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Preparation and Characterization of Isomers of Bis(2-aminoethyl 3-aminopropyl sulfide)cobalt(III) Chloride

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A mixture of isomers of bis(2-aminoethyl 3-aminopropyl sulfide)cobalt(III) chloride has been prepared, and from this mixture four geometric isomers have been isolated on a preparative scale. Three of these latter isomers have been resolved in optical antipodes. The complexes have been characterized by UV–vis absorption, ^{13}C NMR and, in the case of the optically active isomers, also circular dichroism methods. On this basis the structure of the geometric isomers and the absolute configuration of the enantiomers have been assigned. The nomenclature for complexes of this nature is discussed.

Introduction

The sulfur atom in a thioether shows little affinity for coordination to cobalt(III), and there has been a growth of interest in cobalt(III) complexes of chelate ligands containing the thioether function. The first known example of a thioether coordinating to cobalt(III) was reported by Dwyer and Lions.[1-3] They condensed diamines of the general type $H_2N(CH_2)_xS(CH_2)_yS(CH_2)_xNH_2$ with salicylaldehyde and thus obtained hexadentate ligands. With cobalt(III) the ligand having $x = y = 2$ produced a single green isomer whereas the ligand with $x = 3$ and $y = 2$ formed a mixture of green and brown, geometric isomers, respectively. From this work and from subsequent application of a variety of physical methods to obtain structural and spectroscopic information about these and similar complexes, we conclude that the sulfur atom in a chelate thioether is stereochemically more rigid than the nitrogen atom in a secondary amine. However, it is also evident that a thioether sulfur atom coordinated to cobalt(III) has spectrochemical ligand field properties that are not very different from those of a coordinated secondary amine, and the sulfur atom thus behaves as an "innocent" ligand.[4] In this respect the sulfur atom of a thiolate moiety is different, and the spectral features of thiolate cobalt(III) complexes are more complicated due to electron-transfer bands of low energy.[5]

The cumulative stability constants, β_2, for bis[bis(2-aminoethyl) sulfide]cobalt(III), $Co(daes)_2^{3+}$,[6] and for bis(diethylenetriamine)cobalt(III), $Co(dien)_2^{3+}$, have been measured to be $10^{38.3}$ and $10^{48.8}$, respectively.[7] The affinity for the formation of a cobalt(III)–thioether bond is therefore much lower than the affinity for the formation of a cobalt(III)–amine bond. The Co(III)–S(thioether) bond in $Co(daes)_2^{3+}$ has also been shown to be relatively labile, allowing the complex to racemize in acidic aqueous solution with charcoal as a catalyst.[7] Only one geometric isomer of this complex has been characterized,[8] and preliminary force field calculations have provided supporting evidence for a much higher stability of the unsymmetrical facial isomer relative to the symmetrical facial and meridional isomers.[9] Force field calculations were also used to predict the relative stabilities of the isomers of the bis(2-aminoethyl 3-aminopropyl sulfide)cobalt(III) complex in which the ligand might exhibit a higher degree of flexibility than daes in $Co(daes)_2^{3+}$.[9] This prediction is tested and the preparation and characterization of four of these complexes are reported in this paper.

Nomenclature for Bis(linear tridentate ligand)metal Complexes

The IUPAC nomenclature proposals[10] are of great help in the case of complexes of very simple ligands, but in dealing with isomers of a complex ion such as bis(histidinato)cobalt(III), it is necessary to extend the recommended nomenclature. Bagger and Jensen have chosen to characterize the diastereoisomers of this complex according to the geometric arrangement of equivalent ligators from the two ligands.[11] In this case the nomenclature becomes unequivocal because the ligating atoms are easy to distinguish. In complexes of 2-aminoethyl 3-aminopropyl sulfide (aeaps = $NH_2CH_2CH_2SCH_2CH_2CH_2NH_2$) the two terminal ligators are both NH_2 groups, and they differ only in the fact that one is a member of a five-membered chelate ring and the other a member of a six-membered chelate ring. Thus $Co(aeaps)_2^{3+}$ displays cis–trans isomerism due to the positions of the sulfur atoms and also isomerism with respect to the distribution of the chelate rings. According to these elements of diastereoisomerism isomer I in Figure 1 could thus be called *cis*-S-*trans*-6,6 and IV could be *trans*-S-*trans*-5,6 where 5 and 6 are short for five- and six-membered rings, respectively. However, the three meridional forms cannot be described in this manner. They differ only in the combined chiral distribution of the chelate rings and the chirality of the chelated sulfur atoms. They are diastereoisomers in which both elements of isomerism arise only from the presence of elements of chirality. It is therefore possible to characterize the racemates I–IV and the achiral isomer V, but not the racemates of VI–VIII, on the basis of geometric structural elements. In isomers VI–VIII the chelate rings span meridional edges, and since it is practical to distinguish this group of three geometric isomers from the remaining five, we have found it useful to employ a nomenclature based on the use of the terms meridional, symmetric-facial and unsymmetric-facial as employed previously, e.g., for isomers of $Co(dien)_2^{3+}$ and $Co(daes)_2^{3+}$.[8] With the less symmetric ligand aeaps there are three *u-fac* and two *s-fac* isomers. These geometric isomers can be differentiated by a notation that indicates a characteristic trans relationship among the chelate rings. Isomer I is thus *trans*-6,6-*u-fac* and IV is *trans*-5,6-*s-fac*.

