3634 *Inorg. Chem.* **1999,** *38,* 3634−3643

# Cobalt Cage Complexes with $N_3S_3$ Donor Sets and Differing Cavity Sizes: A Novel Macrobicyclic Cage with a Contracted Cap

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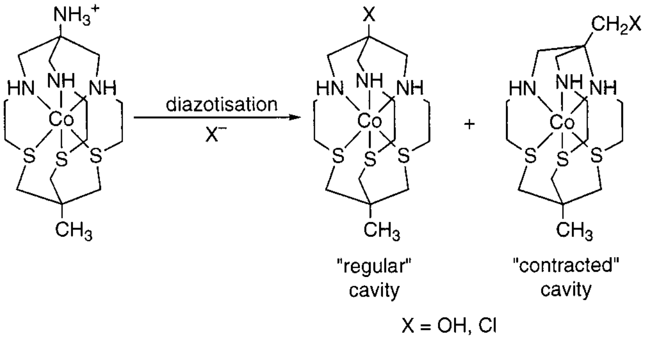
*Received December 2, 1998*

Treatment of the cobalt(III) complex of the hexadentate tripodal $N_3S_3$ ligand ten (4,4′,4″-ethylidynetris(3-thiabutan-1-amine) with propanal and paraformaldehyde under basic conditions, followed by borohydride reduction and reoxidation of the metal center, leads largely to the encapsulated (red) metal complex cation $[Co(Me_2\text{-}N_3S_3sar)]^{3+}$ ($Me_2\text{-}N_3S_3sar$ = 1,8-dimethyl-3,13,16-trithia-6,10,19-triazabicyclo[6.6.6]icosane). Unexpectedly, significant amounts of the homologous (yellow) complex cation $[Co(Me_2\text{-}N_3S_3absar)]^{3+}$ ($Me_2\text{-}N_3S_3absar$ = 1,8-dimethyl-3,13,16-trithia-6,10,19-triazabicyclo[6.6.5]nonadecane) were also obtained. This macrobicyclic complex has a contracted cavity resulting from a cap containing one fewer methylene units than $Me_2\text{-}N_3S_3sar$. The structures of both cobalt(III) complexes have been determined by X-ray crystallography. $[Co(Me_2\text{-}N_3S_3sar)]Cl\cdot ZnCl_4\cdot H_2O$ crystallizes in the cubic space group $P2_13$ with Z = 4, $a$ = 13.9683(11) Å. $[Co(Me_2\text{-}N_3S_3absar)](ClO_4)_3\cdot 0.5CH_3CN\cdot 0.5H_2O$ crystallizes in the triclinic space group $P\bar{1}$ with $Z = 4$, $a = 12.036(4)$ Å, $b = 15.932(9)$ Å, $c = 17.212(14)$ Å, $\alpha = 64.93(7)°$, $\beta = 72.77(5)°$, $\gamma = 88.91(7)°$. The surprising structural rearrangement is examined, along with the spectral and redox properties of both cobalt complexes. The influence of the reduced cavity size in the absar type cage is reflected in a shift of the bands in the electronic spectrum of both the cobalt(II) and cobalt(III) complexes to higher energy, and a more negative value for the Co(III/II) redox potential. The demetalation of the complexes is also described.

## Introduction

As part of a continuing study of the "sarcophagine" type cage complexes and their development as useful redox reagents, a range of related ligands has been prepared, in which the apical substituents, donor groups, and cavity size are varied. In particular, a series of cobalt complexes has been described, in which three of the six secondary amine donors have been replaced by the softer thioether donor groups, giving rise to an $N_3S_3$ donor set.[2,3] Variation of the apical substituent in these cages led to a systematic change in the redox potential. Diazotization of a primary amine group attached to the apical position of the cage also yielded a number of complexes in which the cap nearer to the $N_3$ donor set was contracted by extrusion of a methylene unit (Scheme 1).

**Scheme 1**



The expectation that the contracted cavity would lead to destabilization of the cobalt(II) state and a concomitant decrease in the Co(II)/(III) redox potential was realized. However, the contracted cavity cages were only a minor product of the diazotization reaction, and their separation from the other complexes was tedious. Attempts to prepare a contracted cavity cage by analogy with the base-catalyzed reaction observed for the $[Co(Me,NO_2\text{-}sar)]^{3+}$ complex[4] did not yield the expected contracted cavity cage, but instead it gave rise to a novel pendant arm macrocycle resulting from a dehydrogenation reaction.[5]

The preparation of $N_3S_3$ complexes devoid of functionality in the apical positions, so that the free ligands obtained by demetalation contain only the $N_3S_3$ donor set and no additional binding sites, is also an important synthetic target since it limits the binding possibilities of the metal ion. The capping reaction with nitromethane and formaldehyde gives rise to a nitro-capped species, but it has not been possible to isolate the free ligand with a nitro cap. The demetalation procedures lead to reduction

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10.1021/ic981380g CCC: $18.00

of the nitro group to an amine, or rupture of the cage ligand. The amino-capped cobalt(II) species (obtained by reduction of the nitro-capped complex) can be smoothly demetalated (with cyanide[6,7] or by heating in acid[7]). However, a number of subsequent metal encapsulation reactions have been unsuccessful because the apical primary amino group is also capable of coordination, and some metals coordinate without entering the cavity.[8]

The hydrogen-capped cage complex [Co(H,Me-$N_3S_3$sar)]$^{3+}$ partly meets the synthetic target as it contains no additional functionality. It was prepared by reduction of the nitro-capped cage, followed by diazotization in the presence of chloride, and reductive dechlorination.[3] This complex has also been prepared using an alternative strategy based on a mixed aldehyde capping reaction,[3] analogous to that developed for the $N_6$ sarcophagine system.[9] The corresponding cage ligand in which both apical positions are occupied by methyl groups was also an important synthetic goal. Not only does it lack functionality at the apical sites, but interpretation of the proton NMR spectra of its metal complexes would be considerably simplified by the absence of coupling between protons on adjacent carbon atoms in the cap.

This paper explores the synthesis and characterization of cobalt complexes of the target cage ligand $Me_2$-$N_3S_3$sar, as well as other reaction products.

## Experimental Section

**General Procedures.** $^1$H and proton-decoupled $^{13}$C NMR spectra were recorded with a Varian Gemini 300 MHz Fourier transform NMR spectrometer, using 1,4-dioxane as internal reference for solutions of metal complexes in $D_2O$. The signals of dioxane are taken as $\delta = 3.74$ ppm for $^1$H NMR and $\delta = 67.39$ ppm for $^{13}$C NMR spectra. $^{13}$C peak multiplicities were assigned by the use of DEPT and APT techniques as appropriate. Carbon atoms that are adjacent to N−H groups appear as a pair of isotopomeric peaks in spectra run in 1:1 $H_2O/D_2O$, and this was used to aid in their assignment.[5] Cyclic voltammetry was carried out using a BAS 100 electrochemical analyzer, a glassy carbon working electrode, a platinum wire auxiliary electrode, and a Ag/AgCl/0.1 M NaCl reference electrode (calibrated against a saturated calomel electrode); measurements were made at ambient temperature in 0.1 or 0.2 M aqueous NaCl solution saturated with high-purity argon, and the scan speed was typically 100 mV s$^{-1}$. Electronic absorption spectra were obtained with a Hewlett-Packard 8450A spectrophotometer. [Co(ten)]$Cl_3\cdot 3H_2O$ and [Co(ten)]$Cl_2\cdot ClO_4\cdot H_2O$ were prepared as previously reported.[2,3] All evaporations were carried out at ≤20 Torr in Büchi rotatory evaporators, and the temperature of the water bath did not exceed 50 °C.

**Syntheses.** *Caution! Formaldehyde is a carcinogen, and those reactions in which it is used should be carried out in a well-ventilated fume hood.*

**Capping Reaction.** [Co(ten)]$Cl_2\cdot ClO_4\cdot H_2O$ (1.63 g, 3 mmol) and $NaClO_4$ (5 g) were added to acetonitrile (30 mL) and water (0.64 g), and the solution was stirred for 15 min, during which time some of the complex dissolved. To the stirred suspension were added paraformaldehyde (0.18 g, 6 mmol) and propanal (0.348 g, 6 mmol). After the mixture was stirred for a further 5 min, triethylamine (0.304 g, 3 mmol) was added. The mixture rapidly turned dark brown. After stirring for 4 h, further paraformaldehyde (0.18 g) and propanal (0.348 g) were added, and this procedure was repeated after another 4 h. The reaction mixture was left stirring overnight and then quenched with excess 1 M HCl. A small amount of polymeric organic material was removed by filtration, and the solution was loaded onto a column of Dowex 50W-X2 cation exchange resin. The column was washed with 1 M HCl, to remove aqueous Co$^{2+}$, and then the adsorbed complexes were removed as a single band with 3 M HCl. The eluate was taken to dryness, and the crude product was dissolved in water (30 mL) containing sodium carbonate (3.9 g). $NaBH_4$ (0.15 g) was added, and the solution was stirred for 30 min. The reaction mixture was quenched with 1 M HCl, and air was bubbled through the solution for 15 min. The solution was loaded onto a column of Dowex 50W-X2 cation exchange resin and washed with 1 M HCl (to remove aqueous Co$^{2+}$), and then the adsorbed complexes were removed as a single band with 3 M HCl. The column was then washed with 6 M HCl to remove ten·3HCl. The fraction which contained the metal complexes was stripped to dryness, and the crude product was taken up in water and loaded onto a column of SP-Sephadex C-25. Elution with $Na_2HPO_4$ (0.1 M) gave a small amount of fast-moving brown material, which was discarded, followed by a yellow band ($F_1$) and a slower moving red band ($F_2$). Once the bands were well separated, the concentration of the eluant was increased to 0.15 M. The two bands were loaded onto separate columns of Dowex 50W-X2 cation exchange resin, washed with water, washed with 1 M HCl (to remove Na$^+$), removed with 3 M HCl, and evaporated to dryness. (Yields: $F_1$, ~0.12 g; $F_2$, ~0.40 g). On one occasion, two yellow bands were obtained, and the leading (minor) yellow band ($F_{1a}$) was identified as a carbinolamine complex (see below). The major yellow band corresponded to $F_1$ above.

