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Structural and Electrochemical Studies of Co(III) Cage Amine Complexes with Pendent Thienylmethylamino Groups

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Various 2- and 3-thienylmethylamino-substituted cobalt(III) cage amine complexes, prepared with the objective of obtaining cage-functionalized polythienyls, have been found to be resistant to oxidative polymerization by both electrochemical and chemical procedures. X-ray structure determinations indicate that there is negligible perturbation of the physical dimensions of the thiophene moieties by the cage substituents and thus that the resistance to polymerization must be associated with the high positive charge carried by these substituents.

Introduction

Polymer-modified electrodes[1,2] have attracted considerable interest because of their potential applications in many areas,[3] predominantly those of analytical sensing and electrocatalysis.[4−8] Both the activity and the selectivity of a polymer-modified electrode can be controlled by the introduction of appropriate functionality into the polymer, one avenue to the construction of such electrodes being the electropolymerization of a functionalized monomer. Many cationic thiophene monomers have been successful polymerized, including alkylammonium, imidazolium, and macrocyclic derivatives.[9−15] In pursuit of such an approach, we have previously[16] synthesized materials in which an extremely stable but redox-active metal complex of a macrobicyclic amine was bound to a simple electropolymerizable molecule, the intensely studied thiophene.[17] Preliminary evidence revealed their utility in preparing polymer-modified electrodes from 3-thienylmethyl cage amine conjugates, and the present work concerns development of these observations into a detailed study of attempted polymerization and electropolymerization reactions of thienylmethyl substituted cage amine complex units. We have chosen to prepare both the 2- and 3-thienylmethyl derivatives as they could be used to prepare polymers exhibiting inline[18,19] or pendent[20,21] microstructures, respectively. One complex in its optically resolved form was included in the hope that it might give rise to a more stereoregular polymer than those resulting from racemates.

Results and Discussion

The syntheses presently conducted are outlined in Scheme 1, and the product numbering is given in Table 1. The 2- and 3-thienylmethyl derivatives of $[Co((NH_2)_2sar]^{3+}$ and $[Co((CH_3)(NH_2)sar)]^{3+}$ were all prepared by reductive alkylation of the cage complexes with 2- and 3-thiophene carboxaldehydes using $[BH_3CN]^-$ as the reductant. In earlier

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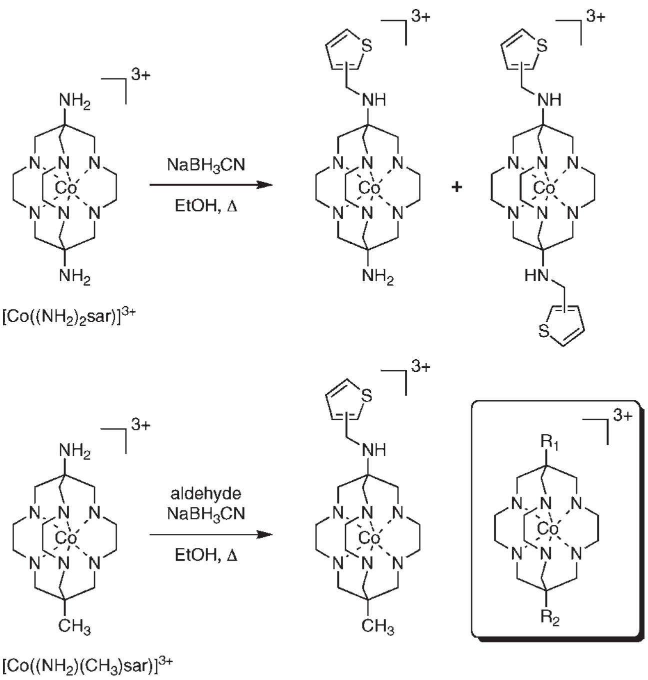
Scheme 1. Reductive Alkylation of $[Co((NH_2)_2sar)]^{3+}$ and $[Co((CH_3)(NH_2)sar)]^{3+}$ with 2- and 3-Thiophenecarboxaldehydes[a]



[a] The inset is the general structure referred to in Table 1.

Table 1. Substituent Patterns and Numbering of Structurally Characterized Known Cage Amine Complexes Bearing Thienylmethyl Pendents

compound	R_1	R_2
1	2-thienylmethylammonio	NH_3^+
2	2-thienylmethylammonio	2-thienylmethylammonio
3	2-thienylmethylammonio	CH_3
4[16]	3-thienylmethylammonio	NH_3^+
5	3-thienylmethylammonio	3-thienylmethylammonio
6	3-thienylmethylammonio	CH_3
7[a]	3-thienylmethylammonio	CH_3

[a] Δ-$[Co((NH_2)(CH_3)sar)]^{3+}$ derivative.

work,[16] efforts were made to completely convert the amino-functionalized cage amine complex plus aldehyde to the imine and then reduce it with $[BH_4]^-$ and, although successful, these reactions proceeded over periods very dependent on the nature of the aldehyde, whereas in the present cases very similar conditions could be applied for all. As in earlier work with $[Co((NH_2)_2sar)]^{3+}$, it was found that use of a 1:1 ratio (complex/aldehyde) of reactants gave rise to a mixture of unreacted, monofunctionalized and difunctionalized products and thus, to simplify and optimize isolation of the desired monofunctionalized products **1** and **4**, a ratio of 1:1.5 was used to ensure negligible residual amounts of reactant. For the $[Co((NH_2)(CH_3)sar)]^{3+}$ derivatives, an excess of aldehyde (3−4 times) was used to ensure near complete monoalkylation. Many of the salts of the dialkylated complexes **2** and **5** exhibited low solubility in water, and particular procedures were developed for their effective chromatographic separation. The complexes were most conveniently isolated in their fully protonated forms.

All the complexes were characterized by ^1H NMR, ^{13}C NMR, and UV−visible spectroscopy, electrospray ionization mass spectrometry (ESI-MS), and elemental analyses, all measurements being consistent with the structures shown.

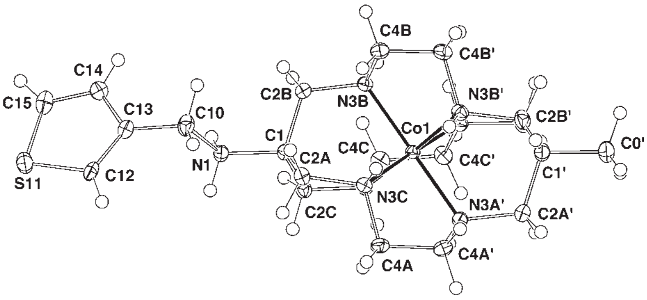


Figure 1. Molecular structure of the cation of **6** showing the major component only of the disordered thiophene group.

Description of the Crystal Structures. The results of the single crystal X-ray studies are consistent with the presented stoichiometries and connectivities. Complexes **3** and **6** are the mono- and diprotonated cations, the monosubstituted 2-thienylmethylammonio species, **3**, crystallizing as a mixed chloride/perchlorate salt and **6** as a chloride salt. Similarly, the structures of **2** and **5** are modeled as diprotonated and unprotonated complexes of the disubstituted 2-thienylmethylammonio ligand, crystallizing as the chloride **2** and mixed chloride/perchlorate **5**. The structures of the cations are similar, with Figure 1 showing **6** being typical in that the normal to the plane of the thiophene ring is approximately perpendicular to the pseudo-3-fold axis of the remainder of the cation. In this complex and the others, the angle defined above tends to lie in the range 74.0(3)−83.78(6)°. The one exception is cation 2 of **3**, shown in Figure 2, where the 2-thienylmethylammonio ligand is now bent, the angle between the normal to the thiophene plane and the axis of the cation being 26.3(1)°. The structures of the cations of **2** and **5** with the disubstituted ligand are similar to those of the monosubstituted species with the cation of **2** shown in Figure 3.

