $N_o = 7314$; $R = 0.099$, $R_w = 0.12$. $|\Delta\rho_{max}| = 3.71(4)$ e Å^{-3}.

Variata: The anion complement was modelled in terms of a total charge of three, made up of one-half of a chloride ion and two-and-a-half nitrate ions, one of the latter being modelled as being disordered over two sets of sites, oxygen occupancies set at 0.5 after trial refinement. The molecules pack as double layers disposed on either side of the plane(s) $x = 0.125$ (etc.), interleaved by layers comprising residues modelled in terms of some anions and water molecule oxygen atoms, about the plane(s) $x = 0$ (etc.). These encompass considerable disorder with a number of site occupancies modelled being set at 0.5 after trial refinement.

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