**[Co($Me_2$-$N_3S_3$absar-7-OH)]$Cl_3\cdot 3H_2O$.** The (minor) leading yellow fraction ($F_{1a}$) was identified by the $^1$H and $^{13}$C NMR spectra as the cobalt(III) complex of the reduced cavity carbinolamine cage 1,8-dimethyl-7-hydroxy-3,13,16-trithia-6,10,19-triazabicyclo [6.6.5]nonadecane. A sample was recrystallized from aqueous 2-propanol. Anal. Calcd (found) for $C_{15}H_{37}CoCl_3N_3O_4S_3$: C, 30.80 (31.0); H, 6.38 (6.0); N, 7.19 (7.0). $^1$H NMR ($D_2O$/DCl): $\delta$ 1.33 (s, 3H, $CH_3C_qN$); 1.40 (s, 3H, $CH_3C_qCH_2S$); 2.92−3.75 (complex pattern of overlapping multiplets, 18H, $CH_2N$ and $CH_2S$); 3.82 (d, *J* 11 Hz, 1H, $CH_2N$); 3.96 (d, *J* 11 Hz, 1H, $CH_2N$); 4.61 (s, 1H, NC*H*(OH)). $^{13}$C NMR ($D_2O$/DCl): $\delta$ 17.91 ($CH_3C_qN$); 29.13 ($CH_3C_qCH_2S$); 37.93, 37.98, 41.35, 42.11, 43.87, 44.43, 46.15, 47.85, 52.65, 52.85 ($CH_2S$ and $CH_2N$); 76.21 ($CH_3C_qN$); 91.09 (N*C*H(OH)$C_q$). The resonance corresponding to $CH_3C_qCH_2N$ overlaps a methylene resonance at 43.87 ppm.

**[Co($Me_2$-$N_3S_3$absar)]$Cl_3\cdot 0.5HCl\cdot 1.5H_2O$.** The yellow fraction ($F_1$) was recrystallized from methanol/diethyl ether, washed with diethyl ether, and dried in vacuo. Anal. Calcd (found) for $C_{30}H_{69}Co_2Cl_7N_6O_3S_6$: C, 32.16 (32.2); H, 6.21 (6.1); N, 7.50 (7.3); S, 17.17 (17.0); Cl, 22.15 (22.3). $^1$H NMR ($D_2O$/DCl): $\delta$ 1.36 (s, 3H, $CH_3C_qN$); 1.41 (s, 3H, $CH_3C_qCH_2S$); 2.9−3.7 (complex pattern of overlapping multiplets, 20H, $CH_2N$ and $CH_2S$); 3.83 (dd, *J* 11, 2 Hz, 1H, $CH_2N$); 3.96 (dd, *J* 11, 2 Hz, 1H, $CH_2N$); 7.3$^\dagger$ (br s, 1H, NH); 7.9$^\dagger$ (br s, 1H, NH); 8.1$^\dagger$ (br s, 1H, NH). The resonances marked with the symbol † disappear when the complex is heated in $D_2O$. $^{13}$C NMR ($D_2O$/DCl): $\delta$ 17.06 ($CH_3C_qN$); 29.14 ($CH_3C_qCH_2S$); 37.89, 38.01, 41.32, 42.13, 43.65, 45.72 ($CH_2S$); 43.95 ($CH_3C_qCH_2S$); 45.03, 52.66, 53.79, 55.09, 63.09 ($CH_2N$); 73.65 ($CH_3C_qN$). Electronic spectrum (water) [$\lambda_{max}$, nm ($\epsilon_{max}$, dm$^3$ cm$^{-1}$ mol$^{-1}$)]: 464 (640), 351 (890), 285 (16 000), 206 (8300).

**[Co($Me_2$-$N_3S_3$absar)]$(CF_3SO_3)_3\cdot 2H_2O$.** A sample of the chloride salt was dissolved in excess triflic acid (neat) under nitrogen and heated at 50 °C for 4 h. The resulting syrup was poured into diethyl ether with vigorous stirring. The precipitate was collected by filtration, washed with diethyl ether, and dried in vacuo. The hygroscopic material was recrystallized from aqueous sodium triflate, giving a crystalline product that was no longer moisture-sensitive. Anal. Calcd (found) for $C_{18}H_{35}CoF_9N_3O_{11}S_6$: C, 24.24 (24.1); H, 3.96 (3.9); N, 4.71 (4.5); Co, 6.61 (6.4).

**[Co($Me_2$-$N_3S_3$absar)]$^{2+}$.** A sample of the cobalt(III) complex was dissolved in water in a spectrophotometer cuvette. A few granules of amalgamated zinc were added, the cuvette was sealed with a rubber septum, and the solution was flushed with nitrogen gas (saturated with water). The spectrum was measured every 15 min until there was no further change, indicating that reduction to cobalt(II) was complete. Electronic spectrum (water) [$\lambda_{max}$, nm ($\epsilon_{max}$, dm$^3$ cm$^{-1}$ mol$^{-1}$)]: 755 (27), 530 (sh, 105), 493 (120), 281 (3600). The magenta solution was subsequently reoxidized by exposure to air (after removal of the

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amalgamated zinc), and the spectrum of the final product was unchanged from that obtained prior to reduction.

**Isolation of the Free Ligand $Me_2$-$N_3S_3$absar.** A solution of [Co($Me_2$-$N_3S_3$absar)]$Cl_3$·0.5HCl·1.5$H_2O$ (200 mg) in water (10 mL) containing NaOH (2 M, 0.1 mL) was flushed with nitrogen. Zinc dust (400 mg) was added, and the mixture was stirred under nitrogen for 15 min. NaCN (600 mg) was added to the magenta solution, and the mixture was stirred under nitrogen for 1 h at ambient temperature and then heated to 100 °C for 5 min to ensure complete demetalation. NaOH (2 g) was added to the pale yellow solution, which was extracted with chloroform (3 × 20 mL). The chloroform extracts were dried ($Na_2SO_4$), and removal of the solvent gave a white microcrystalline material. $^1$H NMR ($CDCl_3$): $\delta$ 0.84 (s, 3H, $CH_3C_q$); 0.91 (s, 3H, $CH_3C_q$); 2.3−2.9 (complex pattern of overlapping multiplets, 20H, $CH_2N$ and $CH_2S$); 3.75 (s, 2 H, $CH_2N$). $^{13}$C NMR ($CDCl_3$): $\delta$ 23.68 ($CH_3C_qN$); 25.31 ($CH_3C_qCH_2S$); 33.17, 35.83$^†$, 40.04$^§$, 42.76, 45.38$^†$, 50.94$^†$, 59.68$^†$ ($CH_2$); 40.04$^§$ ($C_qCH_2S$); 55.30 ($C_qN$). The resonances marked with the symbol † are approximately double the intensity of the remainder. The presence of two overlapping resonances (§) is established by DEPT and APT. The NMR sample was acidified with concentrated DCl, evaporated to dryness, and dissolved in 0.1 M DCl. $^1$H NMR (0.1 M DCl): $\delta$ 1.13 (s, 3H, $CH_3$); 1.35 (s, 3H, $CH_3$); 2.9−3.5 (overlapping multiplets, 22H, $CH_2N$ and $CH_2S$). There are characteristic singlets at 2.91 and 3.44 ppm. $^{13}$C NMR (0.1 M DCl): $\delta$ 19.80 ($CH_3C_qN$); 28.58 ($CH_3C_qCH_2S$); 31.74, 34.85, 41.46, 43.29, 48.74, 52.72 ($CH_2$); 41.16 ($C_qCH_2S$); 57.34 ($C_qN$).

**[Co($Me_2$-$N_3S_3$sar)]$Cl_3$·0.5HCl·1.5$H_2O$.** The red fraction ($F_2$) was recrystallized from aqueous 2-propanol, washed with acetone, and dried in vacuo. Anal. Calcd (found) for $C_{32}H_{73}Co_2Cl_7N_6O_3S_6$: C, 33.46 (33.4); H, 6.41 (6.3); N, 7.32 (7.2); S, 16.75 (16.6); Cl, 21.61 (21.4). $^1$H NMR ($D_2O$/DCl): $\delta$ 0.96 (s, 3H, $CH_3C_qCH_2N$); 1.42 (s, 3H, $CH_3C_qCH_2S$); 2.57$^†$ (d, 3H, $C_qCH_2N$), 2.91$^†$ (d, 6H, overlapping $CH_2CH_2N$ and $C_qCH_2S$), 3.04$^†$ (d, 6H, overlapping $C_qCH_2N$ and $CH_2CH_2S$), 3.23$^†$ (d, 3H, $C_qCH_2S$), 3.64$^†$ (d, 6H, overlapping $CH_2CH_2N$ and $CH_2CH_2S$); 7.5 (br s, 3H, exchangeable NH). (†: each of these $CH_2$ units has a coupling constant of ~12 Hz; additional fine structure, consistent with vicinal coupling in the $CH_2CH_2$ straps, is seen in the resonances centered at 2.91 and 3.04 ppm). $^{13}$C NMR ($D_2O$/DCl): $\delta$ 20.84 ($CH_3C_qCH_2N$); 28.57 ($CH_3C_qCH_2S$); 39.53 ($C_qCH_2S$); 40.99 ($CH_2CH_2S$); 42.25, 42.72 ($C_qCH_3$); 56.15, 56.64 ($CH_2N$). Electronic spectrum (water) [$\lambda_{max}$, nm ($\epsilon_{max}$, dm$^3$ cm$^{-1}$ mol$^{-1}$)]: 487 (940), 369 (1000), 298 (18 000), 231 (12 000).