Hydrogen Bonding. Although the water molecule hydrogen atoms were located and refined in **4** and **6** only, in all the structures there are clearly hydrogen bonding interactions between the cations and the chloride anions. In previous structure determinations of similar metal containing cage compounds[22] it has been observed that where the cation adopts the lel_3 conformation, the anions are commonly involved in hydrogen-bonding between adjacent pairs of hydrogen atoms on the coordinated nitrogen atoms. Such an arrangement may be seen in the structures of **3** (NH···Cl 2.19−2.39 Å), **5** (NH···Cl 2.24−2.41 Å), and **6** (NH···Cl 2.21−2.42 Å), with two chloride and one perchlorate anions in a similar arrangement in **7** (NH···Cl 2.21−2.37 Å, NH···O 1.99, 2.14 Å), where three chloride ions are “chelated” in each case. In both of the structures of **5** and **7**, a chloride anion is also hydrogen bonded to the NH groups of adjacent cations related by a crystallographic 2_1 axis parallel to the *a* axis, forming a one-dimensional hydrogen bonded helical polymer. These are shown in Figures 4a and 4b.

The hydrogen bonding in **3** is similar except that there are two chloride ions bridging the two independent cations so that the cations and chloride anions form a two-dimensional hydrogen bonded polymer in the *ab* plane. This is shown in Figure 4c.

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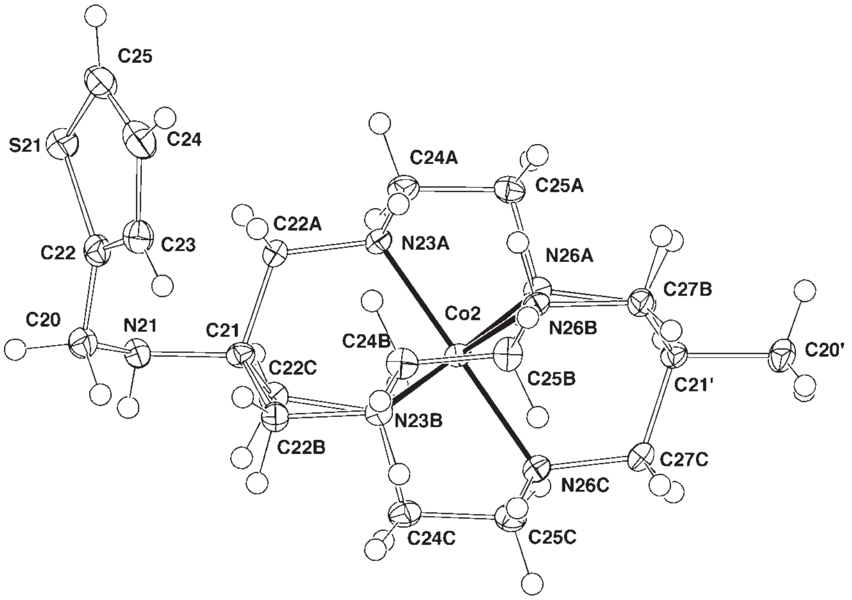

Figure 2. Molecular structure of the second cation of **3**.

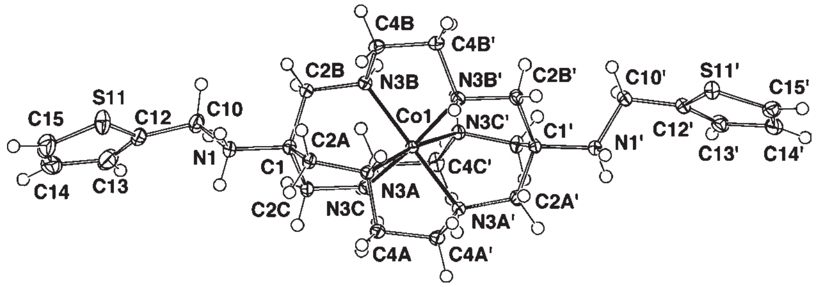

Figure 3. Molecular structure of the cation of **2**.

In contrast to these systems, in **2** only one chloride and one water molecule bridge between two of the hydrogen atoms of the coordinated nitrogen atoms with two water molecules interacting with the remaining pair of hydrogen atoms. The chloride ions in **1** (which is ob_3) are not involved in bridging between the hydrogen atoms of the same molecule but bridge between different molecules as part of a three-dimensional network.

The structure of **3** was analyzed using Hirshfeld surfaces, implemented in Crystal Explorer 2.1, where the authors of this program have provided a means of assessing intermolecular interactions using "a whole-of-molecule approach"[23,24] and can be used to highlight separate interactions.

Figures 5 and 6 show the Hirshfeld surfaces of the two independent cations in the structure of **3**. It is clear that the principal short contacts are those resulting from $H\cdots Cl^-$ interactions with contributions from perchlorate ions and water molecules. The figures clearly define these major contributions to the close contacts in the structure and are more readily interpreted than a simple tabulation of interatomic distances.

A representative fingerprint plot is shown (Figure 7) of molecule 1 in the structure of **3**, and it allows an estimation of the contribution of various interactions. Thus, $H\cdots Cl$ contacts account for only 11.5% (cation 1) and 12.9% (cation 2, plot not shown) of the total contacts from hydrogen atoms within the surface to entities without. However, the short contacts are unequivocally hydrogen-bonds to chloride ions. It is of interest that $H(\text{surface})\cdots O(\text{external})$ contacts {37.2% (mol. 1); 32.5% (mol. 2)} account for a relatively large proportion of the remaining interactions although they are clearly longer than the principal contacts.

Electrochemistry. Cyclic (CV) and Differential Pulse Voltammetry (DPV) were used to define the electrochemistry of the complexes in both water and acetonitrile. The data obtained for aqueous media are given in Table 2. Aqueous acetate media were required for **2** and **5** because of the low solubility of other salts. The pH of the solutions was adjusted to ~7.0 to ensure deprotonation of the apical amine groups as in previous electrochemical studies of cage complexes.[25] The successful deprotonation of the apical amines is supported by the crystallization of **5** from the electrochemical medium with three anions only, **5**$[Cl_2.ClO_4]$. The Co(III)/(II) couple, identified by comparison with earlier studies[26] was found to be most

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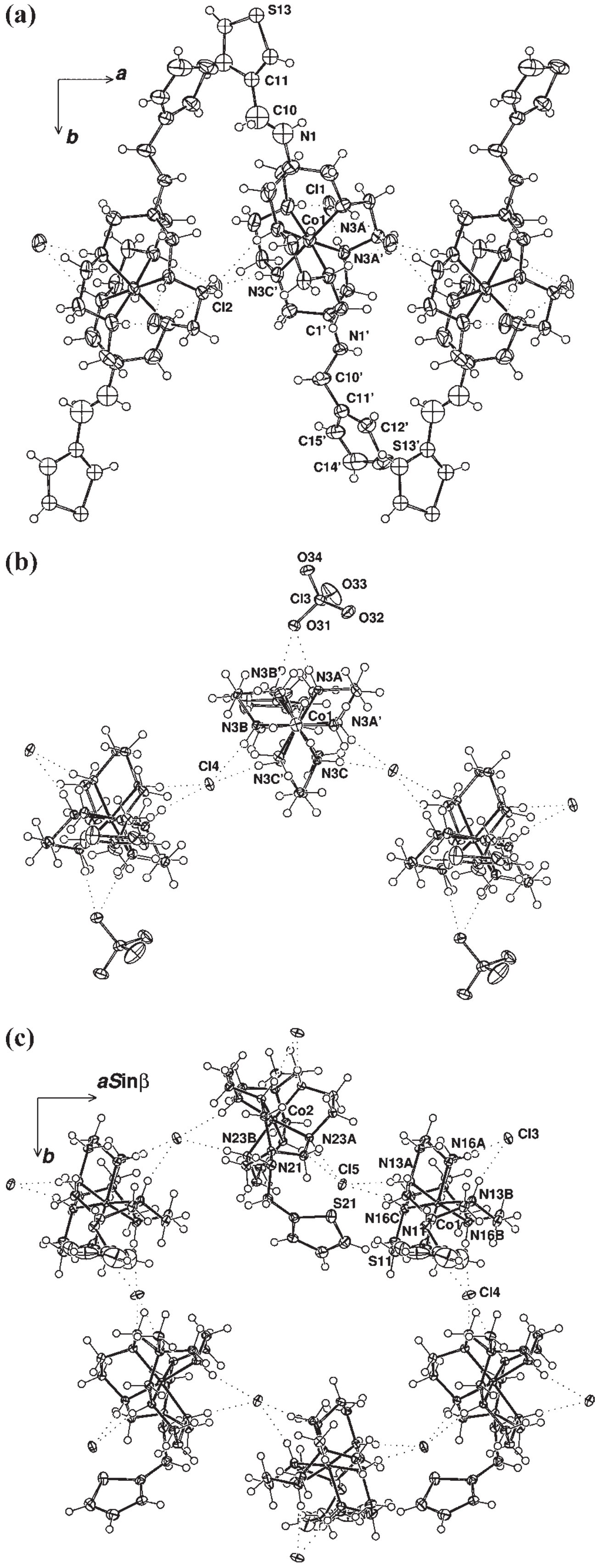

Figure 4. (a) Hydrogen-bonded polymer of **5** involving the cations and the chloride ions. (b) A view, projected along the cation axis, of the hydrogen-bonded supramolecular polymer of **7** involving the cation and the chloride and perchlorate anions. (c) Hydrogen bonding involving the cations and chloride anions in **3**.

