Precursors to New Molecular Tube Ligands. 1. Double-Capped Trinuclear Cobalt Complexes of Aminoethanethiol

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$Co(SCH_2CH_2NH_2)_3$ has been capped on the facial amines through protection of the thiolates by coordination of two such complexes to a central Co(III) ion. The trinuclear species forming the framework is the complex ion $[Co\{Co(SCH_2CH_2NH_2)_3\}_2]^{3+}$, **1**, in meso and rac forms which have been chromatographically separated and identified. Hexaimine derivatives of **1**, $[Co\{Co(SCH_2CH_2N{=}CH_2)_3\}_2]^{3+}$, **2**, have been synthesized in good yield by reaction with excess paraformaldehyde and base in CH_3CN. The hexaimines have been reacted with NH_3 to yield dicapped aza species $[Co\{Co(SCH_2CH_2NHCH_2)_3N\}_2]^{3+}$, **3**, or reacted with nitromethane to yield the nitro-capped ions $[Co\{Co(SCH_2CH_2NHCH_2C)_3CNO_2\}_2]^{3+}$, **4**. The reactions are retentive; i.e., meso reactant yields meso product. All of the products have been characterized by ^1H NMR, ^{13}C NMR, and UV−vis spectroscopy. Electrochemical measurements (CV and dc coulometry) in CH_3CN indicate that the central Co(III) ion in all of the species is reduced first, followed by the two terminal Co(III) centers. The formal potentials show that the Co(III) oxidation state is stabilized by the six thiolate bridging ligands in comparison to six thioether donor atoms, whereas capping has a destabilizing effect.

Introduction

Our group has been interested in the design and synthesis of molecular tube ligands[1] which are capable of encapsulating several metal ions in adjacent octahedral coordination sites, and hence trinuclear species may be useful as potential synthons. The complex hexakis(2-aminoethanethiolato)tricobalt(III), $[Co\{Co(SCH_2CH_2NH_2)_3\}_2]^{3+}$, **1** (Figure 1), is the most prominent of the trinuclear transition metal ion complexes with bridging thiolates.[2−15] Three kinetically inert metal ions hold the ligands in positions which are predisposed for capping of the terminal facial amines; hence, the central sulfur atoms could then be strapped using appropriate modifications of existing synthetic strategies.[16−19]

Aza-, nitromethylidyne- and formylmethylidyne-capping groups are easily attached to tris facial amines,[16,17,19,20] and herein, we describe some successful methods for the trinuclear Co(III) complexes. The synthetic aspects of this work have to some degree advanced the chemistry of encapsulating ligands, as a neutral and insoluble compound such as $[Co(SCH_2CH_2NH_2)_3]$ can be solubilized and capped by utilizing an increase in the overall positive charge of the species by attachment to a central Co^{3+} ion; such a reaction had previously proved difficult. Another aspect of the synthesis was the use of a central metal ion to protect the six sulfur donors, allowing only the amine groups to react with the capping reactants. In addition, these trinuclear complexes offer the ability to synthesize Co(III) complexes of new tripodal S_3N_3 ligands with terminal thiolates, by reduction of the central Co(III) ion. Such complexes are difficult to synthesize by conventional organic methods, and we herein report the electrochemical data which facilitate this route.

Results and Discussion

The trinuclear complex **1** is synthesized in good yield by published procedures.[4,9] The complex exists in meso and rac forms which have been separated by fractional crystallization[5] and by chromatography on Sephadex.[17,21] We have found that