**[Co($Me_2$-$N_3S_3$sar)]Cl·$ZnCl_4$·2$H_2O$.** A sample of the chloride salt was dissolved in hot concentrated HCl, and solid $ZnCl_2$ was added, to give a solution ~2 M in $ZnCl_2$. Upon cooling, the precipitated product was removed by filtration, washed with methanol, and air-dried. Anal. Calcd (found) for $C_{16}H_{37}Cl_5CoN_3O_2S_3Zn$: C, 27.41 (27.3); H, 5.32 (5.6); N, 5.99 (5.8); Cl, 25.28 (25.2).

**[Co($Me_2$-$N_3S_3$sar)]$^{2+}$.** A sample of [Co($Me_2$-$N_3S_3$sar)]$Cl_3$·0.5HCl·1.5$H_2O$ was reduced with zinc amalgam to give a purple solution, as described for the preparation of [Co($Me_2$-$N_3S_3$absar)]$^{2+}$. Electronic spectrum (water) [$\lambda_{max}$, nm ($\epsilon_{max}$, dm$^3$ cm$^{-1}$ mol$^{-1}$)]: 763 (30), 560 (sh, 115), 510 (135), 293 (3700).

**Isolation of the Free Ligand $Me_2$-$N_3S_3$sar.** [Co($Me_2$-$N_3S_3$sar)]$Cl_3$·0.5HCl·1.5$H_2O$ was demetalated following the procedure described above for the preparation of the metal-free cage $Me_2$-$N_3S_3$absar. $^1$H NMR ($CDCl_3$): $\delta$ 0.74 (s, 3H, $CH_3C_qCH_2N$); 0.99 (s, 3H, $CH_3C_qCH_2S$); 2.69 and 2.70 (overlapping t, J 5 Hz, $CH_2CH_2$ and s, $C_qCH_2$, 12H total); 2.91 (t, J 5 Hz, 6H, $CH_2CH_2$); 2.98 (s, 6H, $C_qCH_2$); 3.6 (br s, 3H, NH, disappears with $D_2O$ shake). $^{13}$C NMR ($CDCl_3$): $\delta$ 25.32, 25.73 ($CH_3C_q$); 36.57, 45.00, 51.32, 62,23 ($CH_2$); 38.32, 39.82 ($C_q$). The NMR sample was acidified with concentrated DCl, evaporated to dryness, and dissolved in 0.1 M DCl. $^1$H NMR (0.1 M DCl): $\delta$ 1.11, 1.15 (s, 3H + 3H, $CH_3$); 2.91 (s, 6H, $C_qCH_2$); 3.12 (t, J 5.5 Hz, 6H, $CH_2CH_2$); 3.26 (t, J 5.5 Hz, 6H, $CH_2CH_2$); 3.37 (s, 6H, $C_qCH_2$). $^{13}$C NMR (0.1 M DCl): $\delta$ 20.70 ($CH_3C_qCH_2N$); 28.55 ($CH_3C_qCH_2S$); 31.48, 42.0$^†$, 48.05, 53.4$^†$ ($CH_2$); 36.09 ($C_qCH_2N$); 39.82 ($C_qCH_2S$). Apart from the quaternary carbon signals, all of the resonances are significantly broadened in acidic solution. In particular, the resonances marked with the symbol † have a peak width at half-height ~0.5−1.0 ppm.

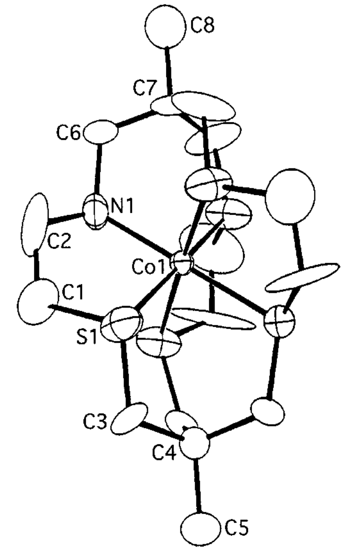

**Figure 1.** ORTEP plot of the cationic unit in [Co($Me_2$-$N_3S_3$sar)]Cl·$ZnCl_4$·$H_2O$ with atom-labeling scheme and vibrational ellipsoids at the 50% probability level.

**X-ray Crystal Structure Determination of [Co($Me_2$-$N_3S_3$sar)]Cl·$ZnCl_4$·$H_2O$.** Crystals of [Co($Me_2$-$N_3S_3$sar)]Cl·$ZnCl_4$·$H_2O$ suitable for single-crystal X-ray diffraction were grown from a solution of concentrated HCl/$ZnCl_2$. Cell dimensions were obtained from 24 reflections with a $2\theta$ angle in the range 27−36° (graphite monochromatized Mo Kα ($\lambda$ = 0.709 30 Å)). The intensity data were collected on an Enraf Nonius CAD-4 diffractometer. Intensity data for reflections *h*, *k*, *l* (*h*, 1 to 14; *k*, 0 to 14; *l*, 0 to 8) were collected using the $\omega$ scan mode up to $2\theta$ = 44.5°. Data were corrected for absorption (transmission range 0.997−0.841). The structures were solved by direct methods using the PC version of the NRCVAX[10] program package implemented on IBM-compatible 80486 computers. Atomic scattering factors for neutral atoms were taken from the literature.[11] Weights based on counting statistics were used, where the weight modifier $K$ in $KF_o^2$ is 0.000 100. Hydrogen atoms were not included in the refinement because of the high thermal motion associated with several of the methylene moieties. The uncoordinated chloride ion appears to be disordered with a water molecule over four sites. This group of atoms was refined as chloride with variable site occupancy factors. The enantiomorph was fixed by collecting and refining Friedel equivalents and refining chirality $\eta$ to 1.1.[12] Maximum and minimum heights in the final difference map were 0.610 and −0.460 e Å$^{-3}$, respectively. An ORTEP[13] drawing of the complex cation is given in Figure 1 showing 50% probability ellipsoids. Crystallographic data are given in Table 1 while selected interatomic distances and angles are given in Table 2.

**X-ray Crystal Structure Determination of [Co($Me_2$-$N_3S_3$absar)]-($ClO_4$)$_3$·0.5$CH_3CN$·0.5$H_2O$.** A sample of [Co($Me_2$-$N_3S_3$absar)]$Cl_3$·0.5HCl·1.5$H_2O$ was dissolved in water and reprecipitated by addition of solid $NaClO_4$. Crystals of [Co($Me_2$-$N_3S_3$absar)]($ClO_4$)$_3$·0.5$CH_3CN$·0.5$H_2O$ suitable for single-crystal X-ray diffraction were grown from aqueous acetonitrile. Cell dimensions were obtained from 24 reflections with a $2\theta$ angle in the range 21−35° (Graphite monochromatized Mo Kα ($\lambda$ = 0.709 30 Å)). The intensity data were collected on an Enraf Nonius CAD-4 diffractometer. Intensity data for reflections *h*, *k*, *l* (*h*, −12 to 12; *k*, 0 to 17; *l*, −16 to 18) were collected using the $\omega$ scan mode up to $2\theta$ = 44.9°. Data were corrected for absorption (transmission range 0.997−0.567). The structures were solved by direct methods using the PC version of the NRCVAX[10] program package implemented

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**Table 1.** Crystallographic Data for $[Co(Me_2\text{-}N_3S_3sar)]Cl\cdot ZnCl_4\cdot H_2O$ (**2**) and $[Co(Me_2\text{-}N_3S_3absar)](ClO_4)_3\cdot 0.5CH_3CN\cdot 0.5H_2O$ (**3**)

| compd | **2** | **3** |
|---|---|---|
| empirical formula | $CoC_{16}H_{30}N_3S_3Cl_5Zn\cdot H_2O$ | $CoC_{15}H_{28}N_3S_3Cl_3O_{12}\cdot {}^1/_2H_2O\cdot {}^1/_2CH_3CN$ |
| fw | 680.23 | 733.43 |
| space group | $P2_13$ | $P\bar{1}$ |
| *a*, Å | 13.9683(11) | 12.036(4) |
| *b*, Å |  | 15.932(9) |
| *c*, Å |  | 17.212(14) |
| α, deg |  | 64.93(7) |
| *β*, deg |  | 72.77(5) |
| *γ*, deg |  | 88.91(7) |
| *V*, Å$^3$ | 2725.40(21) | 2834(3) |
| *Z* | 4 | 4 |
| *T*, K | 293(2) | 293(2) |
| $\rho_{calc}$, g cm$^{-3}$ | 1.658 | 1.72 |
| *μ*, cm$^{-1}$ | 11.5 | 11.6 |
| cryst dimens, mm | 0.20 × 0.25 × 0.30 | 0.10 × 0.30 × 0.40 |
| transm range | 0.841, 0.997 | 0.567, 0.997 |
| *λ*, Å | 0.709 30 | 0.709 30 |
| no. of measd reflns | 3970 | 7670 |
| no. of unique reflns | 1173 | 7374 |
| no. of obsd reflns $I > 3\sigma(I)$ | 722 | 4306 |
| no. of params | 105 | 776 |
| $R_F$, $R_w$, GOF$^a$ | 0.062, 0.055, 2.55 | 0.087, 0.088, 3.84 |

[a] $R_F = \sum(F_o - F_c)/\sum(F_o)$; $R_w = \mathrm{Sqrt}[\sum(w(F_o - F_c)^2/\sum(wF_o^2)]$; GOF $= \mathrm{Sqrt}[\sum(w(F_o - F_c)^2/(\text{no. of reflns} - \text{no. of params})]$.