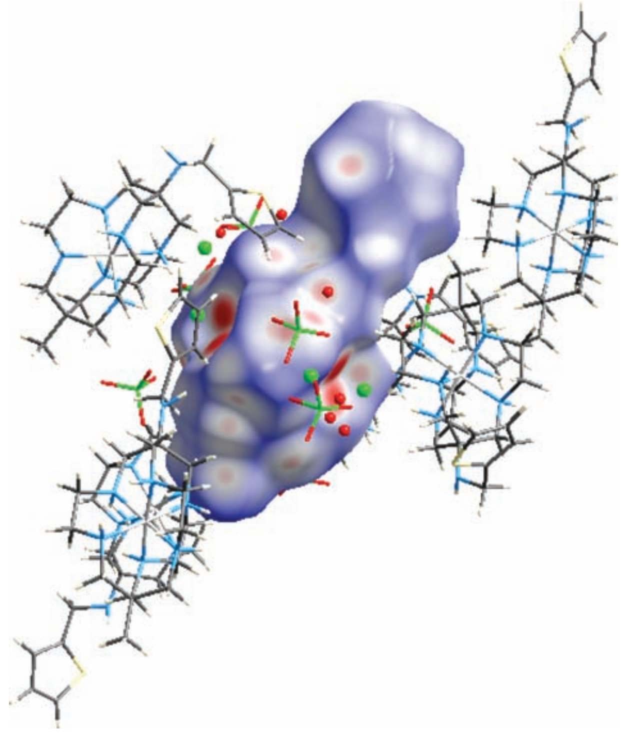

Figure 5. Hirshfeld surface of cation 1 in the structure of **3**, in relation to adjacent species in the cell. Red spheres, H_2O; green spheres Cl^- ions.

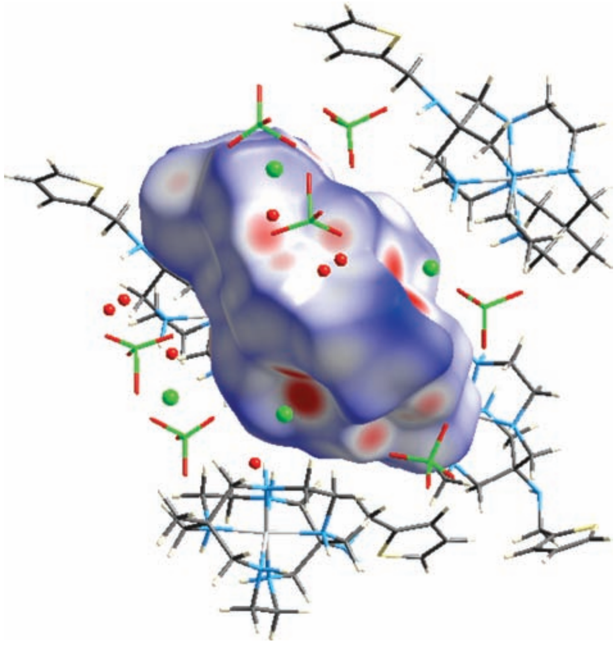

Figure 6. Hirshfeld surface of cation 2 in the structure of **3** with adjacent species in the cell. Red spheres, H_2O; green spheres, Cl^- ions.

quasi-reversible when using glassy carbon electrodes and to occur at potentials similar to those of other cage amine complexes. All the complexes show a decrease in oxidation potential compared to their corresponding starting materials, with the $[Co((NH_2)(CH_3)sar)]^{3+}$ derivatives showing the greatest change.

The electrochemical data for the protonated complexes in acetonitrile is presented in Table 3. Initial scans revealed the presence of poorly reversible Co(III)/(II)

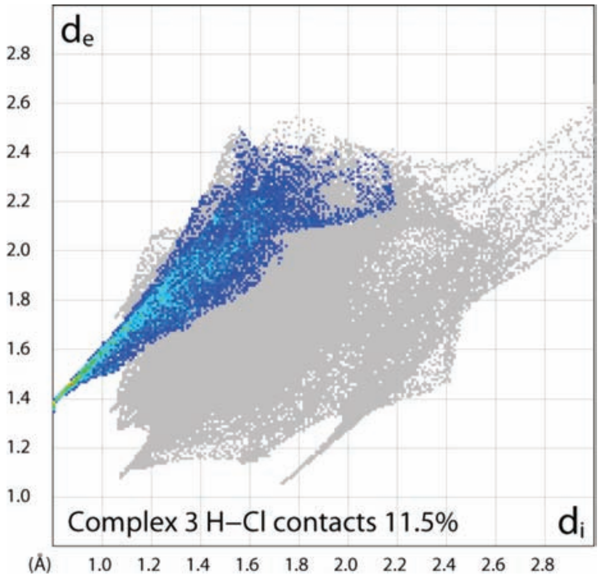

Figure 7. Fingerprint plot highlighting the H−Cl contacts in one of the two independent cations (cation 1) in the structure. Distances to the nearest atoms outside, d_e, and inside, d_i, are defined for points on the surface.

Table 2. Electrochemical Parameters for the Complexes in Water on Glassy Carbon Electrode

complex	$E_{1/2}$ (V, vs Ag/AgCl)	ΔE (mV)	I_a/I_c
$[Co((NH_3)_2sar)]^{5+}$	0.18[a]		
$[Co((NH_2)_2sar)]^{3+}$	−0.73[b]	140	0.94
$[Co((NH_3)(CH_3)sar)]^{4+}$	−0.42[a]		
$[Co((NH_2)(CH_3)sar)]^{3+}$	−0.72[b]	95	0.98
1[c]	−0.62	85	0.95
2[d]	−0.62	90	0.96
3[c]	−0.51	110	0.95
4[c]	−0.63	100	0.95
5[d]	−0.59	125	0.83
6[c]	−0.51	140	0.97

[a] 0.05 M $HClO_4$/0.05 M $NaClO_4$, ref 25. [b] 0.10 M $NaClO_4$, TRIS/$HClO_4$ buffer pH 7.13. [c] Data measured in 0.1 M $NaClO_4$ pH adjusted with 0.1 M TRIS/$HClO_4$ (pH = 7.0). [d] Data measured in 0.1 M NaOAc pH adjusted with 0.1 M TRIS/HOAc (pH = 7.0).

couples along with nearly irreversible peaks assigned to proton reduction, $[RNH_2R']^+ \rightarrow [RNHR']$ based on comparison with the unsubstituted cages and previously reported data,[26] and two to three oxidations between +1 to +2 V. Addition of Li_2CO_3 as a base capable of deprotonating the ammonium sites of the complexes led to voltammograms in which no proton reduction wave was detectable and the Co(III)/Co(II) waves were more nearly reversible, as evidenced by a decrease in the potential peak differences (ΔE) and an increase in the ratio of anodic and cathodic peak currents (I_a/I_c). Deprotonation of the apical amines in this manner was also evident in comparing the ^1H NMR spectra of two solutions of $\mathbf{6}\cdot(OTf)_3\cdot HOTf$ in d_3-MeCN, one with and one without added solid Li_2CO_3. After allowing 1 h for the heterogeneous reaction with Li_2CO_3, major changes in the spectrum were observed, including significant shifts in peaks position and shape. Most notable was the disappearance of a broad peak at ~8.0 ppm, due presumably to $[RNH_2R']^+$, and the appearance of a triplet (J = 6.8 Hz) at 1.75 ppm assigned to the deprotonated apical nitrogen, [RNHR′]. This coincides with a significant shift of the bridging methylene resonance from 4.28 to 3.70 ppm accompanied with increase in complexity of the coupling as a consequence of the presence, of now, diastereotopic protons.