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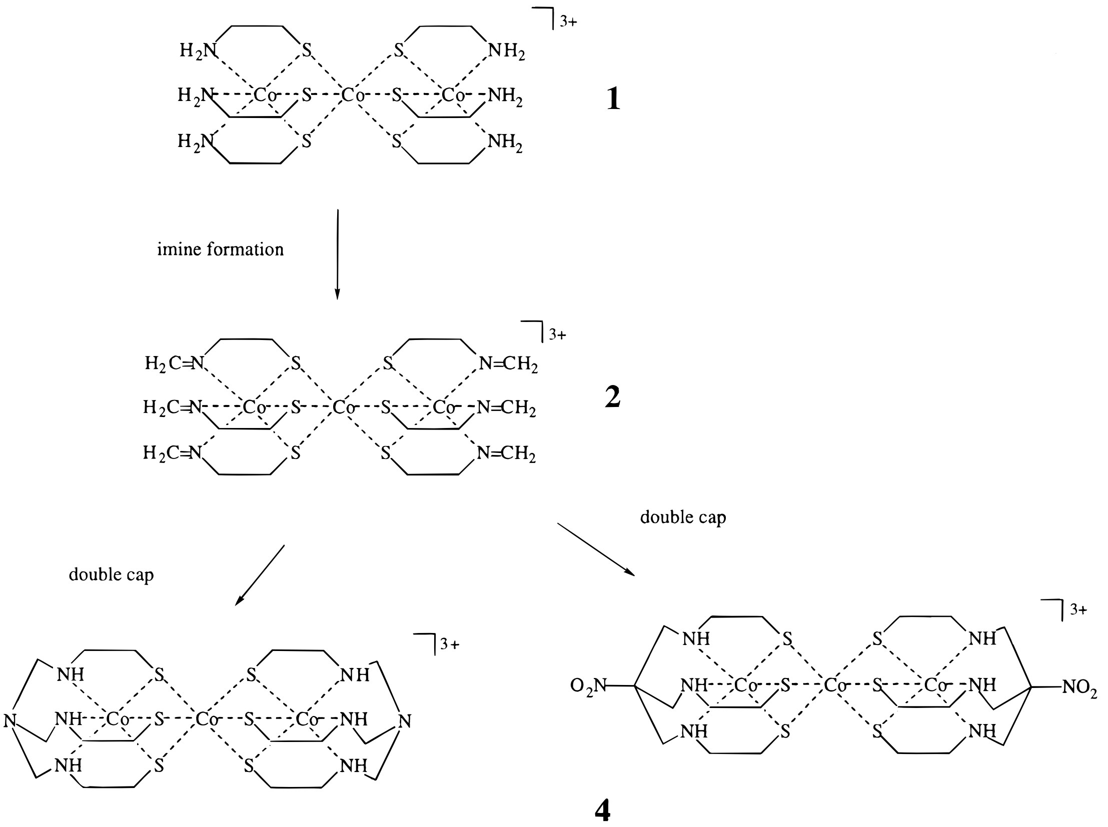

Figure 1. Flow diagram illustrating the potential of trinuclear metal ion substrates as a route to new macrocyclic cage and tube ligands

the two isomers are cleanly separated by ion-exchange chromatography on Dowex and are readily recovered by rotary evaporation or freeze-drying and recrystallization. In the separation, the meso isomer elutes first. The second band was shown to contain the racemate by independent resolution, both by the conventional method using $[Sb_2((+)\text{-tartrate})_2]^{2-}$, which selectively crystallizes the (+) enantiomer,[5] and by chromatographic resolution on Cellex[22] and Sephadex using $K_2[Sb_2((+)\text{-tartrate})_2]$ as the eluant.[21] The efficiency of the resolution is improved if one starts with the pure racemate rather than the meso/rac mixture as originally used.[5,22]

Several preliminary attempts were made to form the capped trinuclear species in a one-step reaction using paraformaldehyde and NH_3, or paraformaldehyde, nitromethane, and base in CH_3CN; however, none of the reactions were successful. The NH_3/formaldehyde and nitromethane/formaldehyde/base mixtures normally undergo side reactions which are slow; however, in our case, the side reactions dominated because of a slower rate of imine formation of the trinuclear species **1**. As the hexaimine complexes are the key intermediates for the capping reactions, we sought to isolate and purify these precursor imines.

The synthetic methodology for the hexaimine was developed from recent capping procedures for $[Co(sen)]^{3+}$,[18,19] and *meso*- and *rac*-hexaimine complexes were obtained in good yield (ca. 80%) by reaction of the *meso*- or *rac*-hexathiolate with a large excess of paraformaldehyde and Et_3N base. The reaction was complete in 10−16 h at room temperature; the corresponding reaction for $[Co(sen)]^{3+}$ is complete in 20−30 min.[18] The exchange rates of the coordinated NH protons are important in determining the reactivity of the complex ions with the formaldehyde electrophile in these reactions, as these rates relate to the acidity of the bound amines.[23] At a given pH, the exchange rates for the NH protons of **1** are in fact slower than those of $[Co(sen)]^{3+}$, as established by H−D exchange experiments (^1H NMR), and are consistent with the observations on the relative rates of imine formation. Activation of the coordinated imine toward nucleophiles may have been expected,[18,19] but in this case, the imines in **2** proved less reactive than those of the $[Co(sen)]^{3+}$ imine intermediate.