The notation recommended by IUPAC for the chiral distribution of a pair of chelate rings in a bis- or tris(bidentate chelate ligand)metal complex is Λ and Δ.[10] This notation is often extended to other dissymmetric complexes of polydentate chelate ligands, and the chelate ring spanning an edge may even be assigned a vector property.[12,13] In isomers I–III there are three chiral pair combinations ΛΔΛ and the overall absolute configuration is thus Λ. The diastereoisomerism in, e.g., isomer I can then be expressed as Λ-*trans*-6,6-*u-fac*-$[Co(aeaps)_2]^{3+}$. It follows that the coor-

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[6] Abbreviations used in this paper are as follows: aeaps = 1,8-diaza-4-thiaoctane; daes = 1,7-diaza-4-thiaheptane; dien = 1,4,7-triazaheptane; en = 1,2-ethanediamine; tn = 1,3-propanediamine; dpt = 1,4,8-triazaoctane.
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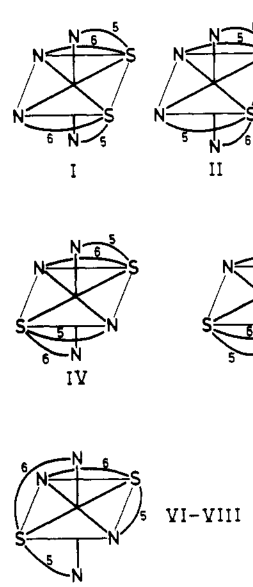

Figure 1. Diastereoisomers of bis(2-aminoethyl 3-aminopropyl sulfide)cobalt(III) ions: I, Λ-*trans*-6,6-*u*-*fac*; II, Λ-*trans*-5,5-*u*-*fac*; III, Λ-*trans*-5,6-*u*-*fac*; IV, Λ-trans-5,6-fac; V, *trans*-5,5-*s*-*fac* VI–VIII, representing three forms all having Λ(5,5)Λ(6,6) meridional configuration and sulfur atoms that on coordination are made chiral ((*R*,*R*)-Co(aeaps)$_2{}^{3+}$, (*S*,*S*)-Co(aeaps)$_2{}^{3+}$, and (*R*,*S*)-Co(aeaps)(aeaps)$^{3+}$).

dinated sulfur atoms in this isomer must assume the *S* absolute configuration, implying that it would be unnecessary for the notation to indicate this for the facial isomers. However, for the meridional forms, it seems necessary to use a detailed notation including the absolute configuration of the chelated sulfur atoms such as, e.g., Λ(5,5)Λ(6,6)-(*R*,*R*)-*mer*-Co(aeaps)$_2{}^{3+}$, leading to a very cumbersome notation for the racemate. Here, Δ(5,5) means that the two lines spanning the edges of the octahedron occupied by the five-membered rings of the two ligands form a right-handed screw.

Experimental Section

Preparations. 2-Aminoethyl 3-Aminopropyl Sulfide (aeaps). 2-Aminoethanethiol (68.6 g, 0.89 mol) prepared according to Nathan and Bogart[14] was suspended in methanol (100 mL). This mixture was added to a solution of sodium (41 g, 1.8 mol) in 400 mL of methanol. To this solution was slowly and with vigorous stirring added 1-amino-3-chloropropane hydrochloride (116.9 g, 0.89 mol, from EGA, Steinheim, West Germany) dissolved in 250 mL of methanol. A precipitate of sodium chloride formed immediately. The mixture was left overnight and then filtered. The filtrate was first concentrated in a rotary evaporator, and the residue was then distilled in vacuum. Distillation at 0.9 torr between 90 and 92 °C gave 88.2 g (0.66 mol, 74%) of the almost pure product. The product was redistilled under the same conditions, giving 81.0 g (0.60 mol, 68%) of aeaps, ^{13}C NMR (22.53 MHz, $CDCl_3$) relative to Me_4Si: δ 29.08, 33.46, 36.24, 40.96, 41.18.