In most cases, three oxidation peaks were observed which may be associated with the oxidation of either the thiophene[27] or the apical amine[28,29] based on their electrochemical potentials. Three peaks were observed regardless of the electrode used, that is, glassy carbon, platinum, or gold. There was generally a shift to lower potential upon treatment with Li_2CO_3, which is consistent with a decrease in overall charge enabling easier cation radical formation for either the amine or the thiophene. It is unlikely the oxidation observed at +1.3 to 1.4 V is associated with the thiophene oxidation as 3-methylthiophene has an oxidation potential of +1.39 V,[30] and this would be expected to shift to higher potential given its proximity to the highly charged Co(III) center.[31,32] Indeed the peaks at +1.54 to 1.88 V are more consistent with thiophene oxidations.[17] The peaks at even higher potential, +1.95 V or more, may be associated with further oxidation of either the thiophene or the amine.

Electropolymerization reactions of all the 3-thienylmethyl derivatives, **4**, **5**, and **6**, and the bis(2-thienylmethyl) derivative, **2**, were investigated in acetonitrile at glassy carbon and platinum electrodes employing both potentiostatic and potentiodynamic techniques. Potentiostatic investigations involved holding the potential at 0.05 V above each of the oxidation potentials given in Table 3 followed by examination of the electrodes using CV and DPV techniques. Under no conditions were any deposited materials detected on the electrodes. Potentiodynamic experiments involved repetitive cycling from −1.0 V to an upper switching voltage ranging from +1.5 to 2.2 V. While there were significant changes in some of the cyclic voltammograms (CVs), including the generation and increase of new peaks, examination of the electrodes did not show any signs of deposited materials.

When a transition-metal-appended thiophene has proven resistant to homopolymerization, two approaches employed to achieve reaction have been copolymerization with another thiophene monomer or grafting of the functionalized thiophene onto a preformed polythiophene-modified electrode.[12,33] Copolymerization of thiophene with all the complexes was investigated in acetonitrile with 1:1 ratios of thiophene to cage monomer (0.05 M each). Polymer films were deposited under both potentiostatic and potentiodynamic conditions, but displayed peaks for only thiophene and none for any Co(III)/Co(II) couple, indicating that the deposited material was solely polythiophene or the amount of cage present was below detectable limits. Changing the ratio of monomers affected only the rate of polythiophene formation. Alternatively, polythiophene-functionalized

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Table 3. Electrochemical Data for the Complexes in MeCN[a]

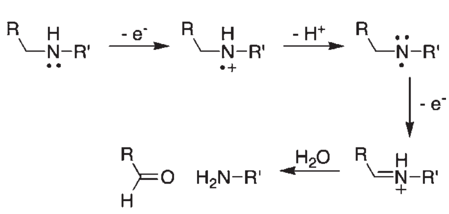
		(Co(III)/(II))				
complex[b]	base	$E_{1/2}$[c]	ΔE[d]	I_a/I_c[d]	$E([RNH_2R']^+)$[c]	E(oxidation)[c]
$[Co((NH_3)_2sar)]^{5+}$		−0.52	330	0.76	−1.11	
	Li_2CO_3	−0.75	190	0.92		
$[Co((NH_2)(CH_3)sar)]^{4+}$		−0.75	130	0.59	−0.56	
	Li_2CO_3	−0.72	130	0.98		
1		−0.70	230	0.88	−0.45	1.40, 1.74, 2.02
	Li_2CO_3	−0.78	180	0.95		1.32, 1.66, 1.96
2		−0.72	180	0.85	−0.42, −1.15	1.33, 1.55
	Li_2CO_3	−0.72	180	0.96		1.36, 1.75
3		−0.52	730	0.42	e	1.33, 1.63, 1.99
	Li_2CO_3	−0.61	220	0.83		1.30, 1.62, 1.98
4		−0.45	665	0.41	e	1.73, 2.08
	Li_2CO_3	−0.63	215	0.75		1.55, 1.88
5		−0.60	230	0.68	−0.33	1.38, 1.58, 2.02
	Li_2CO_3	−0.62	130	0.96		1.37, 1.54, 2.00
6		−0.68	195	0.89	−0.49, −1.04	1.39, 1.55, 1.95
	Li_2CO_3	−0.68	180	0.96		1.40, 1.97

[a] 0.1M LiOTf, GC Electrode. [b] All complexes are as triflate salts. [c] Data from DPV experiments. [d] Data from CV experiments. [e] Only a single peak was observed.

platinum electrodes were placed in solutions containing 0.1 M cage monomer and grafting attempted using both potentiostatic and potentiodynamic methods. No change in the properties of the films were detected even after extended periods.

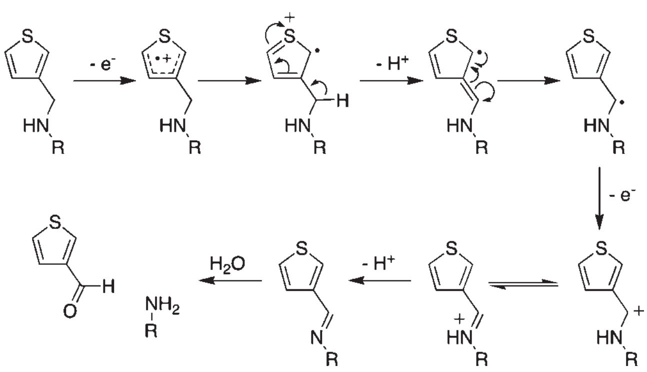
Oxidative Polymerization and Dimerization Investigations. The coupling of thiophenes can be achieved using a wide range of reagents[34] and *N*-alkylamino and alkyl(*N*-alkylamino) substituted thiophenes have been successfully polymerized chemically.[35−40] While a wide range of reagents can be used to couple thiophene,[17,34] we chose to investigate $FeCl_3$ and $(NH_4)_2[Ce(NO_3)_6]$ (CAN); the latter showed promise in prior work with **4**[16] and is a powerful oxidant. The polymerization attempts with $FeCl_3$ were unsuccessful. Polymerizations with CAN were performed in neat nitric acid as previously, though in contrast to preliminary work no highly insoluble material formed upon quenching in water. Analysis of the reaction mixtures revealed no components with higher molecular weight or charges greater than those of the starting materials. For all the complexes significant amounts of $[Co((NH_2)(CH_3)sar)]^{3+}$ and $[Co((NH_2)_2sar)]^{3+}$ were detected, presumably because of cleavage of the thienylmethyl groups. CAN has been shown to oxidatively cleave alkyl and aryl amines,[41−43] and we propose that a similar process is occurring with these complexes. The oxidation potential of CAN is sufficient to oxidize both the amine and the thiophene, so that the mechanism may occur via either of the mechanisms shown in Schemes 2 or 3.

Scheme 2. Electrochemical Oxidation of Amines[a]



[a] R = thienyl, R′ = cage amine.

Scheme 3. Proposed Mechanism for Cleavage of 3-Thienylmethyl Groups



Despite numerous reports of the successful homo- and copolymerization of charged transition metal complex appended thiophenes,[33] similar results could not be obtained with the complexes discussed herein. A number of workers have demonstrated the difficulty of homopolymerizing dicationic complexes,[12,15] and perhaps the increase to a 3+ metal ion charge, resulting in a 4+ charge on the putative radical cation intermediate, eliminates any possibility of polymerization due to charge repulsion. The bulk of the cage substituent may also inhibit homopolymerization, though this should not be a factor in

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copolymerization. Obvious avenues of investigation to the successful incorporation of cage amine units into polythiophene include reduction of the overall charge of the complex by ion-pairing with highly charged anions, use of a metal(II) species bound within the cage and extension of the linkage between the cage and the thiophene, potentially reducing both electrostatic and steric interactions. To avoid oxidative cleavage due to attack on the methylene link, an amide link could be used instead.