Only one major product was observed upon chromatography of the imine product mixture derived from *meso*-**1** or *rac*-**1**. A primary minor band contained an unidentified side product containing imine resonances, while the second major band was the pure *meso*-**2** or *rac*-**2** hexaimine complex. The products were recrystallized by vapor diffusion of a mixture of ethanol and ether into the cooled aqueous solution. The stereoretention of the products implied that the chirality about the cobalt atom is retained under the conditions of the condensation reaction, as expected. The hexaimines are stable in acidic aqueous or nonaqueous solutions but decompose to the corresponding precursor hexathiolates in aqueous basic solution.

The triflate or perchlorate salts of **2** were dissolved in CH_3CN and reacted with NH_3 gas at room temperature for 20 h. After ion-exchange chromatography and recrystallization, the aza-capped complexes **3** (meso or rac) were isolated in approximately 50% yield. Only the dicapped product is observed, even for partly reacted mixtures of the hexaimines; unidentified trace products may have been the monocapped form.

To obtain the nitro-capped complexes, CH_3CN solutions of **2** were reacted with a slight excess of nitromethane in the

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Table 1. ^{13}C NMR Data for the Trinuclear Thiolates $[Co\{Co(NH_2CH_2CH_2S)_3\}_2]^{3+}$ (**1**) and Their Hexaimine (**2**), Aza-Capped (**3**), and Nitro-Capped (**4**) Derivatives[a]

complex	δ/ppm CH_2-S	CH_2-N	$N=CH_2$	CH_2-N_{aza}	CH_2-C_{quat}	C_{quat}-NO_2
meso-**1**	34.73	49.81				
rac-**1**	35.13	49.92				
meso-**2**	32.83	69.99	171.80			
rac-**2**	33.00	70.03	172.02			
meso-**3**	33.38	58.35		71.06		
rac-**3**	33.55	58.48		71.14		
meso-**4**	34.23	57.84			60.86	90.66
rac-**4**	34.41	57.93			61.01	90.68

[a] Recorded at 75.48 MHz; 0.1 mol dm^{-3} DCl at 20 °C; ppm downfield from NaDSS.

Table 2. Visible−UV Data for the Trinuclear and Mononuclear Complexes in Water

complex[c]	λ_{max} ($\epsilon/10^3$ M^{-1} cm^{-1})				
meso-**1**	570 (2.09)	436 (7.23)	350 (20.8)	276 (23.5)	244 (20.5)
rac-**1**	580 (2.26)	440 (6.07)	348 (19.5)	276 (26.2)	
	546 (2.14)	438 (5.62)	347 (18.2)	275 (25.6)[b]	
meso-**2**	530 (4.4)	430 (21.3)	352 (47.2)	268 (53.0)	240 (54.1)
rac-**2**	582 (3.8)	434 (16.2)	348 (47.8)	278 (56.8)	232 (50.1)
meso-**3**	558 (5.3)	434 (16.8)	351 (45.3)	278 (51.8)	248 (43.5)
rac-**3**	578 (5.0)	438 (13.9)	350 (41.2)	278 (55.9)	
meso-**4**	558 (5.3)	438 (17.6)	350 (45.0)	276 (52.2)	250 (46.3)
rac-**4**	566 (5.5)	440 (14.8)	346 (44.3)	276 (57.9)	
monomer[a]	574 (0.74)	438 (17.2)		276 (31.8)	

[a] 1 M $NaClO_4$. [b] Literature values (Brubaker, G. R.; Douglas, B. E. *Inorg. Chem.* **1967**, *6*, 1562). [c] Refer to Figure 1 for the structures of **1**−**4**.

presence of a catalytic amount of Et_3N for 2 days at room temperature. The resulting deeply colored complexes (*meso*-**4** or *rac*-**4**) were isolated in about 60% yield after purification; performing the reaction in an inert atmosphere improves the yield. The nitro-capping reaction is slower than the aza capping under similar conditions, and only dicapped species were observed, as before.