3-Thia-1,6-hexanediyldiammonium Dichloride. A 26.8-g (0.2-mol) sample of aeaps in 50 mL of ethanol was slowly poured into a mixture of 100 mL of ethanol and 33.5 mL of 12 M hydrochloric acid cooled in an ice–salt bath. The mixture was left for 12 h at −20 °C and then filtered. The precipitate was washed with 30 mL of ethanol at 0 °C and then dried in a desiccator over concentrated sulfuric acid. Yield: 28.2 g (69%). Anal. Calcd for $C_5H_{16}N_2SCl_2$: C, 28.99; H, 7.79; N, 13.52; S, 15.48; Cl, 34.23. Found: C, 29.06; H, 7.51; N, 13.45; S, 15.59; Cl, 34.30.

Isomer Mixture of Co(aeaps)$_2$Cl$_3$. Trichlorotris(pyridine)cobalt(III)[15,16] (21.1 g, 0.052 mol) was slowly added to 700 mL of chloroform and kept suspended by vigorous stirring. To this suspension was added aeaps (14 g, 0.104 mol) in 50 mL of chloroform. The color of the suspension changed from green to violet/rose and the viscosity increased. Stirring was continued for 2 to 4 h until all the Co(py)$_3$Cl$_3$ had reacted. The product was isolated by filtration on a large glass filter and washed five times with 200 mL of ether. After most of the ether was removed by suction, the raw product was transferred to 40 mL of 0.5 M hydrochloric acid. Most of the remaining ether was removed by decantion, and the remaining ether was then evaporated in a vacuum desiccator (15 torr). During the evaporation of ether, crystals appeared, and further precipitation was induced by cooling the aqueous mixture in an ice bath for 0.5 h. The precipitate was removed by filtration and washed with three 3-mL aliquots of 96% ethanol. Yield: 2.4 g of a pink fraction, I.

To the combined filtrate and the ethanol washings was added further 60 mL of 96% ethanol, and the mixture was kept at 5 °C for 24 h and then stirred with cooling in an ice bath for 1 h. The precipitate was isolated by filtration and washed with 5 mL of 96% ethanol. Yield: 7.1 g of a dark red fraction, II.

To the mother liquor was added a further 60 mL of 96% ethanol, and the precipitation procedure was repeated. The yield was 7.0 g of an orange fraction, III. The colored mother liquor may contain still more Co(aeaps)$_2{}^{3+}$, but no further crystalline material could be isolated.

Further Fractionation. Fraction I (see above) (2.4 g of Co(aeaps)$_2$Cl$_3$) was dissolved in 60 mL of 0.01 M hydrochloric acid. Insoluble impurities were removed by filtration. To the filtrate was added 60 mL of ethanol, and the solution was kept overnight at 5 °C. Two kinds of crystals appeared: (a) pink needles identified as the meso form *trans*-6,6-*trans*-5,5-*s*-*fac*-Co(aeaps)$_2$Cl$_3$ and (b) compact orange crystals subsequently identified as *trans*-5,5-*u*-*fac*-Co(aeaps)$_2$Cl$_3$. The two kinds of crystals were separated by flotation by repeatedly suspending the crystal mixture in ethanol and removing the slowest settling crystals by decantation. A 0.6-g yield of pure fraction b was obtained. Anal. Calcd for *trans*-5,5-*u*-*fac*-Co(aeaps)$_2$Cl$_3$·3H$_2$O: C, 24.62; H, 7.03; N, 11.48; S, 13.15; Cl, 21.80. Found: C, 24.56; H, 7.14; N, 11.46; S, 12.95; Cl, 21.83.

The pink fraction was found by microscopy to contain small amounts of isomer b and was recrystallized. A 0.25-g sample of nearly pure isomer a was dissolved in 15 mL of 0.01 M hydrochloric acid. After filtration 15 mL of ethanol was added to the filtrate, and the solution was kept at 5 °C for 14 h. Yield: 0.20 g of pure isomer a. Anal. Calcd for *trans*-6,6-*trans*-5,5-*s*-*fac*-Co(aeaps)$_2$Cl$_3$·2H$_2$O: C, 25.57; H, 6.87; N, 11.93; S, 13.65; Cl, 22.64; Co, 12.54. Found: C, 25.50; H, 6.79; N, 12.10; S, 14.12; Cl, 22.50; Co, 12.55.