**Table 2.** Selected Interatomic Distances and Angles for $[Co(Me_2\text{-}N_3S_3sar)]Cl\cdot ZnCl_4\cdot H_2O^a$

| Distances (Å) |  |  |  |
|---|---|---|---|
| Co1−S1 | 2.235(4) | Co1−N1 | 2.022(11) |
| Co1−S1a | 2.235(5) | Co1−N1a | 2.022(13) |
| Co1−S1b | 2.235(5) | Co1−N1b | 2.022(14) |
| **Angles (deg)** |  |  |  |
| S1−Co1−S1a | 90.27(18) | S1a−Co1−N1b | 177.9(3) |
| S1−Co1−S1b | 90.27(19) | S1b−Co1−N1 | 177.9(4) |
| S1−Co1−N1 | 91.1(4) | S1b−Co1−N1a | 88.1(4) |
| S1−Co1−N1a | 177.9(4) | S1b−Co1−N1b | 91.1 (4) |
| S1−Co1−N1b | 88.1(3) | N1−Co1−N1a | 90.5(6) |
| S1a-Co1−S1b | 90.27(16) | N1−Co1−N1b | 90.5(5) |
| S1a-Co1−N1 | 88.1(4) | N1a−Co1−N1b | 90.5(5) |
| S1a−Co1−N1a | 91.1 (3) |  |  |

[a] Symmetry transformations used to generate equivalent atoms: a, *y*, *z*, *x*; b, *z*, *y*, *x*.

on IBM-compatible 80486 computers. Atomic scattering factors for neutral atoms were taken from the literature.[11] Weights based on counting statistics were used, where the weight modifier *K* in $KF_o^2$ is 0.000 050. Hydrogen atoms could not be located via difference Fourier map inspection. The structure consists of two independent cations, one independent acetonitrile and one independent water molecule. Cation A is disordered as follows: S1, S2, and S3 were refined with site occupancies of 0.85 whereas S1A, S2A, and S3A were refined with site occupancies of 0.15. Cation B has disorder at S, N, and two carbon atoms (C41 and C62). These atoms were refined with site occupancies of 0.60, whereas their disordered counterparts were refined with site occupancies of 0.40. Maximum and minimum heights in the final difference map were 1.050 and −0.740 e Å$^{-3}$, respectively. An ORTEP[13] drawing of the complex cation is given in Figure 2 showing 50% probability ellipsoids. Crystallographic data are given in Table 1 while selected interatomic distances and angles are given in Table 3.

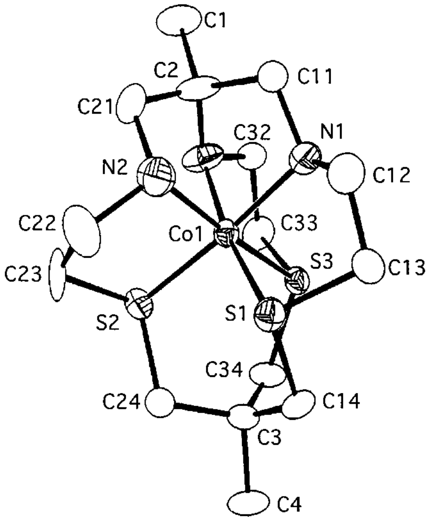


**Figure 2.** ORTEP plot of the cationic unit “A” in $[Co(Me_2\text{-}N_3S_3absar)](ClO_4)_3\cdot 0.5CH_3CN\cdot 0.5H_2O$ with atom-labeling scheme and vibrational ellipsoids at the 50% probability level.

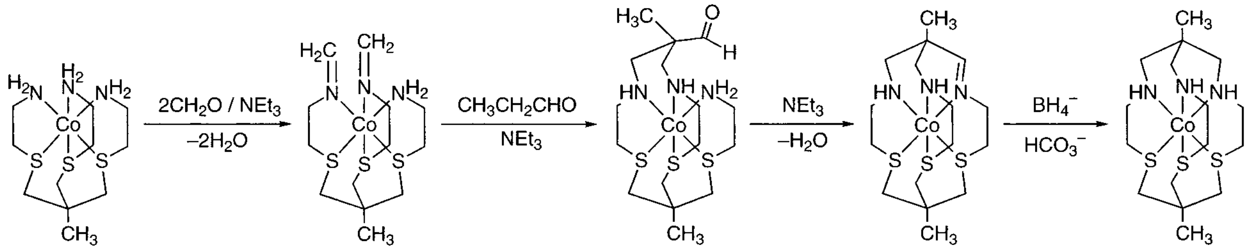
**Table 3.** Selected Interatomic Distances and Angles for $[Co(Me_2\text{-}N_3S_3absar)](ClO_4)_3\cdot 0.5CH_3CN\cdot 0.5H_2O$

| Distances (Å) |  |  |  |
|---|---|---|---|
| Co1−S1 | 2.215(5) | Co2−S4 | 2.261(7) |
| Co1−S1A | 2.23(3) | Co2−S4A | 2.073(9) |
| Co1−S2 | 2.185(5) | Co2−S5 | 2.241(6) |
| Co1−S2A | 2.30(3) | Co2−S5A | 2.263(9) |
| Co1−S3 | 2.207(5) | Co2−S6 | 2.131(6) |
| Co1−S3A | 2.09(3) | Co2−S6A | 2.281(9) |
| Co1−N1 | 1.995(12) | Co2−N4 | 2.054(17) |
| Co1−N2 | 1.989(12) | Co2−N4A | 1.92(3) |
| Co1−N3 | 1.931(11) | Co2−N5 | 1.909(17) |
|  |  | Co2−N6 | 1.936(18) |
|  |  | Co2−N6A | 1.90(3) |
| **Angles (deg)** |  |  |  |
| S1−Co1−S2 | 95.85(18) | S4−Co2−S5 | 94.30(24) |
| S1−Co1−S3 | 92.81(19) | S4−Co2−S6 | 90.0(3) |
| S1−Co1−N1 | 87.9(4) | S4−Co2−N4 | 86.6(5) |
| S1−Co1−N2 | 91.7(4) | S4−Co2−N5 | 174.0(5) |
| S1−Co1−N3 | 170.8(4) | S4−Co2−N6 | 90.6(6) |
| S1A−Co1−S2A | 90.2(10) | S4A−Co2−S5A | 93.4(3) |
| S1A−Co1−S3A | 95.4(10) | S4A−Co2−S6A | 93.4(4) |
| S2−Co1−S3 | 90.85(18) | S4A−Co2−N4A | 96.2(8) |
| S2−Co1−N1 | 175.6(4) | S4A−Co2−N6A | 95.3(8) |
| S2−Co1−N2 | 90.9(4) | S5−Co2−S6 | 93.9(3) |
| S2−Co1−N3 | 93.2(4) | S5−Co2−N4 | 90.0(5) |
| S2A−Co1−S3A | 92.7(10) | S5−Co2−N5 | 90.1(5) |
| S3−Co1−N1 | 91.2(4) | S5−Co2−N6 | 170.4(5) |
| S3−Co1−N2 | 175.0(4) | S5A−Co2−S6A | 91.3(3) |
| S3−Co1−N3 | 88.5(4) | S5A−Co2−N4A | 88.1(8) |
| N1−Co1−N2 | 86.7(5) | S5A−Co2−N6A | 169.8(8) |
| N1−Co1−N3 | 82.9(5) | S6−Co2−N4 | 175.0(5) |
| N2−Co1−N3 | 86.6(5) | S6−Co2−N5 | 93.7(6) |
|  |  | S6−Co2−N6 | 94.3(5) |
|  |  | S6A−Co2−N4A | 170.4(8) |
|  |  | S6A−Co2−N6A | 93.5(9) |
|  |  | N4−Co2−N5 | 89.4(7) |
|  |  | N4−Co2−N6 | 82.1(7) |
|  |  | N4A−Co2−N6A | 85.7(11) |
|  |  | N5−Co2−N6 | 84.5(7) |

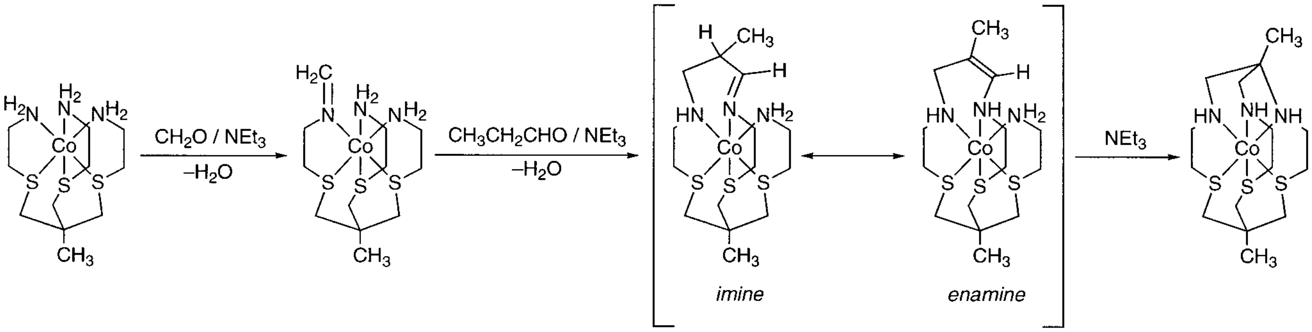
## Results and Discussion.