Although not attempted, the optically resolved hexaimine and bis(nitromethyl)- and diaza-capped trinuclear ions can obviously be synthesized from the resolved forms of the *rac*-hexathiolato complex by the above methods, without resort to direct resolution methods.

^{13}C NMR Spectra. Although the meso and rac isomers of **1** have been previously reported,[5,22] ^{13}C NMR data have only been reported for one (unassigned) isomer.[6] The ^{13}C NMR spectrum of each isomer is distinct, with resonances of the meso isomer appearing upfield from those of the rac complex. A consistent difference is observed between meso and rac pairs of the hexaimines and their nitro- and aza-capped derivatives (Table 1). The simple two-, three-, or four-line ^{13}C NMR spectrum for each of these complexes is consistent with the anticipated S_6 or D_3 symmetry.

Complex **1** displays only two resonances. From ^{13}C NMR studies of several well-characterized Co(III) complexes with N and S donor atoms,[24,25] the high-field assignment is made to the carbon atom α to the S donor.

The ^{13}C NMR spectra of **2** display simple three-line patterns. There is a downfield shift of more than 20 ppm for the carbon adjacent to the imine nitrogen relative to the parent, and there is a new resonance at ca. 172 ppm in the imine region. The shifts are similar to those observed for other imines, including those derived from $[Co(sen)]^{3+}$.[18,19]

The aza-capped complexes **3** also display three-line spectra. *meso*-**3** has a resonance at 58.35 ppm for the carbon atom on N, approximately 12 ppm upfield from the corresponding signal of the parent hexaimine. Also, the resonance at 71 ppm for the NH carbon in the cap is over 100 ppm upfield from the parent imine carbon resonance. These shifts are in accordance with the change from the $N=CH_2$ structure of the imine to the NCH_2N of the product.

The nitro-capped species **4** each exhibit a four-line spectrum. As expected, there is a low-intensity, low-field resonance at 90.7 ppm, typical of a capping nitromethyl carbon atom.[25] Other resonances at approximately 34, 58, and 61 ppm are assigned to CS, CN, and NC (in the cap), by comparison with spectra of the starting materials and related structures.

^{1}H NMR Spectra. These are more complicated than the ^{13}C NMR spectra, and only the general features are discussed. For a given ligand system, meso and rac pairs are very similar, but the hexathiolate, hexaimine, nis(nitromethyl)-capped, and diaza-capped species reveal systematic and characteristic differences.

The starting trinuclear ions show the expected multiplets in the $-S-CH_2-$ (δ ca. 2 ppm), $-N-CH_2-$ (δ ca. 3 ppm), and NH (δ ca. 5 ppm) regions. For the perchlorate salt of the rac ion in Me_2SO-d_6, these appear at δ 1.75 (dt, 6H), 2.17 (m, 6H), 2.8 (m, 6H), and 2.85 (m, 6H) and at δ 4.72 (NH, br s, 6H) and 4.96 (NH, br s, 6H). All six terminal $-NH_2$ groups are equivalent, but the gem NH protons on each are diastereotopic—hence the NH doublet. For the hexaimines, these NH proton signals are absent and are replaced by lower field imine proton signals. For example, the methylenes in the *meso*-hexaimine complex appear as a doublet of doublets centered at δ 7.30 (6H) and 7.95 (6H), with a double-bond cis H−H (geminal) coupling constant of 10 Hz, both features typical for terminal $N=CH_2$. The other signals of this complex are at δ 3.85 (dt, 6H) and 4.15 (dd, 6H) ($-N-CH_2$), now at lower field because of the adjacent imine nitrogen, and at δ 2.35 (dd, 6H) and 2.06 (dt, 6H)) ($-S-CH_2-$). The bis(nitromethyl)-capped ions reveal the reappearance of an NH signal (δ 7.1 (br s, 6H), at lower field than for the parent ions since these are now secondary amines. For the meso bis(nitromethly)-capped complex, the other resonances appear at δ 3.52 (t, 6H), 3.15 (m, 6H), 3.3 (m, 6H), and 2.88 (m, 6H) ("inner and outer" $-N-CH_2-$) and at δ 2.45 (d, 6H) and 1.8 (dt, 6H) ($-S-CH_2-$). The additional two multiplets (12H) in the $-N-CH_2-$ region are attributable to the capping residues. Similarly, the ^{1}H spectra of the diaza-capped species (meso) reveal a low-field NH singlet (δ 6.6, 6H), capping $-N-CH_2-N-$ resonances at δ 4.4 (m, 6H) and 3.28 (m, 6H), and $-N-CH_2-CH_2-$ resonances at δ 3.18 (m, 6H) and 2.80 (m, 6H), with $-S-CH_2-$ signals at δ 2.44 (d, 6H) and 1.75 (t, 6H).