Conclusions

We have developed an efficient method for preparing thienylmethyl cage amine complexes employing reductive amination. As found with related Co(III) cage complexes, protonation-deprotonation of the apical amino substituents significantly influences their electrochemistry. Readily accessible thiophene oxidations were found, though all attempts to electropolymerize the complexes were unsuccessful. Chemically induced oxidative polymerization by $NH_4[Ce(NO_3)_6]$ was also unsuccessful, but did reveal cleavage of the thienylmethyl groups, presumably because of oxidation to the imine and subsequent hydrolysis.

Experimental Section

General Conditions. $[Co((NH_3)_2sar)]Cl_5$[44] and $[Co((NH_3)(CH_3)sar)]Cl_4$[44] were prepared as previously described. Δ-$[Co((NH_2)(CH_3)sar)]Cl_4$ was prepared from Δ-$[Co(sen)]^{3+}$[45] using analogous procedures to those previously described.[44] The complexes were converted to their acetate salts by slow passage of aqueous solutions through a column of acetate-form Dowex 1 × 2 anion exchange resin, the eluates being taken to dryness and the crude products recrystallized from $EtOH/Et_2O$. 2-Thiophenecarboxaldehyde (Aldrich) and 3-thiophenecarboxaldehyde[46] were distilled under reduced pressure and stored under argon in a freezer. AcOH (AR glacial), CaH_2, $(NH_4)_2[Ce(NO_3)_6]$, anhydrous CF_3SO_3H, $FeCl_3$ (anhydrous), $HClO_4$ (60% solution in water), HCl (32% solution in water), HNO_3 (68% in water), Li_2CO_3, NBu_4Br, $NaBH_3CN$, and $NaClO_4$ were used as received. AR absolute EtOH was stored over freshly activated 3 Å molecular sieves. Solvents for general use (CH_2Cl_2, EtOAc and EtOH) were distilled prior to use.

Chromatographic separations were performed using H^+ form Dowex 50Wx2 or Na^+ form SP Sephadex C-25 cation exchange resins under gravity flow. Dowex columns were eluted with varying concentrations of hydrochloric acid (0.5−8M) prepared from 32% aqueous hydrochloric acid and Millipore Milli-Q deionized water. Sephadex columns were eluted with various salt solutions prepared from AR grade salts and Millipore Milli-Q water, the complex cations present in the eluates being recovered by absorption of the eluates on Dowex 50Wx2, re-elution with HCl and evaporation of these eluates to dryness. Solvent removal was performed under reduced pressure (ca. 40 mmHg) on a rotary evaporator, using bath temperatures of about 50 °C for aqueous solutions and less than 50 °C for most organic solutions.

Nuclear Magnetic Resonance (NMR) spectra were obtained on either a Bruker ARX300 (^1H at 300.14 MHz and ^{13}C at 75.47 MHz), a Bruker AV500 (^1H at 500.13 MHz and ^{13}C at 125.8 MHz), or a Bruker AV600 (^1H at 600.13 MHz and ^{13}C at 150.90 MHz) spectrometer. Assignments of ^1H and ^{13}C resonances were made with the aid of DEPT, COSY, HSQC, and HMBC sequences. Spectra acquired in D_2O were referenced internally to either acetone (^1H, CH_3 at 2.22 ppm; ^{13}C, CH_3 at 30.89 ppm and C(O) at 215.94 ppm) or ethanol (^1H, CH_3 at 1.17 ppm and CH_2 at 3.65 ppm; ^{13}C, CH_3 at 17.47 ppm and CH_2 at 58.05 ppm). Electronic spectra of the pure complexes were collected in Milli-Q water using a HP8452 spectrophotometer. Mass spectra of cage amine complexes were collected using the ESI-MS technique either on a VG AutoSpec at the University of Western Australia or at the Mass Spectrometry Unit of the Australian National University. Elemental analyses (C, H, and N) were performed at the Research School of Chemistry Microanalytical Unit, Australian National University, Canberra, ACT. Prior to analysis, samples were dried under vacuum at 50 °C for at least 4 h. Electrochemical measurements were performed using a MacLab Potentiostat controlled by an Apple Power Macintosh G3 computer equipped with AD Instruments Echem Software (v 1.5.2). A standard 3-electrode system was employed using a platinum counter electrode, Ag/AgCl reference electrode (Cypress Systems "no-leak" Ag/AgCl or Teflon Ag/AgCl reference electrode) and either a circular (1 mm diameter) platinum, gold or glassy carbon in PEEK working electrode. Electrodes were polished using alumina (Griffin, fast cutting) on a polishing cloth, rinsed with solvent, and then sonicated for 10 min in the electrolyte to be used. Unless otherwise stated, CVs were collected in the range of ± 2 V or ± 5 V at sweep rates of 100 and 250 mV/s respectively. DPV conducted in the range of ± 2 V or ± 5 V was performed at sweep rates of 10 and 25 mV/s. All other parameters were kept constant, pulse width and height being set at 50 μs and 25 mV, respectively.

Purification of Solvents and Electrolytes for Electrochemistry. Water was purified using a Millipore Milli-Q system. MeCN (Unichrom 190 grade 99.7%) was passed through a column of neutral alumina (Fluka, 0.05−0.15 mm pH 7.0 ± 0.5; dried at 500 °C) and distilled from CaH_2 with the first 20% of the distillate being discarded. TRIS (tris(hydroxymethyl)aminomethane, Ajax, 99%) was recrystallized from $H_2O/EtOH$ and dried under vacuum for 4 h at 40 °C. NBu_4PF_6 was used as received (Aldrich, 99.5%) or prepared as previously described,[47] (using NBu_4Br in place of NBu_4I) and was recrystallized twice from hot absolute AR EtOH and dried under vacuum overnight at 100 °C. $LiClO_4$ (Fluka, 99%) was recrystallized twice from hot MeCN and dried under vacuum overnight at 50 °C. All solvents and electrolyte solutions were stored in the dark at 25 °C. Aqueous electrolytes were buffered by addition of TRIS to 0.1 M in the electrolyte followed by adjustment of the pH to ∼7.0 by addition of the conjugate acid of the electrolyte anion. Aqueous solutions were filtered through SGS 25 mm − Nylon 0.45 μm membrane syringe filters before use. Nonaqueous solutions were filtered through Phenomonex Phenex 13 mm − PTFE 22 μm syringe filters before use. Solutions were degassed by bubbling argon through the solution for at least 10 min. Deprotonation of the apical amino groups of the complexes under electrochemical investigation was achieved by treatment with Li_2CO_3 and conducted by stirring the electrolyte solution of the complex with ∼100 mg of anhydrous Li_2CO_3 followed by filtration through a 22 μm syringe filter (see above).