Fraction II (see above) was a nearly pure isomer contaminated with only small amounts of other isomers. A 5-g sample of fraction II was dissolved in 30 mL of 0.5 M hydrochloric acid, giving a nearly saturated solution. To filtered solution was added 30 mL of ethanol, and the mixture was kept at 5 °C overnight. Large dark red crystals precipitated during this time and they were later identified as isomer c, *trans*-6,6-*u*-*fac*-Co(aeaps)$_2$Cl$_3$·H$_2$O. Yield: 2.6 g. In some of our repetitions of this procedure, this fraction still contained other isomers in the form of small crystals, much of which could be removed by flotation as in the separation of fraction I. In this case 2.3 g of crude isomer c was purified further by dissolution in 10 mL of 0.5 M hydrochloric acid followed by reprecipitating by the addition of 10 mL of ethanol and cooling. Yield: 1.55 g of pure isomer c. Anal. Calcd for *trans*-6,6-*u*-*fac*-Co(aeaps)$_2$Cl$_3$·3H$_2$O: C, 26.58; H, 6.70; N, 12.40; S, 14.19; Cl, 23.54. Found: C, 26.38; H, 7.02; N, 12.31; S, 14.24; Cl, 23.80.

Fraction III could not be fractionated further by crystallization of the chloride salt of the isomers present. Instead, the separation of the two dominating isomers (approximately 30% isomer c and 60% isomer d) was accomplished by precipitation with perchlorate ions. A 5-g sample of fraction III (0.01 mol) was dissolved in 20 mL of 0.005 M perchloric acid, and 3 mL of 70% perchloric acid was added to the filtered solution. Storage at 5 °C resulted in the formation of 3.6 g of nearly pure perchlorate of isomer d. A 3.0-g sample of this product was reprecipitated from 25 mL of 0.005 M perchloric acid by the addition of 3 mL 70% perchloric acid and cooling. Yield: 2.5 g of isomer d, *trans*-5,6-*u*-*fac*-Co(aeaps)$_2$(ClO$_4$)$_3$·H$_2$O. Anal. Calcd for isomer d: C, 18.65; H, 4.69; N, 8.70; S, 9.96; Cl, 16.52. Found: C, 18.54; H, 4.82; N, 8.62; S, 10.00; Cl, 16.55.

To the filtrate remaining after isolation of 3.6 g of isomer d was added a further 3 mL of 70% perchloric acid, and the mixture was cooled in an ice bath. A 1.3-g yield of pure *trans*-6,6-*u*-*fac*-Co(aeaps)$_2$(ClO$_4$)$_2$Cl precipitated. Anal. Calcd for this double salt: C, 21.38; H, 5.02; N, 9.97; S, 11.41; Cl, 18.93. Found: C, 21.22; H, 5.16; N, 9.84; S, 11.62; Cl, 19.60.

Separation by Means of Column Chromatography. Materials. Ion-exchange chromatography on SP Sephadex C-25 was performed with Pharmacia K 26/100 and K 26/40 columns. Each eluted isomer was isolated on a Pharmacia K 9/15 column packed with 4 cm × 0.9 cm (i.d.) of Dowex 50W X8, which was connected to the outlet of the larger column. Geometric isomers were separated by elution through 25 cm × 2.6 cm (i.d.) SP Sephadex with 0.15 M sodium sulfate acidified to pH 3 with sulfuric acid at a rate of 100 mL/h. Resolution in enantiomers was accomplished by elution with 0.15 M sodium bis(μ-(*R*,*R*)-tartrato-

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(4−))diantimonate(III) at a rate of 50 mL/h through 90 cm × 2.6 cm (i.d.) Sephadex in a cold room (5 °C). All eluent passed replaceable Dowex columns in order to collect the separated materials from several chromatographic runs and in order to make it possible to reuse the eluent in case of enantiomeric separations.

Recovery of Complexes. Pure isomers were recovered from the Dowex ion exchanger after 0.5 M lithium chloride acidified with hydrochloric acid (pH 3) was first passed through the column until all the previous eluent was removed. The complex ion was then eluted with 4 M hydrochloric acid and the colored eluate was concentrated in a vacuum desiccator over concentrated sulfuric acid and solid sodium hydroxide until a volume of less than 5 mL was obtained. Crystallization was then induced by the addition of variable amounts of ethanol.

Chromatographic Runs. A 0.5-g sample of Co(aeaps)$_2$Cl$_3$, fraction I, was dissolved in 30 mL of 0.015 M sodium sulfate acidified to pH 4. The filtered solution was applied to the column and eluted with the 10-fold diluted eluent until all the complex was bound to the uppermost 5–10 mm of ion-exchange material. Elution with 0.15 M sodium sulfate (pH 3) gave a clear separation after ca. 4 h. The dominating isomer is *trans*-5,5-*u*-*fac*-Co(aeaps)$_2^{3+}$, which is eluted faster than the *s*-*fac* isomer. Small amounts of other isomers can be detected as weak bands eluted faster than the two main ones.