The equivalence of the two "ends" for each of the trinuclear ions and the C_3 symmetry are evident in all the spectra, which are relatively simple.

UV−Visible Spectra. The UV−visible spectra (Table 2) for all of the new trinuclear complexes are very similar to those observed previously[5,6,26] for the original starting material **1** and its analogues. Formation of the hexaimine has a minor effect on the chromophore, and capping even less so. Data for the blue mononuclear complex[27,28] are included for comparison; however, note that the ligand field exerted by the thiolate sulfur

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Table 3. Cyclic Voltammetric Data for the Trinuclear Complexes in CH_3CN with 0.1 Mol dm^{-3} Bu_4NBF_4 Electrolyte[a]

complex	$E_{pc/mV}$	$E_{pa/mV}$	$E_{1/2}$/mV	ΔE/mV
meso-**1**	−460 −940	−400	−430	60
rac-**1**	−500 −950	−450	−475	50
meso-**2**	−390 −840	−300	−340	90
rac-**2**	−430 −840	−340	−385	90
meso-**3**	−460 −990	−360	−410	100
rac-**3**	−480 −1200	−340	−410	100
meso-**4**	−460 −950	−330	−390	130
rac-**4**	−470 −1010	−340	−405	120

[a] Ag/AgCl reference electrode in 3 mol dm^{-3} KCl; scan rate 100 MV/s; internal standard $E_{1/2}(Fc/Fc^+) = +\ 0.456$ V.

is different from that of the bridging thiolate donors of the trinuclear complexes.

The lowest energy visible absorption band at 550 nm is due to the d−d transition of the $^1A_{1g} \rightarrow {}^1T_{1g}$ parentage for a Co(III) ion in octahedral symmetry, and the second absorption band at 430 nm is at a higher energy than the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition. From the spectra, it is evident that these broad asymmetric bands have more than one contributing component, consistent with a departure from octahedral symmetry and with an overlap of transitions from essentially two chromophores, terminal $Co^{III}N_3S_3$ and central $Co^{III}S_6$. The molar extinction coefficients for these absorption bands, even corrected for the presence of three Co atoms, are much greater than those for mononuclear hexaamine Co(III) species, due in part to mixing from the charge-transfer transitions involving the soft sulfur donors.

The ultraviolet absorption bands observed for these complexes at ca. 350, 270, and 240 nm are much more intense than the visible bands, and the tail into the visible region accounts for the near-black appearance of the compounds. These bands are attributable to ligand to metal charge transfer among the terminal cobalt ions, the sulfur bridges, and the central metal ion. Molar extinction coefficients in Table 2 have not been corrected for the presence of three cobalt atoms. The absorption band at ca. 350 nm is assigned to the bridged sulfur to metal charge-transfer transition; this band is not present in the spectrum of the mononuclear complex.

Electrochemistry. Cyclic voltammograms for all of the trinuclear complexes display one quasi-reversible couple, with $E_{1/2}$ ranging from −340 to −475 mV, and an irreversible reduction, with E_{pc} ranging from −840 to −1200 mV (see Table 3). By comparison with the closely related $[Co\{Co((R)\text{-cysteinate})_3\}_2]^{3-}$ [29] and $[Co(RhL_3)_2]^{3+}$ where L = 2-aminoethanethiolate,[13] the first redox process for **1** can be assigned to the central Co(II/III) redox couple corresponding to the reaction

$$[Co^{III}(Co^{III}N_3S_3)_2]^{3+} + e^- \rightleftharpoons [Co^{II}(Co^{III}N_3S_3)_2]^{2+}$$