Structure Determinations. The crystal data for compounds **1**−**3** and **5**−**7** are summarized in Table 4 with the structures depicted in Figures 1 to 4, where displacement enevlopes have been drawn at the 50% probability amplitude level. Crystallographic data for the structures were collected at 100(2) K (150K for **2**, 170 K for **6**) using CCD area-detector instruments fitted with graphite-monochromated Mo Kα radiation (λ = 0.7107 Å), yielding N_{total} reflections, these merging to N unique after multiscan absorption correction (R_{int} cited), with N_o reflections having $I > 2\sigma(I)$. The structures were refined against F^2 with full-matrix least-squares using the program SHELXL-97.[48]

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Table 4. Crystal and Refinement Data

	complex					
	1	**2**	**3**	**5**	**6**	**7**
empirical formula	$C_{19}H_{46}Cl_5CoN_8O_7S$	$C_{24}H_{54}Cl_5CoN_8O_5S_2$	$C_{20}H_{41}Cl_3CoN_7O_{6.50}S$	$C_{24}H_{45}Cl_3CoN_8O_{5.50}S_2$	$C_{20}H_{54}Cl_4CoN_7O_7S$	$C_{20}H_{46}Cl_4CoN_7O_{15}S$
formula	$C_{19}H_{40}CoN_8S \cdot ClO_4 \cdot 4Cl \cdot 3H_2O$	$C_{24}H_{44}CoN_8S_2 \cdot 5Cl \cdot 5H_2O$	$C_{20}H_{39}CoN_7S \cdot 1.375ClO_4 \cdot 1.625Cl \cdot H_2O$	$C_{24}H_{42}CoN_8S_2 \cdot ClO_4 \cdot 2Cl \cdot 1.5H_2O$	$C_{20}H_{40}CoN_7S \cdot 4Cl \cdot 7H_2O$	$C_{20}H_{46}CoN_7 \cdot 3ClO_4 \cdot Cl \cdot 3H_2O$
formula weight	766.88	835.05	680.94	763.08	737.49	857.43
crystal system	monoclinic	triclinic	monoclinic	orthorhombic	triclinic	orthorhombic
space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P2_12_12_1$	$P\bar{1}$	$P2_12_12_1$
a (Å)	13.9924(3)	10.4870(10)	14.3458(2)	13.5627(4)	9.9640(8)	11.5396(3)
b (Å)	14.0651(5)	12.1800(10)	22.6817(3)	13.8650(3)	11.9100(10)	14.5424(4)
c (Å)	16.3511(5)	14.986(2)	18.2093(2)	17.5765(5)	14.7250(12)	19.7738(5)
α (deg.)	90	73.433(2)	90	90	95.0180(10)	90
β (deg.)	104.631(3)	89.839(2)	92.888(1)	90	93.2580(10)	90
γ (deg.)	90	79.880(2)	90	90	105.5250(10)	90
V (Å^3)	3113.62(16)	1803.9(3)	5917.55(13)	3305.21(15)	1671.4(2)	3318.31(15)
Z	4	2	8	4	2	4
ρ (g cm^{-3})	1.636	1.537	1.529	1.533	1.465	1.716
μ (mm^{-1})	1.10	1.01	0.97	0.94	0.94	0.98
$T_{min/max}$	0.64	0.88	0.88	0.82	0.79	0.94
crystal dimensions (mm)	0.23 × 0.14 × 0.12	0.45 × 0.28 × 0.21	0.41 × 0.39 × 0.30	0.34 × 0.12 × 0.05	0.58 × 0.52 × 0.37	0.32 × 0.21 × 0.19
θ_{max} (deg.)	39.1	33.5	35.0	29.4	28.6	37.2
N_{total}	87983	27427	201121	32757	14430	102379
N	17471	13026	26026	8339	7599	16695
R_{int}	0.081	0.019	0.041	0.063	0.018	0.043
N_o [$I > 2\sigma(I)$]	10507	11017	16521	4717	6600	11837
data/restraints/parameters	17471/16/411	13026/15/483	26026/106/786	8339/17/419	7599/31/434	16695/6/450
goodness-of-fit	1.16	0.95	1.09	0.94	1.06	1.00
R_1, wR_2 [$I > 2\sigma(I)$]	0.059, 0.164	0.034, 0.089	0.057, 0.176	0.052, 0.104	0.032, 0.083	0.039, 0.094
R_1, wR_2 [all data]	0.100, 0.218	0.042, 0.095	0.086, 0.201	0.112, 0.125	0.037, 0.084	0.056, 0.096
a(,b)	0.115	0.055(1.3)	0.120	0.061	0.048(0.55)	
$\lvert\Delta\rho_{max}\rvert$ (e Å^{-3})	3.1	1.34	2.7	0.65	0.74	1.34

Anisotropic displacement parameters were refined for the non-hydrogen atoms, hydrogen atom treatment following a riding model. Reflection weights were $(\sigma^2(F)^2 + (aP)^2(+bP))^{-1}$ $(P = (F_o^2 + 2F_c^2)/3)$. Neutral atom scattering factors were employed.

Individual variations in procedure were as follows:

(1) The hydrogen atoms for water molecule O(6) were not located. Those for O(5) and O(7) were refined with restrained geometries.

(2) All solvent water molecule hydrogen atoms were located and refined with geometrical restraints.

(3) The perchlorate and chloride anions 1−5 were easily identifiable. Two tetrahedral groups were identified in the remaining electron density and were modeled as perchlorate anions with occupancies constrained to 0.5 and 0.25 after trial refinement. A large residual peak was assigned to a chloride ion, Cl(8), with occupancy set at 0.5 after trial refinement. Other surrounding peaks were modeled as oxygen atoms of water molecules with occupancies set at 0.5. Geometries of perchlorate anions (6) and (7) were restrained to ideal values. Hydrogen atoms were located on N(11) and N(21), consistent with the cation charge +3. The associated geometries were refined with restraints. Solvent water molecule hydrogen atoms were not located.

(5) Both CH_2NH-thiophene chains were disordered over two sets of sites with occupancy factors refined to 0.658(5) and 0.833(8) and their complements for the unprimed and primed parts, respectively. The atoms of both components of the unprimed section were refined with isotropic displacement parameters. The perchlorate anion was rotationally disordered about the Cl(3)−O(31) bond, occupancies being constrained to be the same as those for the atoms C(10)−C(15) after preliminary refinement gave almost identical values. Water molecule 2 was refined with constrained occupancy of 0.5 after trial refinement; the hydrogen atoms for both solvent water molecules were not located, X_{abs} was −0.032(2).

(6) The thiophene group was rotationally disordered with occupancies refined to 0.694(3) and complement for the two components. Geometries of the minor component were restrained to ideal values. Water molecule hydrogen atoms were located and refined with restrained geometries.

(7) Water molecule hydrogen atoms for O(2) and O(3) were included with the water molecule geometries restrained to ideal values. Those for water molecule O(1) were less obvious and subsequently omitted from the model.

Full details of the structure determinations for six compounds have been deposited with the Cambridge Crystallographic Data Centre as **CCDC** 746907 **1**, 746908 **2**, 746909 **3**, 746910 **5**, 746911 **6**, and 746912 **7**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223−336−033; or e-mail: deposit@ccdc.cam.ac.uk.

Synthesis of the Complexes 1−7: General Procedure. The following is a generalized procedure used for the synthesis of the 2- and 3-thienyl derivatives of the $[Co((NH_2)_2sar)]^{3+}$ and

$[Co((NH_2)(CH_3)sar)]^{3+}$. The particular quantities of reagents used and workup procedures for each separate reaction are detailed subsequently.

The cage amine complex, $[Co((NH_2)_2sar)][OAc]_3$ or $[Co((NH_2)(CH_3)sar)][OAc]_3$ and 3 Å molecular sieves were placed in a 2-neck round-bottomed flask fitted with a reflux condenser, and dried under vacuum for 30 min. To the flask was added Absolute AR EtOH, and the mixture stirred until all of the cage complex had dissolved. Thiophene carboxaldehyde, $NaBH_3CN$, and AcOH were then added, and the mixture was heated at reflux. The progress of the reactions was monitored on SP-Sephadex mini-columns (0.05−0.2 M trisodium citrate eluant) until no further change occurred. The reaction mixture was filtered through a pad of Celite to remove the now powdered molecular sieves and washed thoroughly with EtOH and H_2O. The EtOH in the filtrate was removed under reduced pressure, and the residue dissolved in water. This solution was washed with both CH_2Cl_2 (×2) and EtOAc. The traces of CH_2Cl_2 and EtOAc in the aqueous fraction were removed under reduced pressure, and the solution was diluted further with deionized water prior to absorption on a chromatography column for separation of the products.

Preparation of the Complexes 1 and 2. The reaction was performed using $[Co((NH_2)_2sar)][OAc]_3$ (507 mg, 0.921 mmol), 2-thiophenecarboxaldehyde (299 mg, 2.67 mmol), $NaBH_3CN$ (235 mg, 3.74 mmol), 3 Å molecular sieves (∼2 g), EtOH (70 mL), and AcOH (2 mL). Chromatographic separation was achieved on SP-Sephadex using 0.25−1.0 M aqueous NaOAc giving 2 bands, **B1** and **B2**.