**Formation of the Complexes.** The synthesis of the encapsulated cage complex $[Co(Me_2\text{-}N_3S_3sar)]^{3+}$ proceeds via a template-assisted mixed-aldehyde condensation (Scheme 2), which is analogous to that proposed for the formation of the related $N_6$ complex.[9] The exact sequence in which the formaldehyde and propanal units add to the cobalt complex is not known, but it is likely that formaldehyde condenses first and then is attacked by the carbanion of propanal. The principal product of the capping reaction is the monoimine cage complex shown in Scheme 2, and this is reduced with borohydride to give the target cage. The monoimine product was readily identified in the reaction mixture by a number of characteristic

**Scheme 2**



**Scheme 3**



features in the $^1$H and $^{13}$C NMR spectra. The single sharp imine proton signal at 8.5 ppm ($>$N=C(R)*H*) was a useful indicator of the progress of the reaction. $^{13}$C NMR peaks at 19.3 ppm ($CH_3$ resonance in the imine-containing cap) and 187.7 ppm (cap imine) fell close to the corresponding shifts in the $N_6$ donor system (19.1 and 188.3 ppm).[9] The isolation and full characterization of the intermediates and byproducts of the $N_3S_3$ system will be the subject of a separate study.[14]

One notable difference between the capping of the $N_3S_3$ donor and $N_6$ donor systems is the complication introduced by the facile reduction of the Co(III) center to give the low-spin Co(II) complex in the sulfur-containing system. The ease of reduction of cobalt(III) complexes is enhanced by the replacement of amine groups by the more polarizable thioether donors. Furthermore, the thioether donor is a considerably poorer donor than the amine nitrogen for first-row transition metals. Under the capping conditions, there was a significant amount of reduction of the template $[Co(ten)]^{3+}$ (up to 30%); in the chromatographic workup of the reaction, $Co^{2+}$ and the protonated ligand ten are isolated. This facile formation of $[Co(ten)]^{2+}$ and its reduced stability compared to $[Co(sen)]^{2+}$ appear to be the principal causes for the lower yield of the $N_3S_3$ cage in comparison to the $N_6$ analogue.

Upon addition of triethylamine to the reaction mixture, all of the $[Co(ten)]^{3+}$ dissolves, but a brown precipitate is rapidly formed. This appears to be an insoluble salt of deprotonated $[Co(ten)]^{3+}$, as isolation of this material followed by dissolution in DCl shows the presence of only $[Co(ten)]^{3+}$ in the NMR spectrum. The use of a different counteranion (such as trifluoromethane sulfonate) did increase the solubility, but led to a decrease in the yield. The conditions of the capping reaction have been varied extensively, and the synthesis given in the Experimental Section represents the best conditions found thus far. Addition of more (or less) base, changing the nature of the base, and the use of more solvent, different anions, shorter reaction times, or different proportions of the aldehydes either have no significant effect on the reaction or lead to a reduction in the yield.

The imine precursors[14] to the saturated cage complex were reduced with borohydride ion. After the reduction mixture was quenched with acid, the cobalt(II) complexes were reoxidized to cobalt(III) by bubbling with a vigorous stream of air. Two products were separated by chromatography, corresponding to the expected "regular" cavity complex (red) and the unexpected "contracted" cavity complex (yellow). There has been no evidence for the formation of a corresponding contracted $N_6$ cage complex during the capping of $[Co(sen)]^{3+}$.[7,9]

The contracted cavity complex is inaccessible via the normal reaction sequence in the mixed-aldehyde capping reaction (Scheme 2). A proposed reaction sequence for its formation is outlined in Scheme 3. Condensation of a single formaldehyde unit and one propanal with $[Co(ten)]^{3+}$ is followed by rearrangement of the product imine to the enamine. The final step of the capping involves attack at the more substituted end of the double bond. Although this would normally be the less favored position for attack, attack at the other end of the double bond would give rise to a highly strained four-membered chelate ring fused to a six-membered chelate ring. A small amount of the contracted cavity carbinolamine species $[Co(Me_2\text{-}N_3S_3\text{absar-7-OH})]^{3+}$ (which arises through hydration of an imine) is also formed, and the mechanistic aspects of its formation will be the subject of a subsequent publication.[14]

**Isolation of the Free Ligands.** Both the regular and contracted cavity cage complexes were smoothly demetalated to give the free ligands by reducing the inert cobalt(III) center to cobalt(II) with zinc dust under an inert atmosphere in the presence of cyanide. On heating, the metal was removed and complexed as $[Co(CN)_6]^{3-}$, and the free ligand was extracted into chloroform. Both ligands are white, microcrystalline, air-stable materials, insoluble in water, although their hydrochloride salts are water soluble.

Demetalation of the cage ligands is more facile for the $N_3S_3$ cage ligands than for the corresponding $N_6$ cage systems. Thioethers are considerably weaker donors for the first-row transition metals than are amines. Demetalation of $[Co(Me_2\text{-}sar)]^{2+}$ has only been effected in poor yield and under extreme

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(14) Angus, P. M.; Sargeson, A. M. In preparation.

(15) Geue, R. J.; Osvath, P.; Sargeson, A. M.; Walker, G. W. Unpublished.

conditions,[15] whereas $[Co(Me_2\text{-}N_3S_3sar)]^{2+}$ is demetalated by cyanide at 100 °C in a matter of minutes.The corresponding process for $[Co(Me_2\text{-}S_6sar)]^{2+}$ is complete in a matter of seconds at 20 °C.[7] The extrusion of the cobalt(II) center from the contracted cavity $Me_2\text{-}N_3S_3absar$ is noticeably faster than that for $Me_2\text{-}N_3S_3sar$, and this is an indication of the poorer fit of the cobalt(II) ion into the smaller cavity. This size mismatch is also seen in a comparison of the electronic properties of cobalt complexes formed with the two cage ligands (see below).

Both the amine-capped ligand $NH_2,Me\text{-}N_3S_3sar$ and the hydrogen-capped $H,Me\text{-}N_3S_3sar$ have been prepared in good yield by heating of their cobalt(II) complexes in concentrated hydrochloric acid.[7] However, the insolubility of the neutral $Me_2\text{-}N_3S_3absar$ and $Me_2\text{-}N_3S_3sar$ ligands in aqueous solution makes workup considerably simpler using the cyanide demetalation coupled with chloroform extraction, and it is therefore the method of choice, despite the attendant risks of cyanide ion.

**Spectral and Electronic Properties.** The spectral and electronic properties of the $[Co(Me_2\text{-}N_3S_3sar)]^{3+}$ complex cation are consistent with a fully encapsulated cobalt(III) ion coordinated to an $N_3S_3$ donor set. Both the $^1H$ and $^{13}C$ NMR spectra show that the complex cation has average $C_3$ symmetry. The $^1H$ NMR spectrum shows the two expected singlets corresponding to the apical methyl groups. The methylene protons in the caps give rise to pairs of AB doublets, and those in the straps give AA′BB′ multiplets. However, in common with most of the cage complexes, a number of the methylene protons were in similar environments, leading to overlapping signals and making detailed analysis difficult. The eight-line $^{13}C$ NMR spectrum was assigned by a combination of the DEPT spectrum and a comparison of the chemical shifts with those observed for the related complexes with averaged $D_3$ symmetry ($[Co(Me_2\text{-}N_6sar)]^{3+}$ and $[Co(Me_2\text{-}S_6sar)]^{3+}$). In addition, in a 1:1 mixture of $H_2O/D_2O$, the carbon atoms that are adjacent to the isotopomeric N−H and N−D groups showed slightly different chemical shifts,[5] and this technique was used to establish which carbon atoms were adjacent to exchangeable N−H groups.

Treatment of aqueous $[Co(Me_2\text{-}N_3S_3sar)]^{3+}$ with base gave rise to a dark purple solution. The resonances in the $^1H$ spectrum were significantly broadened, while most of the resonances in the $^{13}C$ NMR spectrum were lost, with only the quaternary carbons and the methyl resonances appearing as sharp peaks. It seems likely that one of the N−H amines is deprotonated, and that there is rapid exchange of the remaining two protons between the three equivalent sites. When base was added to solutions of the corresponding $N_6$ cage complexes, an intense purple color was also observed,[4,16] although in those cases the resonances in the NMR spectra did not show significant broadening. It is possible that the increased accessibility of the cobalt(II) state in the presence of the more polarizable thioether donors leads to some net reduction and rapid electron transfer between traces of the low-spin cobalt(II) complex and the cobalt(III) complex. This could be responsible for the broadening of the $^1H$ signals and the loss of the $^{13}C$ signals, since the electron transfer rates for the $N_3S_3$ cages are $\sim 10^4$ greater than those of the corresponding $N_6$ cages. It is clear from the NMR studies that there is no H exchange at the carbon atoms (see below), and the N-proton exchange and conformational changes that normally take place rapidly with the cobalt(III)−$N_6$ cages do not cause such broadening.

Even though the resonances corresponding to carbon atoms at the thioether end of the cage molecule were also broadened in basic solution, there was no indication of $CH_2$−S deprotonation in $[Co(Me_2\text{-}N_3S_3sar)]^{3+}$. Furthermore, reacidification of a sample of the deprotonated species dissolved in $D_2O$ with concentrated DCl (after 24 h) gave quantitative recovery of the parent complex with no sign of any C−H exchange, or Co−C bond formation, as has been reported for $[Co([9]aneS_3)_2]^{3+}$,[17] and for a number of mixed N−S donor systems.[18−23] The C−H bonds adjacent to the coordinated thioethers in $[Co(Me_2\text{-}N_3S_3sar)]^{3+}$ do not have the appropriate orientation for the stabilization of a carbanionic species through a $d\pi-p\pi$ interaction, and the structure is considerably more rigid than the linear tridentate ligands for which such deprotonations have been reported. The secondary N−H protons in $[Co(Me_2\text{-}N_3S_3sar)]^{3+}$ are significantly more acidic than those in ordinary cobalt(III) secondary amines, in line with that reported for the $N_6$ cages.[24−26] Despite the ready deprotonation of a coordinated amine center in the $N_3S_3$ cage complex, the lack of $S-CH_2$ proton exchange (assisted by amine deprotonation) is consistent with the reported stereospecificity of this process.[20−23]

The $[Co(Me_2\text{-}N_3S_3absar)]^{3+}$ complex shows the expected lack of symmetry in the $^{13}C$ NMR spectrum arising from the lack of a methylene unit in one strand of the cage. The $^1H$ NMR spectrum again shows two singlets for the apical methyl groups. The methylene region of the spectrum contains resonances corresponding to 22 inequivalent protons, each coupled to one or more protons, over a chemical shift range of 1.1 ppm, so it is not possible to make a detailed assignment. However, the patterns of the $^1H$ and $^{13}C$ NMR spectra parallel those obtained for the related contracted-cavity cages obtained from the diazotization reaction of $[Co(NH_3^+,Me\text{-}N_3S_3sar)]^{3+}$.[3] The $^{13}C$ resonances have been assigned by a combination of the DEPT technique and the isotopomeric method described above.