It may also be advantageous to separate the isomers constituting fraction III chromatographically since the chlorides could not be separated by fractional recrystallization. The fastest moving isomer is *trans*-6,6-*u*-*fac*-Co(aeaps)$_2^{3+}$ (isomer c) while the *trans*-5,6-*u*-*fac* isomer (d) is the dominant isomer. The presence of small amounts of other isomers would show as weak bands eluted more slowly than the two abundant isomers.

Resolution of Isomers. Each diastereoisomer of *u*-*fac* configuration was resolved chromatographically at 5 °C on SP Sephadex C-25 with 0.15 M sodium bis(μ-(R,R)-tartrato(4−))diantimonate(III), "sodium antimonyl tartrate", as the eluent. The diastereoisomers were applied to the column in portions of ca. 300 mg of chloride salt dissolved in 40 mL of 0.015 M "antimonyl tartrate". The separated enantiomers from several chromatographic runs were collected on Dowex ion exchanger and recovered as described above. The enantiomers were eluted from SP Sephadex in the following order: b, $(-)_{589}$-Δ-*trans*-5,5-*u*-*fac*-Co(aeaps)$_2^{3+}$ faster than the $(+)_{589}$ isomer; c, $(+)_{589}$-Δ-*trans*-6,6-*u*-*fac*-Co(aeaps)$_2^{3+}$ faster than the $(-)_{589}$ isomer; d, $(-)_{589}$-Δ-*trans*-5,6-*u*-*fac*-Co(aeaps)$_2^{3+}$ faster than the $(+)_{589}$ isomer.

Isomer b was most difficult to resolve in enantiomers, and it was found necessary to double the column length in order to obtain a clear separation. Even then the slowest moving enantiomer was obtained with low purity. The optically active chlorides of isomer b are very soluble, and it was therefore found advantageous to precipitate with perchloric acid, which resulted in diperchlorate chlorides. Anal. Calcd for $(-)_{589}$-*trans*-5,5-*u*-*fac*-Co(aeaps)$_2$(ClO$_4$)$_2$Cl·1.5H$_2$O: C, 20.40; H, 5.30; N, 9.52; S, 10.89; Cl, 18.07. Found: C, 20.67; H, 4.90; N, 9.64; S, 10.30; Cl, 17.50. $[M]_{589} = -6500°\ M^{-1}\ cm^{-1}$. The slowly eluting enantiomer of isomer b gave $[M]_{589} = +3000°\ M^{-1}\ cm^{-1}$.

The resolved *trans*-6,6-*u*-*fac* isomers were isolated as chlorides. Anal. Calcd for $(+)_{589}$-*trans*-6,6-*u*-*fac*-Co(aeaps)$_2$Cl$_3$·1.5H$_2$O: C, 26.06; H, 6.78; N, 12.16; S, 13.92; Cl, 23.08; Co, 12.79. Found: C, 25.91; H, 7.03; N, 12.06; S, 13.90; Cl, 23.40; Co, 12.76. $[M]_{589} = +2800°\ M^{-1}\ cm^{-1}$.

The resolved *trans*-5,6-*u*-*fac* geometric isomer could also be isolated as the chloride. Anal. Found for $(-)_{589}$-*trans*-5,6-*u*-*fac*-Co(aeaps)Cl$_3$·1.5H$_2$O: C, 26.12; H, 60.86; N, 12.48; S, 13.92; Cl, 23.40; Co, 12.81. $[M]_{589} = -1500°\ M^{-1}\ cm^{-1}$.

Rearrangement of the Isomer Mixture to Isomer b. The ether-washed crude product containing the mixture of isomers was dissolved in 40 mL of water. The excess ether was decanted off and the residual ether removed by evaporation in connection with a filtration. The neutral solution was kept at 5 °C overnight, giving a good yield of *trans*-5,5-*u*-*fac*-Co(aeaps)$_2$Cl$_3$, which was isolated by filtration. After recrystallization as described earlier, 9.7 g of *trans*-5,5-*u*-*fac*-Co(aeaps)$_2$Cl$_3$·3H$_2$O was isolated.

Physical Measurements. Optical rotation was measured on a Perkin-Elmer 141 polarimeter. Concentrations were kept near 10^{-3} M in 0.040 M hydrochloric acid, and the molar rotation was calculated from $[M] = 100\alpha/(cl)$, where α is the observed rotation in degrees, c the molar concentration, and l the path length in cm.