This in direct contrast to an earlier reported assignment.[6] Preliminary constant potential coulometric results for *meso*-**1**, indicate that a 1-electron process (0.9 ± 0.2 e$^-$) is associated with reductions occurring at potentials of −450 mV.[30] Attempts to coulometrically measure the second reduction were problematic due to the apparent instability of the Co(II) complex, and dissociation occurred with the formation of a precipitate on the working electrode.[31] Preliminary results were obtained using direct current (dc) sweep voltammetry, where the 2-electron nature of the second reduction was observed at higher potentials. The nature of the second reduction appears to be dependent upon the functions at the terminal N_3 face, as evidenced by the E_{pc} values, and can be written as

$$[Co^{II}(Co^{III}N_3S_3)_2]^{2+} + 2e^- \rightarrow [Co^{II}(Co^{II}N_3S_3)_2]^0 \rightarrow \text{decomposition products}$$

The $E_{1/2}$ values due to the central Co(III/II) couples of the corresponding meso and *rac* pairs are very similar; however, changes are observed due to a change in the terminal N_3 face of the complexes. Values of the formal potentials for the capped **3** and **4** complexes are almost 70 mV more positive than those for the uncapped analogues **1**, indicative of a stabilization of the Co(II) oxidation state relative to the Co(III) state upon capping. The formation of the imines from complexes **1** results in a positive shift in potential by approximately 100 mV, again indicating the stabilization of the Co(II) oxidation state by imine functions. This behavior can be ascribed to the stronger π-accepting ability and increased ligand field strength of imines compared with amines.[32] In contrast, formation of the aza-capped species **3** resulted in a negative shift in potential up to 70 mV. This may be partly due to the better electron-donating ability of alkylated nitrogens, hence stabilizing the Co(III) oxidation state. Other factors which influence the electrochemical behavior of encapsulated metal ions include cavity size and conformation[33] and rigidity of the ligand.[34−37] Hence, capped complexes may have an increased resistance to accommodating the larger Co(II) ion. With the capped complexes **4**, the situation becomes more complicated due to the strong electron-withdrawing nature of the nitromethyl group; $E_{1/2}$ values are not vastly different from those of the aza-capped complexes.

Comparisons could be made between these complexes with a central Co(III) ion having six bridging thiolate ligands and cobalt complexes having six thioether donors, e.g. $[Co^{III}(RSR')_6]^{3+}$. However, the electrochemical behavior of the latter complexes is vastly different. In general, thioether coordination strongly stabilizes Co(II) with respect to Co(III), as evidenced by data for $[Co^{III/II}(RSR')_6]$, where $E_{1/2}$ values are in the range +600 to +900 mV vs NHE (ca. +350 to +650 mV vs Ag/AgCl in 3 mol dm^{-3} KCl).[38−41] These values are in contrast to our results for the bridging thiolate complexes, where $E_{1/2}$ values are at negative potentials of ca. −400 mV vs Ag/AgCl in 3 mol dm^{-3} KCl. The disparity in values indicates that the

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(30) Unpublished results. The CV measurements, on a short time scale, are uncomplicated by dissociation of the Co(III) “ends” from the Co(III)−Co(II)−Co(III) product. The coulometric measurements, on much longer time scales, are plagued with this problem.

(31) Unpublished observation. The precipitate is probably the uncharged Co(III)-capped monomer. Chemical reduction using Zn/HCl produces a white product which has been established to be the hydrochloride salt of the reduced form of the previously unknown, terminal ligand.

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Co(III) oxidation state is stabilized in a coordinated hexathiolate environment, whereas in a hexathioether environment, Co(II) is stabilized; capping only marginally reduces the overall effect. In studies of ruthenium complexes,[42] it has also been observed that coordination by thiolate ligands causes a shift to negative reduction potentials, relative to thioether coordination.

Experimental Section

Instrumentation. ^{1}H and ^{13}C NMR spectra were recorded using a Varian XL-300 spectrometer operating at 299.5 and 75.48 MHz, respectively. Chemical shifts (δ) are reported in parts per million (ppm) relative to tetramethylsilane (Me_4Si, 0 ppm) in Me_2SO-d_6 for both ^{1}H and ^{13}C NMR spectra. The reference for ^{1}H and ^{13}C NMR spectra recorded in D_2O or D_2O/0.1 mol dm^{-3} DCl was sodium 2,2-dimethyl-2-silapentane-5-sulfonate (NaDSS, 0 ppm), together with an internal reference of 1,4-dioxane at 69.26 ppm. All spectra were recorded at room temperature. Proton exchange in $[Co(sen)]^{3+}$ [17,18] and the *rac*- and *meso*-hexathiolate complexes in unbuffered D_2O containing dioxane was followed by ^{1}H NMR spectroscopy. UV−visible spectra (ϵ, M^{-1} cm^{-1}) were measured on a Hewlett-Packard 8452A diode array spectrophotometer in a 1 cm path length cell with H_2O or CH_3CN solutions at room temperature.