In contrast to the $[Co(Me_2\text{-}N_3S_3sar)]^{3+}$ complex, deprotonation of the contracted-cavity cobalt(III) complex gave a reddish complex, and although the $^1H$ NMR spectrum showed some broadening, the $^{13}C$ resonances remained sharp. The peaks that have been assigned to the $CH_2N$ resonances undergo varying degrees of shift, as expected, but the remainder of the carbon signals remain largely unchanged. This difference in behavior is consistent with the greater difficulty associated with adding electron density to the cobalt(III) center when it is encapsulated in the contracted cavity. Once again, there were no signs of carbanion formation or proton exchange at $S-CH_2$, but this is consistent with the geometry of the complex cation.

Cyclic voltammetry shows reversible 3+/2+ couples for the cobalt complexes of both $Me_2\text{-}N_3S_3sar$ and $Me_2\text{-}N_3S_3absar$. Reversible electrochemistry is observed for the cobalt complexes

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**Table 4.** Redox Potentials for the Co(III)/(II) Cage Couples with $N_xS_{6-x}$ Donor Groups

| complex | $E_{1/2}$ (V)[a] |
|---|---|
| $[Co(Me_2\text{-}N_6sar)]^{3+/2+}$ | −0.484 |
| $[Co(H,Me\text{-}N_4S_2sar)]^{3+/2+}$ | −0.156[b] |
| $[Co(Cl,Me\text{-}N_4S_2sar)]^{3+/2+}$ | −0.037[b] |
| $[Co(Me_2\text{-}N_3S_3sar)]^{3+/2+}$ | −0.104 |
| $[Co(H,Me\text{-}N_3S_3sar)]^{3+/2+}$ | −0.092 |
| $[Co(HO,Me\text{-}N_3S_3sar)]^{3+/2+}$ | −0.031 |
| $[Co(Cl,Me\text{-}N_3S_3sar)]^{3+/2+}$ | +0.010 |
| $[Co(Me_2\text{-}N_3S_3absar)]^{3+/2+}$ | −0.181 |
| $[Co(Me,HOCH_2\text{-}N_3S_3absar)]^{3+/2+}$ | −0.160 |
| $[Co(Me,ClCH_2\text{-}N_3S_3absar)]^{3+/2+}$ | −0.121 |
| $[Co(Me_2\text{-}S_6sar)]^{3+/2+}$ | +0.244 |

[a] Vs SHE at 20 °C. $I = 0.2$ M NaCl. Values in 0.1 M NaCl are 10−20 mV more positive.[3] [b] 0.1 M $NaClO_4$, ref 28.

of the related cage ligands from $N_6$ through $S_6$ donor sets[3,26−28] and is attributed to the enhanced stability engendered by the encapsulating nature of the ligand. The redox potentials are listed in Table 4, together with those of related complexes, redetermined under the same conditions. The variations in redox potential for a series of hexaamine cage complexes with varying cavity size and apical substituent have previously been analyzed in terms of a Hammett type correlation,[29] and the $N_3S_3$ cages show the same trend, although the differences in redox potential are smaller.

The replacement of N donors by S thioether donors in the sar-based cages raises the redox potential in a near linear progression, and the value measured for $[Co(Me_2\text{-}N_3S_3sar)]^{3+/2+}$ (−104 mV) is approximately midway between the values for the corresponding $N_6$ and $S_6$ cage complexes. The redox potential of $[Co(Me_2\text{-}N_3S_3absar)]^{3+/2+}$ is ∼80 mV more negative, as the larger cobalt(II) ion is not accommodated as readily in the smaller cavity as is the cobalt(III) ion, leading to a destabilization of the former state. The combination of the contracted cavity and the inductive effect of the methyl group gives $[Co(Me_2\text{-}N_3S_3absar)]^{3+}$ the most negative redox potential recorded thus far for the $N_3S_3$ donor set.[3] This alleviates the problems associated with the use of these complexes as electron transfer agents in the photosplitting of water,[3,30,31] and its use in this context has recently been reported.[32]

The dramatic difference in the color of the two cobalt(III) complexes arises from a 20 nm shift in the positions of the d−d transitions to higher energies in the contracted cavity cage with respect to the $[Co(Me_2\text{-}N_3S_3sar)]^{3+}$ complex. In fact all of the bands in the UV/visible spectrum are shifted to higher energies (Figure 3). This is a consequence of the higher ligand field imposed by the tighter cavity. A similar (but smaller) hypsochromic shift has been reported for the corresponding $N_6$ cages.[4,16]

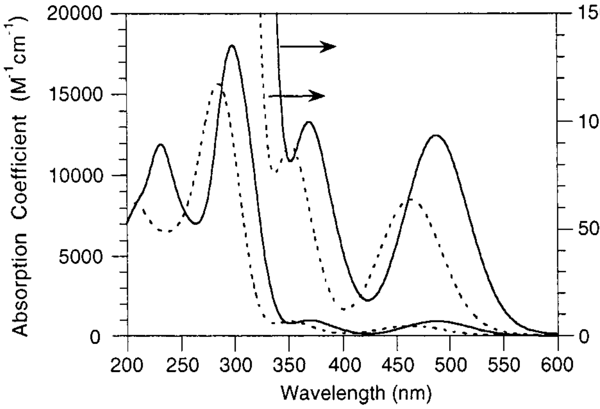

**Figure 3.** Absorption spectra of $[Co^{III}(Me_2\text{-}N_3S_3sar)]^{3+}$ (—) and $[Co^{III}(Me_2\text{-}N_3S_3absar)]^{3+}$ (- - -) in $H_2O$.

**Table 5.** Band Positions and Ligand Field Parameters for Cobalt(III) Cage Complexes[a]

| complex | $E(^1A_{1g} \rightarrow {}^1T_{1g})$ | $E(^1A_{1g} \rightarrow {}^1T_{2g})$ | $\Delta_{O_h}$ | $B$ | ref |
|---|---|---|---|---|---|
| $[Co(Me_2\text{-}N_6sar)]^{3+}$ [b,c] | 21 050 | 29 100 | 23 440 | 598 | |
| $[Co(Me,NH_3^+\text{-}N_6sar)]^{4+}$ [b] | 21 200 | 29 000 | 23 530 | 575 | 16 |
| $[Co(Me,CH_2Cl\text{-}N_6absar)]^{3+}$ [b] | 21 835 | 29 940 | 24 240 | 599 | 16 |
| $[Co(Me,NH_3^+\text{-}N_5Ssar)]^{4+}$ [d,e] | 20 660 | 28 330 | 22 880 | 566 | 33 |
| $[Co(Me,NH_3^+\text{-}N_4S_2sar)]^{4+}$ [b] | 20 450 | 27 700 | 22 610 | 530 | 34 |
| $[Co(Me,H\text{-}N_4S_2sar)]^{3+}$ [b] | 20 490 | 27 550 | 22 600 | 514 | 34 |
| $[Co(Me,NH_3^+\text{-}N_3S_3sar)]^{4+}$ [b] | 20 490 | 27 100 | 22 480 | 475 | 3 |
| $[Co(Me,NH_3^+\text{-}N_3S_3sar)]^{4+}$ [d,f] | 20 460 | 26 960 | 22 610 | 465 | 35 |
| $[Co(Me_2\text{-}N_3S_3sar)]^{3+}$ [b,c] | 20 530 | 27 100 | 22 510 | 471 | |
| $[Co(Me_2\text{-}N_3S_3absar)]^{3+}$ [b,c] | 21 550 | 28 490 | 23 640 | 499 | |
| $[Co(Me_2\text{-}S_6sar)]^{3+}$ [b] | 20 240 | 26 315 | 22 080 | 432 | 27 |

[a] Values quoted in $cm^{-1}$. [b] $B$ and $\Delta_{O_h}$ were calculated from spectral data reported in the references, using LIGFIELD,[36] with $C = 6B$. [c] This work. [d] $B$, $C$, and $\Delta_{O_h}$ were calculated from spectral data reported in the references, using LIGFIELD.[36] [e] Spectra recorded at 11 K, in Nafion film. The energies of the transitions ($^1A_{1g} \rightarrow {}^3T_{1g}$) 13 750 $cm^{-1}$ and ($^1A_{1g} \rightarrow {}^3T_{2g}$) 17 500 $cm^{-1}$ were also used in the calculation. $C =$ 3300 $cm^{-1}$. [f] Spectra recorded at 10 K, in Nafion film. The energies of the transitions ($^1A_{1g} \rightarrow {}^3T_{1g}$) 14 145 $cm^{-1}$ and ($^1A_{1g} \rightarrow {}^3T_{2g}$) 17 240 $cm^{-1}$ were also used in the calculation. $C = 3070$ $cm^{-1}$.

The ligand field parameters for the cobalt(III) complexes, based on the solution spectra (∼20 °C), are given in Table 5, together with those of related complexes, calculated using the reported band maxima.[3,16,27,33−35] The calculations were carried out with the program LIGFIELD[36] employing a symmetry-based parametrical model and the full $d^6$ configuration. The ligand field is perceived as a sum of octahedral and lower symmetry contributions, and the complete Hamiltonian is a sum of these ligand field contributions, electron repulsion, and spin−orbit coupling.