Absorption spectra were recorded on a Cary 118 spectrophotometer. The circular dichroism (CD) spectra were measured on a CNRS Roussel-Jouan Dichrographe III instrument in combination with a Tektronix 4051 microcomputer, which averages many measurements at each wavelength and substracts a base line curve from the measured CD spectrum. Solutions for spectral measurements were made in 0.040 M hydrochloric acid, and owing to variable water content in the complex salts, all solutions were analyzed for cobalt to establish the concentrations.

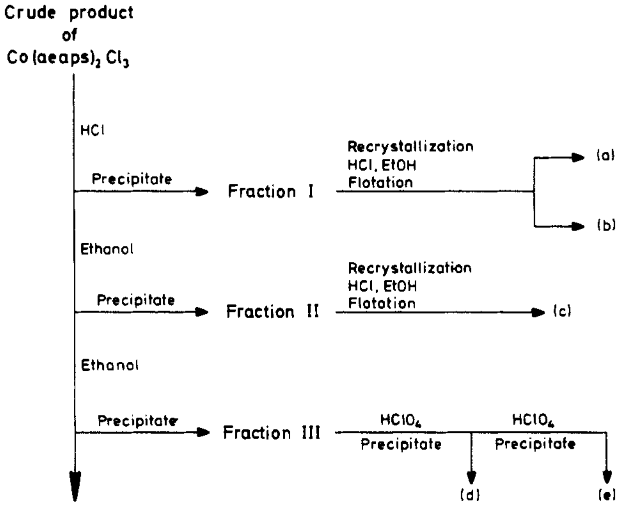

Figure 2. Schematic separation of four geometric isomers of Co(aeaps)$_2^{3+}$ by fractional crystallization: (a) *trans*-5,5-*s*-*fac*-Co(aeaps)$_2$Cl$_3$·2H$_2$O; (b) *trans*-5,5-*u*-*fac*-Co(aeaps)$_2$Cl$_3$·3H$_2$O; (c) *trans*-6,6-*u*-*fac*-Co(aeaps)$_2$Cl$_3$·H$_2$O; (d) *trans*-5,6-*u*-*fac*-Co(aeaps)$_2$(ClO$_4$)$_3$·H$_2$O; (e) *trans*-6,6-*u*-*fac*-Co(aeaps)$_2$(ClO$_4$)$_2$Cl.

The analyses were performed on a Perkin-Elmer 403 atomic absorption spectrophotometer after destruction of the complexes by evaporation with perchloric acid. Direct analyses of solutions of the complexes were found to be unsatisfactory.

^{13}C NMR spectra were recorded on a JEOL FX 90Q spectrometer with tetramethylsilane (Me$_4$Si) as internal standard for CDCl$_3$ solutions and sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as internal standard for D$_2$O solutions.

X-ray powder diffraction photographs were obtained with a XDC 700 Guinier-Hägg focusing camera using Cu Kα radiation (quartz monochromator).

Results and Discussion

Preparations. Attempts to prepare a mixture of isomers of Co(aeaps)$_2^{3+}$ by oxidation of a mixture of cobalt(II) and the ligand in aqueous solution with activated charcoal failed. This negative result is not really surprising in view of the results obtained by Hammershøi and Larsen[7] on the stability of bis[bis(2-aminoethyl) sulfide]cobalt(III), Co(daes)$_2^{3+}$. For the latter complex a formation constant $\beta_2 = 10^{38.3}$ was found, which can be compared with $\beta_2 = 10^{48.8}$ for Co(dien)$_2^{3+}$. The two values show clearly that the thioether function has very little affinity for cobalt(III), and this is expected to be even more pronounced with aeaps than with daes, since the former ligand introduces less steric strain on the position of the thioether group near the metal ion.

Co(aeaps)$_2^{3+}$ itself was prepared from the neutral complex trichlorotris(pyridine)cobalt(III), which is soluble in chloroform and is both relatively labile and unstable. Thus a solution of Co(py)$_3$Cl$_3$ in chloroform exhibits a slow change in the visible absorption spectrum due to the formation of (Co(py)$_4$Cl$_2$)$_2$CoCl$_4$. With the free ligand aeaps in chloroform, the green Co(py)$_3$Cl$_3$ reacts over a period of a few hours to give a red-brown isomer mixture according to

$$\mathrm{Co(py)_3Cl_3 + 2aeaps \rightarrow Co(aeaps)_2Cl_3 + 3py}$$

The reaction mixture is soluble in water, and the red aqueous solution changes pH and absorption, indicating destruction and possibly rearrangement of the isomers. However, the addition of acid to give pH <4 appears to inhibit destruction, and all solutions of the complex were therefore kept in this pH range.