Electrochemical measurements were performed using a Princeton Applied Research scanning potentiostat (PAR model 362) with a Ag/AgCl reference electrode in 3 mol dm^{-3} KCl, a platinum disk working electrode, and a platinum wire auxiliary electrode. Complex concentrations approximated 0.001 mol dm^{-3} in 0.1 mol dm^{-3} Bu_4NBF_4 in CH_3CN. The cell was purged with Ar between scans. Coulometric experiments were performed using a Princeton Applied Research 174A polarographic analyzer, with a platinum basket working electrode, a Ag/AgCl in 0.05 mol dm^{-3} Bu_4NBF_4 in CH_3CN reference electrode, and a platinum wire auxiliary electrode.

Bio-Rad analytical grade Dowex 50W-X2 (200−400 mesh, H$^+$ form) and Pharmacia SP Sephadex C-25 (Na$^+$ form) ion-exchange resins were used for the cation-exchange chromatography. For the electrochemical measurements, CH_3CN (Aldrich HPLC grade) was stored over dried molecular sieves under N_2. The supporting electrolyte, Bu_4NBF_4, was prepared by neutralization of HBF_4 with Bu_4NOH and purified by recrystallization from MeOH and twice from ethyl acetate and ether[42] and drying under vacuum. All solutions were degassed with nitrogen or argon prior to the experiments. All chemicals, except where otherwise indicated, were AnalaR grade or the equivalent. All evaporations were carried out at <30 °C on Büchi rotary evaporators.

All complexes analyzed satisfactorily for C, H, and N and, where appropriate, F, S, and Cl. Early on, many of the trinuclear compounds tended to crystallize with varying degrees of occluded acid (HCl for Cl$^-$ salts, CF_3SO_3H for triflates). The problem was overcome by using sodium salts as precipitants for triflates and perchlorates and water/alcohol as the recrystallization medium for the Cl$^-$ salts.

[CAUTION! Perchlorates are potentially explosive and should be handled only in small quantities.]

Synthesis. $[Co(SCH_2CH_2NH_2)_3]$[4,27,28] and $[Co\{Co(SCH_2CH_2NH_2)_3\}_2](NO_3)_3$[9] were prepared by published procedures. The meso and rac isomers of the trinuclear material, **1**, were separated by ion-exchange chromatography on Dowex. Approximately 30 g of the starting mixture was sorbed onto the column (10 × 50 cm) and eluted with 3 mol dm^{-3} HCl to give two clearly separated bands. The chloride salts of the products were easily isolated after evaporation or freeze-drying of the solutions. The crude products were recrystallized from water with the addition of EtOH. Yields: approximately 15 g of each. The first band off the column was the meso isomer, as shown by taking small samples of each of the crude products (0.02 g) and chromatographing on a Sephadex column (2 25 cm) using $Na_2[Sb_2((+)\text{-tartrate})_2]$ (0.2 mol dm^{-3}) as the eluant. Only the rac form separated into two bands; the resolving agent was subsequently removed on a Dowex column in the Na$^+$ form, by resorption, copious washing with H_2O, and then elution with 2 mol dm^{-3} HCl. Both bands were active, with equal and opposite α/A ratios at selected wavelengths. The chloride salts were converted into either triflate or perchlorate salts. Triflate salts were formed by rapid treatment with neat CF_3SO_3H;[34] N_2 was used to purge HCl gas, and the triflate salts were reprecipitated using diethyl ether. Perchlorate salts were obtained by recrystallization of the crude products with H_2O and $NaClO_4$, with addition of EtOH and ether to yield black crystals. The meso isomer is more soluble than the rac form, and in solution, the rac form is olive-green, while the meso is dark brown.