Since the absorption bands of the spin-forbidden transitions ($^1A_{1g} \rightarrow {}^3T_{1g}$ and $^1A_{1g} \rightarrow {}^3T_{2g}$) were not observed, only two parameters can be fitted; the remaining parameters in the total energy expression were fixed. The parameters to be fitted were chosen as Racah $B$ and $\Delta_{O_h}$, while the lower symmetry ligand field parameters as well as the spin−orbit coupling were set to 0. Racah $C$ was fixed at $6B$, rather than using the usual assumption that $C \approx 4B$.[37] This somewhat unorthodox choice of the $C$:$B$ ratio is justified by LIGFIELD calculations on the complexes $[Co(NH_3^+,CH_3\text{-}N_5Ssar)]^{4+}$ and $[Co(NH_3^+,CH_3\text{-}$

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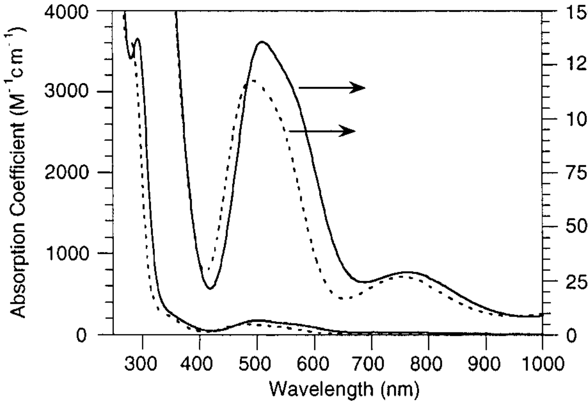

**Figure 4.** Absorption spectra of $[Co^{II}(Me_2\text{-}N_3S_3sar)]^{2+}$ (—) and $[Co^{II}(Me_2\text{-}N_3S_3absar)]^{2+}$ (- - -) in $H_2O$.

$N_3S_3sar)]^{4+}$ where the two spin-forbidden transitions to the triplet states have been observed.[33,35] These calculations yield *C*:*B* ratios of 5.8 and 6.6, respectively (Table 5). It has been argued previously that for cobalt(III) amine complexes a *C*:*B* ratio of 6 is more appropriate than the conventional choice of 4.[33−35] It is worth noting, however, that altering the *C*:*B* ratio from 6 to 4 has only a marginal effect on the values of the ligand field parameters, and the observed *trends* remain unaffected.

There is a smooth but rather modest decrease in the value of $\Delta_{O_h}$ as amine donor groups are successively replaced by thioethers (~200 $cm^{-1}$ for each donor group). This indicates that the thioether donor exerts a slightly weaker ligand field than the secondary amine nitrogen. An earlier ligand field analysis of a series of analogous cage complexes indicated that there was a significant reduction, of unclear origin, on replacement of the first amine donor, followed by a very small decrease upon the replacement of subsequent amine groups.[33] The reduction of *B* as successive amine donors were replaced by thioethers was much more pronounced. Similar trends for *B* have previously been noted for cage and macrocyclic complexes with mixed N−S donor sets.[33,38]

In contrast, contraction of the $N_3S_3$ cage cavity has a dramatic effect on the value of $\Delta_{O_h}$, whereas the value of *B* is affected only to a modest extent. For the corresponding cobalt(III) complexes of $N_6$sar and $N_6$absar,[16] a similar increase is seen for $\Delta_{O_h}$, while there is little effect on *B*.

The UV/visible bands in the cobalt(II) complexes are shifted hypsochromically in the contracted cavity cage (Figure 4), although the effect is less pronounced than in the cobalt(III) state. Assignment of the bands for the cobalt(II) systems proved to be less than straightforward for the high-spin ($N_6$) and low-spin ($N_3S_3$ and $S_6$) systems alike. Consequently, the calculated ligand field parameters were poorly determined, giving unacceptably large standard deviations. The model framework is inadequate in that it does not take into account the differential nephelauxetic effects[37] arising from the covalency differences in octahedral symmetry between the $t_{2g}$ and $e_g$ d orbitals. A satisfactory reproduction of the experimental transition energies from the calculations may require the use of different Racah *B* and *C* electron repulsion parameters for transitions to excited states which give rise to very different electron distributions.

The electronic self-exchange rate constants for both $[Co(Me_2\text{-}N_3S_3sar)]^{3+/2+}$ and $[Co(Me_2\text{-}N_3S_3absar)]^{3+/2+}$ are ~$10^4$ $M^{-1}$ $s^{-1}$, and together with a series of related complexes, they form the subject of a separate study.[39] These rates are about the same as that for $[Co(Me_2\text{-}S_6sar)]^{3+/2+}$ but approximately 4 orders of magnitude greater than those of the corresponding $N_6$ donor cobalt(III/II) cage complexes.[27,39−43] Electron transfer in the $N_6$ cage systems is accompanied by a high-spin cobalt(II)/low-spin cobalt(III) change.[27,40] In contrast, both the cobalt(II) and cobalt(III) states in the $N_3S_3$ and $S_6$ cage complexes have a low-spin electronic configuration and, consequently, lesser reorganization energies.

Both the $^1H$ and $^{13}C$ NMR spectra of the free $Me_2\text{-}N_3S_3$sar ligand show average $C_3$ symmetry, and the protons corresponding to the "cap" methylene groups register as singlets, since in the absence of a metal ion in the cavity, the individual protons on the same cap carbon are degenerate through a rapid trigonal twist about the $C_3$ axis. In DCl solution, the positions of the resonances in the proton spectrum are shifted in a manner consistent with protonation of the amine nitrogens, but the average $C_3$ symmetry is preserved, showing the dynamic nature of amine protonation in contrast to the effect of coordinating an inert metal center to the amines. Interestingly, the $^{13}C$ NMR spectrum shows a marked change upon protonation. With the exception of the quaternary carbon resonances, the remainder of the signals are significantly broadened, although the overall symmetry of the spectrum is retained. In particular, the resonances at 42.0 and 53.4 ppm are ~1 ppm wide. There are two reasons for this difference. Although there are three secondary amines that can in principle be protonated in $Me_2\text{-}N_3S_3$sar, the structure of the ligand is such that full protonation will only be possible in very concentrated acid, as the electrostatic repulsions generated by three ammonium ion centers held in such close proximity are considerable. Thus under the conditions of the NMR measurement (0.1 M DCl) there will be more than one protonated species at equilibrium, and each will have slightly different chemical shifts. In addition, the exchange rate for the protons is reduced in acidic solution, which will also lead to broadening. Nevertheless, the average $C_3$ symmetry of the molecule is still evident on both the $^1H$ and $^{13}C$ NMR time scales.

The methylene region of the proton spectrum of the unprotonated $Me_2\text{-}N_3S_3$absar is complicated, owing to the lower symmetry in this molecule compared with $Me_2\text{-}N_3S_3$sar. However, the $^{13}C$ NMR contains only 11 resonances, which is consistent with the presence of two equivalent "straps" in the cage, and one different. This molecule is also quite flexible, and the equivalent methylene units in different straps are averaged on the NMR time scale. Once again, the $^{13}C$ NMR spectrum of the protonated ligand in DCl shows broadening, although not to the same extent as that seen in $Me_2\text{-}N_3S_3$sar. In this instance, as a result of the lower symmetry, the methylene units in one strap are differentiated from those of the other two, and so the proton exchange processes between the amine groups in the different types of strap will lead to separate signals rather than broadening.

**Crystal Structure of $[Co(Me_2\text{-}N_3S_3sar)]Cl\cdot ZnCl_4\cdot H_2O$.** The structure of the complex cation $[Co(Me_2\text{-}N_3S_3sar)]^{3+}$ (Figure 1) clearly shows the complete encapsulation of the cobalt center

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by the cage ligand and the coordination of the three secondary amine nitrogens and three thioether sulfurs. As noted for all of the sar-type cage complexes that have been structurally characterized, there is only one absolute configuration of the donor atoms for any particular configuration about the cobalt center. Thus a $\Lambda$ configuration about the cobalt requires an *S* configuration about the donor atoms.

In the complex cation $[Co(Me_2\text{-}N_3S_3sar)]^{3+}$, the Co−S bond length is 2.235(5) Å. The closely related $N_3S_3$ cage complex cations $[Co(aza,Me\text{-}N_3S_3sar)]^{3+}$ and $[Co(NO_2,CH_2SCH_2CH_2NH_3^+\text{-}N_3S_3sar)]^{4+}$ have averaged Co−S bond lengths of 2.226(1) Å[2] and 2.215 Å,[44] respectively. The corresponding values in the $N_5S$ and $N_4S_2$ donor cage complexes $[Co(NH_3^+,Me\text{-}N_5Ssar)]^{4+}$ and $[Co(NO_2,Me\text{-}N_4S_2sar)]^{3+}$ are 2.219(1)[33] and 2.214(5) Å.[34] Similarly, the open tripodal complexes $[Co(ten)]^{3+}$ and $[Co(N_4S_2ten)]^{3+}$ both have averaged Co−S bond lengths of 2.211(7) Å.[34,35] Although these bond lengths have previously been described as being "at the short end of $Co^{III}$−S bond lengths",[33−35,44] the comparison is perhaps not appropriate, since the species with significantly longer Co−S bonds involve acyclic ligands with a coordinated terminal −S−Me group in the form of methionine (2.301 Å)[45] or *S*-methylcysteine (2.272 Å).[46] A more valid comparison involves thioether donors in the middle of a polymethylene unit that is anchored at each end by other thioether or amine groups. In this case, the Co−S bond lengths found in $[Co(Me_2\text{-}N_3S_3sar)]^{3+}$ (2.235 Å), in particular, fall in the middle of a relatively narrow range observed for such systems (2.217 Å for *cis*-$[Co([9]ane\text{-}N_2S)_2]^{3+}$ [47] to 2.256 Å for $[Co([18]ane\text{-}N_2S_4)]^{3+}$ [48]). The Co−S bond length is the same within experimental error as that found in the structure of the related homoleptic thioether cage $[Co(Me_2\text{-}S_6sar)]^{3+}$ (2.237(7) Å).[49] This is not too surprising as coordinating thioethers have a relatively modest effect on the bond distance of the ligand coordinated in the trans position (e.g., the Co−S bond lengths in $[Co([9]aneS_3)_2]^{3+}$ and $[Co([9]aneN_3)([9]aneS_3)]^{3+}$ are 2.253(5)[50] and 2.247(9) Å,[51] respectively).