Separation of Isomers. The reaction mixture was dissolved in weak hydrochloric acid, and fractional crystallization from this solution gave three main fractions according to the scheme shown in Figure 2. The least soluble chloride fraction (I) consists of two kinds of crystals, namely pink needle-formed crystals (isomer a) and compact orange crystals (isomer b). We have separated these two forms by flotation as well as by ion-exchange chromatography on SP-Sephadex. The latter method is of particular value as an analytical tool for checking isomeric purity. Recently,

Table I. Diagonal Energies for the Transitions $^1A_{2g} \leftarrow {}^1A_{1g}$ and $^1E_g \leftarrow {}^1A_{1g}$ in *cis*- and *trans*-$Co^{III}N_4S_2$ Given in Terms of the Cubic Ligand Field Parameters Δ_N and Δ_S and the Racah Parameter C

chromophore	$E(^1A_{2g} \leftarrow {}^1A_{1g})$	$E(^1E_g \leftarrow {}^1A_{1g})$
cis-$Co^{III}N_4S_2$	$^1/_2(\Delta_N + \Delta_S) - C$	$^3/_4\Delta_N + {}^1/_4\Delta_S - C$
trans-$Co^{III}N_4S_2$	$\Delta_N - C$	$^1/_2(\Delta_N + \Delta_S) - C$

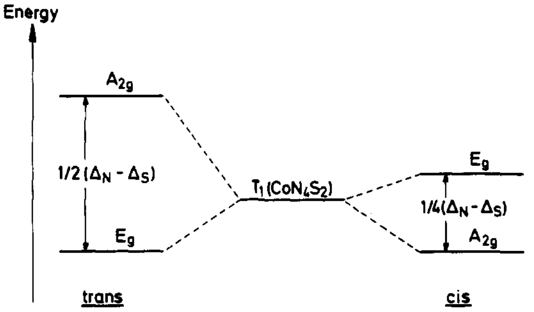

Figure 3. Splitting of the lowest lying, singlet excited state in the two different holohedrized symmetries derived from *cis*- and *trans*-CoN_4S_2 complexes.

Table II. Experimental ^{13}C NMR Chemical Shifts (ppm) Relative to Me_4Si (Solvent $CDCl_3$) and DSS (Solvent D_2O) for Potential Ligands and the ^{13}C NMR Chemical Shifts Calculated from Eggert and Djerassi's Results and from the Influence of a Sulfur Atom

			numbering of the atoms							
solvent	origin	ligand	1	2	3	4	5	6	7	8
D_2O	measd	aeaps	N	42.8	37.1	S	31.4	34.9	42.7	N
$CDCl_3$	measd	aeaps	N	41.0	36.2	S	29.1	33.5	41.2	N
C_6D_6	calcd	aeaps	N	42.5	36.8	S	30.7	34.3	42.5	N
D_2O	measd	daes	N	43.3	37.1	S	37.1	43.3	N	
$CDCl_3$	measd	daes	N	41.5	35.9	S	35.9	41.5	N	
C_6D_6	calcd	daes	N	42.5	36.8	S	36.8	42.5	N	
D_2O	measd	dien	N	43.3	54.1	N	54.1	43.3	N	
$CDCl_3$	measd	dien	N	41.9	52.7	N	52.7	41.9	N	
C_6D_6	calcd	dien	N	43.3	53.9	N	53.9	43.3	N	

also an ion-exchange HPLC microanalytical method has been developed.[17]

Fraction II consists mainly of the chloride of one isomer (c), whereas the mother liquor contains two soluble isomers. It proved convenient to precipitate a complex perchlorate (isomer d) by the addition of a small amount of perchloric acid. After removal of this salt, further addition of perchloric acid precipitated a chloride diperchlorate (isomer e). These perchlorates were converted to the chlorides by cation exchange. The chloride of fraction e was shown by X-ray powder diffraction to be identical with isomer c, and a total of four isomers were thus isolated. The presence of other isomers in relatively small amounts cannot been excluded, and HPLC results indicate the presence of other isomers in the starting material.[17]

Isomer Characterization. The chloride salts of the four isomers have slightly different appearances, and the visible–UV absorption spectra are sufficiently different to allow the isomers to be distinguished. The band assigned as the $T_{1g} \leftarrow A_{1g}$ transition of octahedral parentage varies as follows (ν_{max}/cm^{-1}, ϵ_{max}/M^{-1} cm^{-1}): (a) 19900, 145; (b) 20000, 207; (c) 20000, 235; (d) 20100, 252.