B1: 1. This band was absorbed onto a column of H^+ Dowex 50Wx2, the column washed with deionized H_2O and 1 M HCl, and the complex eluted with 3 M HCl. This eluate was taken to dryness under reduced pressure, and the residue recrystallized from 1 M HCl/EtOH, 127 mg. ^1H NMR (D_2O): δ (ppm) 2.89−3.00 (cm, 12H, cage methylene), 3.44−2.61 (cm, 12H, cage methylene), 4.39 (cm, 2H, bridging CH_2), 7.10 (dd, 1H, $J_1 = 5.1$ Hz, $J_{12} = 3.6$ Hz, thienyl), 7.23 (dd, 1H, $J_{11} = 3.5$ Hz, $J_{12} = 0.5$ Hz, thienyl), 7.52 (dd, 1H, $J_{11} = 5.1$ Hz, $J_{12} = 1.0$ Hz, thienyl) $^{13}C\{^1H\}$ NMR (D_2O): δ (ppm) 41.22 (CH_2, bridging methylene), 51.48, 51.95, 54.80, 54.84 (CH_2, cage methylene), 56.56, 61.55 (C_q, cage cap), 128.45, 128.85, 130.47 (CH, thienyl), 134.71 (C_q, thienyl) ESI-MS$^+$ (H_2O) {Molecular Ion = $[C_{19}H_{38}CoN_8]^{3+}$} *m*/*z* (Cl^- Salt) 234.6 $[C_{19}H_{37}CoN_8]^{2+}$ = MI − H^+; 467.2 $[C_{19}H_{36}CoN_8]^+$ = MI−2H^+; 503.2 $[C_{19}H_{37}CoN_8Cl]^+$ = MI −H^++Cl^-; 503.2 $[C_{19}H_{38}CoN_8Cl_2]^+$ = MI + 2Cl^- Analysis Found: C, 32.60; H, 6.27; N, 15.41. Calcd for $CoC_{19}H_{40}N_8SCl_5.3H_2O$: C, 32.47; H, 6.60; N, 15.94% UV−vis (H_2O): {λ_{max} (ε_{max})} 472 (150 L mol^{-1} cm^{-1}), 234 (11700 L mol^{-1} cm^{-1}). Crystals of the tetrachloride-monoperchlorate suitable for single crystal X-ray diffraction were isolated by slow evaporation of the chloride salt from a 0.1 M $NaClO_4$ acidified with $HClO_4$.

B2: 2. Upon standing, a small amount of the material precipitated from solution and was dissolved by warming before absorption onto a column of H^+ Dowex 50Wx2. The column was washed with deionized H_2O, 1 M HCl and 3 M HCl, the product was eluted with 50/50 8 M HCl/EtOH (Note: Elution with just HCl reduces the recoveries). The eluate was reduced to dryness and the crude product recrystallized from 2 M HCl, 346 mg. ^1H NMR (D_2O): δ (ppm) 2.92−3.06 (cm, 12H, cage methylene), 3.45−3.51 (cm, 6H, cage methylene), 3.57−3.62 (cm, 6H, cage methylene), 4.40 (AB quartet, 4H, bridging methylene), 7.10 (dd, 2H, $J_{11} = 5.2$ Hz, $J_{12} = 3.5$ Hz, thienyl), 7.23 (dd, 2H, $J_{11} = 3.5$ Hz, $J_{12} = 1.2$ Hz, thienyl), 7.53 (dd, 2H, $J_{11} = 5.1$ Hz, $J_{12} = 1.2$ Hz, thienyl) $^{13}C\{^1H\}$ NMR (D_2O): δ (ppm) 41.21 (CH_2, bridging methylene), 51.51, 54.00 (CH_2, cage methylene), 61.19 (C_q, cage cap), 128.46, 128.88, 130.51 (CH, thienyl), 134.59 (C_q, thienyl) ESI-MS$^+$ (H_2O) {Molecular Ion = $[C_{24}H_{40}CoN_8S_2]^{3+}$} *m*/*z* ($Cl^-$ Salt) 281.9 $[C_{24}H_{39}CoN_8S_2]^{2+}$ = MI−H^+; 562.8 $[C_{24}H_{38}CoN_8S_2]^+$ = MI−2H^+; 598.7 $[C_{24}H_{39}CoN_8S_2Cl]^+$ = MI −H^++ Cl^-; 634.7 $[C_{24}H_{40}CoN_8S_2Cl_2]^+$ = MI + 2Cl^- UV−vis (H_2O): {λ_{max} (ε_{max})} 472 (140 L mol^{-1} cm^{-1}), 234 (29500 L mol^{-1} cm^{-1}). Crystals of the pentachloride hydrate suitable for single crystal X-ray diffraction were isolated by slow evaporation of an aqueous solution.

Preparation of Complex 3. The reaction was performed using $[Co((NH_2)(CH_3)sar)][OAc]_3$ (1.05 g, 1.91 mmol), 2-thiophenecarboxaldehyde (625 mg, 5.57 mmol), $NaBH_3CN$ (475 mg, 7.56 mmol), 3 Å molecular sieves (∼1 g), EtOH (50 mL), and AcOH (1 mL). After general workup the mixture was absorbed onto a column of H^+ Dowex 50Wx2, which was washed with deionized H_2O and 1 M HCl, before elution with 2H HCl produced one band (**B1**) and a further band (**B2**) was eluted with 5 M HCl.

B1: $[Co((NH_2)_2sar)]^{3+}$. The eluate was reduced to dryness and the ^1H NMR spectrum showed it to be unreacted starting material.

B2: 3. This band was absorbed onto a column of H^+ Dowex 50Wx2, the column washed with deionized H_2O, 1 M HCl, 3 M HCl, and the complex eluted with 5 M HCl. The eluate was taken to dryness under reduced pressure, and the crude product recrystallized from H_2O/MeOH, 876 mg. ^1H NMR (D_2O): δ 0.94 (s, 3H, cage Me), 2.40−3.59 (cm, 24H, cage), 4.34−4.45 (cm, 2H, bridging CH_2), 7.10 (dd, $J_{11} = 5.15$ Hz, $J_{12} = 3.55$ Hz, 1H, thiophene), 7.23 (dd, $J_{11} = 3.55$ Hz, $J_{12} = 1.2$ Hz, 1H, thiophene), 7.52 (dd, $J_{11} = 5.15$ Hz, $J_{12} = 1.2$ Hz, 1H, thiophene). $^{13}C\{^1H\}$ NMR (D_2O): δ 19.97 (CH_3, cage Me), 41.15 (CH_2, bridging methylene), 42.89 (C_q, cage), 51.61, 55.13, 55.24 (CH_2, cage methylene), 61.44 (C_q, cage), 128.46, 128.89, 130.54 (CH, thiophene), 134.58 (C_q, thiophene) ESI-MS$^+$ (H_2O) {Molecular Ion = $[C_{20}H_{39}CoN_7S]^{3+}$} *m*/*z* ($Cl^-$ salt) 466.3 $[C_{20}H_{37}CoN_7S]^+$ = MI − 2H^+; 502.5 $[C_{20}H_{38}CoN_7SCl]^+$ = MI − H^+ + Cl^-, 538.3 $[C_{20}H_{38}CoN_7SCl_2]^+$ = MI + Cl^- UV−vis (H_2O): {λ_{max} (ε_{max})} 472 (120 L mol^{-1} cm^{-1}), 236 (19700 L mol^{-1} cm^{-1}). Crystals of the tetrachloride hydrate suitable for single crystal X-ray diffraction were isolated by slow evaporation of an aqueous solution of the complex.

Preparation of Complexes 4 and 5. The reaction was performed using $[Co((NH_2)_2sar)][OAc]_3$ (1.02 g, 1.85 mmol), 3-thiophenecarboxaldehyde (612 mg, 5.46 mmol), $NaBH_3CN$ (251 mg, 3.99 mmol), 3 Å molecular sieves (∼2 g), EtOH (60 mL), and AcOH (1 mL). Chromatographic separation was achieved on SP-Sephadex using 0.25−1.0 M aqueous NaOAc giving 3 bands, **B1**, **B2**, and **B3**.