By contrast, the Co−N bonds in $[Co(Me_2\text{-}N_3S_3sar)]^{3+}$ are unusually long (2.022 Å). The normal range of Co−N bond lengths in the analogous $[Co(N_6sar)]^{3+}$ type cages spans a range of 1.96−2.00 Å,[52−54] and even tripodal structures such as $[Co(sen)]^{3+}$ and $[Co(tame)_2]^{3+}$ have Co−N bond lengths around 1.97 Å.[55,56] However, the cage complexes with $N_3S_3$ donor sets all show longer Co−N bonds (2.009 Å in $[Co(aza,Me\text{-}N_3S_3sar)]^{3+}$,[2] 2.007 Å in $[Co(NO_2,CH_2SCH_2CH_2NH_3^+\text{-}N_3S_3sar)]^{4+}$).[44] The unusually long Co−N bonds observed in the $N_3S_3$ donor cages are not the result of any trans effect, since the longest reported Co−N bond in a cobalt(III) cage complex (2.042 Å), which is found in the $[Co(NO_2,Me\text{-}N_4S_2sar)]^{3+}$ complex cation, is trans to a nitrogen donor.[34] Furthermore, the Co−N bonds in $[Co(Me[9]aneN_3)_2]^{3+}$ average 1.974 Å,[57] while those with each N donor trans to a thioether donor in $[Co([9]aneN_3)([9]aneS_3)]^{3+}$ average 1.961 Å.[51] In macrocyclic complexes with secondary amine donors, such elongated Co−N bonds are usually a reflection of a degree of cumulative ring strain (e.g., $[Co([18]aneN_5)Br]^{2+}$ has Co−N bonds (trans to secondary amines) ranging from 2.014 to 2.065 Å).[58] However, for $[Co(Me_2\text{-}N_3S_3sar)]^{3+}$, the geometry around the central cobalt center is close to octahedral, with all of the L−Co−L (L = N, S) angles within ∼2° of the ideal value for octahedral symmetry, and the trigonal twist angle defined by the planes of the $N_3$ and $S_3$ donor sets is 57.4° (60° for regular octahedral geometry). It seems likely, therefore, that the differences in Co−N and Co−S bond lengths are imposed by the geometric constraints of the cage ligand itself, rather than the inherent properties of the donor set. Thus the Co−N bond lengths in the $N_5S$ complex (average 1.98(1) Å)[33] more closely resemble those of the corresponding $N_6$ cages. By contrast, the sole elongated Co−N bond in the $N_4S_2$ structure (2.042(4) Å) is the one in the cap containing the two thioether donor atoms, and it is proposed that the geometric constraints of the cage make this amine more akin to the pair of adjacent thioether donors that make up this $NS_2$ "cap".[34]

The gross structural features of the complex cation reflect trigonal symmetry. The complex has the conformation that is most commonly observed for the "sar"-based cobalt cage complexes with amine, thioether, or mixed N,S donor sets (*lel*$_3$),[59] i.e., all three five-membered N−C−C−S chelate rings are in the *lel* conformation. The methylene units of the caps are almost eclipsed with respect to the donor groups (the N cap is twisted ∼4° from the fully eclipsed position while the S− cap is rotated ∼10°), and the two caps are staggered with respect to each another. These conformational characteristics were also observed in the cation geometries of the $N_3S_3$ cages $[Co(aza,Me\text{-}N_3S_3sar)]^{3+}$ [2] and $[Co(NO_2,CH_2SCH_2CH_2NH_3^+\text{-}N_3S_3sar)]^{4+}$,[44] as well as the related $N_4S_2$,[34] $N_5S$,[33] and $N_6$[16,52] cage complexes. It can be seen from the ORTEP diagram that the thermal ellipsoids of the methylene groups in the "straps" in particular are large. Similar conformational flexibility has been observed around the Co−S bonds in most of the cobalt cage structures containing thioether donor groups, and this reflects a degree of disorder.[28,35,44]

**Crystal Structure of $[Co(Me_2\text{-}N_3S_3absar)](ClO_4)_3\cdot 0.5CH_3CN\cdot 0.5H_2O$.** The structure of the complex cation $[Co(Me_2\text{-}N_3S_3absar)]^{3+}$ (Figure 2) not only shows the encapsulation of the cobalt center by the cage ligand and the coordination of the three secondary amine nitrogens and three thioether sulfurs but also establishes the unexpected formation of the contracted cavity, resulting from the condensation of a propanal and a single formaldehyde unit with the tripodal $[Co(ten)]^{3+}$.

The complex cation $[Co(Me_2\text{-}N_3S_3absar)]^{3+}$ shows substantial disorder. There are two distinct cations in the unit cell. One of these (cation "A") has disorder at the three thioether sulfur atoms which were refined with site occupancies of 0.85 and 0.15. The

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other (cation “B”) has disorder at all six donor groups and at two methylene groups, which are refined with site occupancies of 0.60 and 0.40. The effective rotation of the $N_3$ and $S_3$ donor sets (in opposite directions) between the two forms of cation “B” is accommodated by a different connectivity between the two “caps”, and the two forms effectively differ significantly only in the position of one “strap” *C*$H_2$N methylene unit. The structures of both cations A and B are in fact quite similar (with the exception of the distorted form of cation “A”, which corresponds to the 15% site occupancy in the refinement).

Despite the complexities of the structure, the effects of encapsulation within the contracted cavity are clearly apparent. The modest changes around the central metal core are consistent with the observations reported for the only other crystallographically characterized “absar” based cage complexes, [Co(Me,OH-absar)]$^{3+}$ [4] and [Co(Cl,$CH_2$Cl-absar)]$^{3+}$.[52] Furthermore, there is no significant difference between the mean Co−S bond length in the [Co($Me_2$-$N_3S_3$absar)]$^{3+}$ cation (2.21(7) Å) and that in the [Co($Me_2$-$N_3S_3$sar)]$^{3+}$ cation (2.235(5) Å) nor between the mean Co−N bond lengths in the “regular arms” of [Co($Me_2$-$N_3S_3$absar)]$^{3+}$ (2.00 Å) and [Co($Me_2$-$N_3S_3$sar)]$^{3+}$. However, the Co−N bond length in the “contracted arm” of [Co($Me_2$-$N_3S_3$absar)]$^{3+}$ is significantly shortened (1.93 Å), and this is in contrast to the $N_6$-based absar complexes, where the Co−N bond lengths in the “regular” and “contracted” arms were not significantly different (1.97 Å).

There is some deviation from normal octahedral geometry around the central Co−$L_6$ (L = N, S) core. Although most of the L−Co−L angles are within ∼3% of the normal values for octahedral coordination, in cation “A” the N1−Co−N3 angle is compressed to 82.9° and the S1−Co−S2 angle opposite is expanded to 95.9°, corresponding to a slight shift of the cobalt center away from the $N_3$ donor set. (In cation “B” similar behavior is observed.) The trigonal twist angle defined by the planes of the $N_3$ and $S_3$ donor sets is surprisingly close to 60°, considering the distortion imposed by the contracted cavity. The rotations required to eclipse the N−S pairs related by chelating strands is ∼59(±1)° for the two “normal strands” whereas that for the strand with one fewer methylene units is 56(±1)°. The geometry is thus effectively octahedral, with the amine donor group in the contracted strand having suffered a slight displacement from its normal position.

Although it would seem that the metal center largely dictates the geometry of the immediate coordination environment, the accommodation of the metal ion within the contracted cavity shows up much more markedly in the structural rearrangement of the ligand framework itself. The cap containing the sulfur donors is twisted 35° (cation “A”) and 24° (cation “B”) away from the eclipsed position, and this is a significant increase over the value observed for the [Co($Me_2$-$N_3S_3$sar)]$^{3+}$ structure (10°). (The entire cap at the nitrogen end is tilted as a result of the absence of one methylene unit, so it is not really meaningful to compare the torsion angle of the amine cap of [Co($Me_2$-$N_3S_3$sar)]$^{3+}$ with that of [Co($Me_2$-$N_3S_3$absar)]$^{3+}$.)

One notable feature that is present in all three structurally characterized “absar” based cage complexes is the *lel*$_2$*ob* conformation of the three S(N)−C−C−N five-membered chelate rings.[4,52] Furthermore, in each case, the chelate ring having the *ob* conformation is not in the strand that is missing the methylene unit.

## Conclusion

The mixed-aldehyde capping of the cobalt complex of a tripodal $N_3S_3$ donor ligand, followed by reduction, leads to a pair of related cage ligand complexes. The major product has the same ligand framework as that observed in related capping reactions, whereas the minor product has a smaller cavity, arising from the formation of a cap containing one fewer methylene units. These complexes can be readily demetalated to give the corresponding free ligands, which possess no additional functionality, so their potential coordination chemistry is simplified. They represent an interesting case where a closely related but intrinsically different pair of cage ligands can both be readily prepared, separated, and demetalated. As such they offer a valuable probe of the effect of cavity size on the complexation properties for different metal ions, since the size and nature of the coordination cavity are well-defined.

The properties of the cobalt complexes clearly reflect the influence of the different cavity size on the metal center. The preparation of metal complexes with other first-row transition metals in particular should provide interesting insights into the control of electronic and magnetic properties (spin state, oxidation potential, electron self-exchange rates) via control of the available cavity within which the metal must be accommodated.

**Acknowledgment.** We thank Dr. P. M. Angus for helpful discussions and the ANU Microanalytical Service. Support from the Natural Sciences and Engineering Research Council (Canada) is also gratefully acknowledged.

**Supporting Information Available:** Tables of full crystallographic data, atomic parameters, bond lengths, angles, and thermal parameters. This material is available free of charge via the Internet at http://pubs.acs.org. Tables of calculated and observed structure factors are available from the authors upon request.

IC981380G