***meso*- and *rac*-$[Co\{Co(SCH_2CH_2N{=}CH_2)_3\}_2]Cl_3$ (2).** *rac*-$[Co\{Co(SCH_2CH_2NH_2)_3\}_2](CF_3SO_3)_3$ (3.0 g) was dissolved in 250 cm^3 of CH_3CN with warming, and 100 cm^3 of Et_3N and 40 g of paraformaldehyde were added. The mixture (pH 10−11) was stirred with warming (ca. 50 °C) for 2 h and then at room temperature for 12 h. A small sample of the mixture was withdrawn, filtered, and evaporated to dryness. A ^{13}C NMR spectrum of the crude sample showed that the hexaimine had formed with no apparent starting material remaining. The reaction was quenched with 1 mol dm^{-3} HCl, and the mixture was sorbed onto Dowex. The product was washed with H_2O, 1 mol dm^{-3} HCl, and 3 mol dm^{-3} HCl, and the major band was eluted with 4 mol dm^{-3} HCl. The solution was evaporated to dryness, and the remaining black product was recrystallized from H_2O, with addition of a saturated ethanolic solution of $NaClO_4$ to yield a fine crystalline product, *rac*-**2**. Yield: 2.3 g, 82%.

meso-$[Co\{Co(SCH_2CH_2N{=}CH_2)_3\}_2](ClO_4)_3$ was prepared by a method identical method to that described above. The resulting chloride salt was converted to the perchlorate by using aqueous $NaClO_4$ with vapor diffusion of EtOH. Yield: 75%.

***meso*- and *rac*-$[Co\{Co(SCH_2CH_2NHCH_2)_3N\}_2]Cl_3$ (3).** Ammonia was bubbled through CH_3CN and then through a solution of $[Co\{Co(SCH_2CH_2N{=}CH_2)_3\}_2](ClO_4)_3$ (0.2 g) dissolved in 15 cm^3 of CH_3CN for 24 h at room temperature. The mixture was diluted with H_2O (50 cm^3), and the solution was sorbed onto Dowex (1 × 3 cm), washed with H_2O and 1 mol dm^{-3} HCl, and eluted with 5 mol dm^{-3} HCl. After evaporation of the solvent, the black residue of *meso*-$[Co\{Co(SCH_2CH_2NHCH_2)_3N\}_2]Cl_3{\cdot}7H_2O$ (*meso*-**3**) was recrystallized from H_2O by vapor diffusion of EtOH. Yield: 0.1 g, 53.5%.

The chloride salt ($6H_2O$) of *rac*-**3** was prepared from *rac*-**2** by a method identical to that described above. Yield: 48%.

***meso*- and *rac*-$[Co\{Co(SCH_2CH_2NHCH_2)_3CNO_2\}_2]Cl_3$ (4).** *meso*-$[Co\{Co(SCH_2CH_2N{=}CH_2)_3\}_2](ClO_4)_3$ (3 g was dissolved in 150 cm^3 of CH_3CN. To this black solution were added CH_3NO_2 (1.3 g) and Et_3N (5 cm^3) with stirring. The solution became warm with some formation of a precipitate. The mixture was stirred at room temperature for approximately 60 h, and the reaction was then quenched with 10 cm^3 of 5 mol dm^{-3} HCl. The mixture was diluted with 1 L of H_2O, and the solution was sorbed onto Dowex (5.5 × 30 cm), washed with H_2O, 1 mol dm^{-3} HCl, and 3 mol dm^{-3} HCl, and finally eluted with 5 mol dm^{-3} HCl. The second major band was collected and evaporated to dryness. The resulting crude product *meso*-$[Co\{Co(SCH_2CH_2NHCH_2)_3CNO_2\}_2]Cl_3{\cdot}6H_2O$ (*meso*-**4**, 1.7 g) was recrystallized from H_2O in almost quantitative yield. Yield: 1.69 g, 62%.

rac-$[Co\{Co(SCH_2CH_2NHCH_2)_3CNO_2\}_2]Cl_3{\cdot}6H_2O$ (*rac*-**4**) was prepared by a method similar to that above, except the reaction was conducted under a N_2 atmosphere. The crude product was recrystallized from H_2O. The crystalline product was filtered off, washed with EtOH and diethyl ether, and vacuum-dried. Yield: 7 g, 77%.

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Supporting Information Available: Table S1, listing microanalytical data for salts of *meso*- and *rac*-**2**, -**3**, and -**4**. This material is available free of charge on the Internet at http://pubs.acs.org.

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