B1: $[Co((NH_2)_2sar)]^{3+}$. Recovery of the complex via Dowex/HCl treatment enabled its identification as unreacted starting material.

B2: 4. This band was absorbed onto a column of H^+ Dowex 50Wx2, the column washed with deionized H_2O and 1 M HCl, and the complex eluted with 3 M HCl. The eluate was taken to dryness, and the crude product recrystallized from 1 M HCl/EtOH, 214 mg. Spectroscopic data were consistent with previously characterized material.[16] UV−vis (H_2O): {λ_{max} (ε_{max})} 472 (130 L mol^{-1} cm^{-1}), 234 (20600 L mol^{-1} cm^{-1}).

B3: 5. This band was absorbed onto a column of H^+ Dowex 50Wx2, the column washed with deionized H_2O, 1 M HCl, 3 M HCl, and the complex eluted with 50/50 8 M HCl/EtOH. The eluate was taken to dryness, and the crude product recrystallized from 1 M HCl, 683 mg. Spectroscopic data were consistent with those of previously characterized material.[16] UV−vis (H_2O): {λ_{max} (ε_{max})} 472 (140 L mol^{-1} cm^{-1}), 234 (24200 L mol^{-1} cm^{-1}). Crystals suitable for single crystal X-ray diffraction were isolated by slow cooling from 100 °C in a Dewar flask, of a saturated solution of the chloride salt in 0.1 M $NaClO_4$ buffered to pH 7 with TRIS/$HClO_4$, to yield the mixed chloride-perchlorate salt.

Preparation of Complex 6. The reaction was using $[Co((NH_2)(CH_3)sar)][OAc]_3$ (998 mg, 1.82 mmol), 3-thiophenecarboxaldehyde (598 mg, 5.33 mmol), $NaBH_3CN$ (448 mg, 7.12 mmol), 3 Å molecular sieves (~1 g), EtOH (60 mL), and AcOH (1 mL). After general workup the mixture was absorbed onto a column of H^+ Dowex 50Wx2, which was washed with DeI H_2O and 1 M HCl. Elution with 2H HCl produced one band, **B1**, and a further band, **B2**, was eluted with 5 M HCl.

B1: **$[Co((NH_2)_2sar)]^{3+}$.** The eluate was reduced to dryness, and the ^1H NMR spectrum of the crude product revealed it was starting material.

B2: 6. This band was absorbed onto a column of H^+ Dowex 50Wx2, the column washed with deionized H_2O, 1 M HCl, 3 M HCl, and the complex eluted with 5 M HCl. The eluate was taken to dryness under reduced pressure, and the crude product recrystallized from H_2O/EtOH, 847 mg. ^1H NMR (D_2O): δ 0.94 (s, 3H, cap Me), 2.42−3.62 (m, 24H, cage), 4.31 (m, 2H, bridge CH_2), 7.19 (dd, $J_{11} = 5.0$ Hz $J_{12} = 1.3$ Hz, 1H), 7.53 (dd, $J_{11} = 5.0$ Hz, $J_{12} = 3.0$ Hz, 1H), 7.61 (d, $J_1 = 1.6$ Hz, 1H) $^{13}C\{^1H\}$ NMR (150.9 MHz, D_2O, EtOH ref): δ 19.95 (CH_3, cap Me), 41.56 (CH_2, bridging methylene), 42.99 (C_q, cage), 50.99, 55.16, 55.17, 55.27 (CH_2, cage), 61.50 (C_q, cage), 128.31, 128.48, 128.60 (CH, thiophene), 131.52 (C_q, thiophene) ESI-MS^+ (H_2O) {Molecular Ion = $[C_{20}H_{39}CoN_7S]^{3+}$} *m*/*z* ($Cl^-$ salt) 466.4 (100%) $[C_{20}H_{37}CoN_7S]^+$ = MI − $2H^+$; 502.5 (5%) $[C_{20}H_{38}CoN_7SCl]^+$ = MI − H^+ + Cl^- FAB-MS^+ (NAOB) *m*/*z* 124.0 (57%), 137.0 (74%), 154.0 (100%), 242.0, 307.0 (15%), 391.3 (16%), 466.1 (22%) $[C_{20}H_{37}CoN_7S]^+$ = MI − $2H^+$; 502.0 (11%) $[C_{20}H_{38}CoN_7SCl]^+$ = MI − H^+ + Cl^- UV−vis (H_2O): {λ_{max} (ε_{max})} 472 (140 L mol^{-1} cm^{-1}), 238 (20500 L mol^{-1} cm^{-1}). Crystals suitable for single crystal X-ray diffraction were isolated by slow evaporation of an aqueous solution of the complex.

Preparation of Complex 7. The reaction was performed using {Δ-$[Co((NH_2)(CH_3)sar)]$}$[OAc]_3$ (357 mg, 0.65 mmol), 3-thiophenecarboxaldehyde (211 mg, 1.88 mmol), $NaBH_3CN$ (176 mg, 2.80 mmol), 3 Å molecular sieves (~1 g), EtOH (30 mL), and AcOH (0.5 mL). After general workup the mixture was absorbed onto a column of H^+ Dowex 50Wx2, which was washed with deionized H_2O and 1 M HCl. Elution with 2H HCl produced one band, **B1**, and a further band, **B2**, was eluted with 5 M HCl.

B1: **$[Co((CH_3)(NH_2)sar)]^{3+}$.** The eluate was reduced to dryness, and the ^1H NMR spectrum of the crude product was consistent with it being starting material, $[Co((NH_2)_2sar)]^{3+}$

B2: [**7**]. This band was absorbed onto a column H^+ Dowex 50Wx2, the column washed with deionized H_2O, 1 M HCl, 3 M HCl, and the complex eluted with 5 M HCl. The eluate was taken to dryness under reduced pressure, and the crude product recrystallized from H_2O/EtOH, 286 mg. ^1H NMR (D_2O): δ (ppm) 0.94 (s, 3H, cap Me), 2.42−2.50 (m, 3H, cage), 2.72−2.92 (cm, 6H, cage), 2.97−3.10 (m, 6H, cage), 3.34−3.53 (cm, 6H, cage), 3.54−3.61 (m, 3H, cage), 4.30 (AB quartet, 2H, bridge CH_2), 7.19 (m 1H, thiophene), 7.53 (m, 1H, thiophene), 7.60 (d, $J = 1.6$ Hz, 1H, thiophene) $^{13}C\{^1H\}$ NMR (D_2O): δ (ppm) 19.95 (CH_3, cap Me), 41.54 (CH_2, bridging methylene), 42.97 (C_q, cage), 51.04, 55.16, 55.17, 55.26 (CH_2, cage), 61.48 (C_q, cage), 128.21, 128.47, 128.56 (CH, thiophene), 131.70 (C_q, thiophene). Crystals suitable for single crystal X-ray diffraction determination were isolated by slow evaporation of an aqueous solution of the mixed chloride-perchlorate salt.

General Method for Conversion of Complexes to Acetate and Triflate Salts. **Acetate Salts.** The chloride salts of complexes **1** to **7** were converted to the corresponding acetate salts by slow passage through a column of Dowex 1 × 2 anion exchange resin (OAc^- form). The eluates were reduced to dryness, redissolved in EtOH, and reduced to dryness repeatedly until no odor of acetic acid could be detected. The crude products were recrystallized from EtOH/Et_2O and dried under vacuum at 50 °C overnight.

Triflate salts. The acetate salts were dissolved in a minimum volume of absolute EtOH and cooled in an ice bath before addition of neat CF_3SO_3H. The precipitate was collected, recrystallized from MeCN/Et_2O, and dried under vacuum at 60 °C overnight.

Perchlorate Salts. ***Caution!*** *As per the triflate salts, except $HClO_4$ (60% in H_2O) was used instead of CF_3SO_3H. In practice minimal amounts of perchloric acid were added to the ice-cold ethanol behind a safety-shield.*

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Supporting Information Available: X-ray crystallographic data in CIF format, Tables S1−S3, and Figures S1−S17. This material is available free of charge via the Internet at http://pubs.acs.org.