The low molar absorbance of isomer a compared to those of isomers b–d is striking and suggests the presence of a center of inversion in this complex. In keeping with this, we have been unable to resolve this isomer in enantiomers. Only one isomer possesses a centrosymmetric structure, namely the *s-fac* isomer, and the correctness of this assignment has since been verified by an X-ray diffraction analysis.[18]

On the basis of the similarity of the spectra of Co(daes)$_2^{3+}$ (ν_{max}, ϵ_{max}: 20600, 215) and isomers b–d the latter have been assigned the *u-fac* structures with the two sulfur atoms cis. The theoretical energy differences between the transitions of the first absorption bands in *cis*- and *trans*-$Co^{III}N_4S_2$ with holohedral D_{4h} symmetry are given in Table I to illustrate this point. The absolute values for Δ_N and Δ_S are difficult to assess, but comparison of the spectra of *u-fac*-Co(diene)$_2^{3+}$ and *u-fac*-Co(daes)$_2^{3+}$ shows that Δ_S is smaller than Δ_N. This leads to a splitting of the first excited state as shown in Figure 3. For these isomers the splittings are much smaller than the bandwidths, and the splittings will therefore only cause broadening of the absorption bands and relatively small shifts in the maxima of the band envelopes. For isomers a–d we find widths at 50% of maximum absorption of 3600, 3100, 3200, and 3200 cm^{-1}, respectively. By comparison, a value of 3200 cm^{-1} is found for *u-fac*-Co(daes)$_2^{3+}$, and on this basis alone it would be reasonable to conclude that isomers b–d are unsymmetrical-facial. The near-UV absorption band assigned as S → Co(III) charge-transfer transitions (vide infra) has its maximum at 33000 cm^{-1} for isomers b–d, while for isomer a this maximum is found at 30000 cm^{-1} and is thus displaced considerably toward lower energy. A similar variation in the position of a postulated S → Co(III) charge-transfer band has been used to assign structures for cis–trans isomers.[19] In support of this conclusion the Δ-*trans*-5,5 structure has been established by X-ray diffraction techniques for *u-fac*-Co(aeaps)$_2$ClO$_4$·S$_2$O$_6$·2H$_2$O derived from isomer c.[18]

^{13}C NMR. A number of investigations have shown that it is possible to predict the ^{13}C chemical shift for a carbon nucleus in a given molecular environment.[20] Thus it is possible to calculate the ^{13}C chemical shifts of aeaps as a perturbed molecule of *n*-octane in which the methyl groups are replaced by amino groups and a methylene group is replaced by the thioether function. Lindemann and Adams[21] have discussed the chemical shifts for carbon atoms in alkanes, and following this approach, Eggert and Djerassi have studied the influence on ^{13}C shifts of the introduction of amino groups in alkanes.[22] The influence of a thioether can be judged from the spectra of cyclohexane (δ = 26.9) and cyclothiahexane (δ_α = 29.4 ppm, $\delta_\beta = \delta_\gamma$ = 26.9 ppm) in CS$_2$ relative to Me$_4$Si. These results suggest a change in chemical shift of +2.5 ppm for the α-carbon atom alone. Using this correction and Eggert and Djerassi's results, we calculated the ^{13}C chemical shifts listed in Table II together with the experimental shifts obtained for D$_2$O and C$_6$D$_6$. It can be seen that except for the two NCH$_2$ carbon atoms, the assignment of the chemical shifts is consistent.

The ^{13}C NMR spectra of the four isomers of Co(aeaps)$_2^{3+}$ have been used to characterize the compounds and also to clarify structural features. The number of stereochemically nonequivalent carbon atoms in the complexes is ten for the two isomers *trans*-5,6-*u-fac*-Co(aeaps)$_2^{3+}$ and *mer*-(*R*,*S*)-Co(aeaps)(aeaps)$^{3+}$ both of which lack symmetry elements whereas all of the remaining six isomers have only five nonequivalent carbon atoms. The measured ^{13}C chemical shifts for the complexes can be assigned according to procedures similar to those used for the free ligand. However, for the complexes, the changes in ^{13}C chemical shift are the results of two influences, viz. an electronic effect of cobalt(III) on the carbon atoms and an effect that has its origin in the steric distribution of the carbon atoms and the flexible conformations of the puckered chelate rings.

Figure 4 shows schematically the proton decoupled ^{13}C NMR spectra of some reference complexes, and Figure 5 shows the spectra of daes and aeaps and their cobalt(III) complexes. From the reference spectra we draw the following conclusions:

(i) ^{13}C chemical shifts of methylene groups are augmented slightly when a ligand such as ethylenediamine forms a five-

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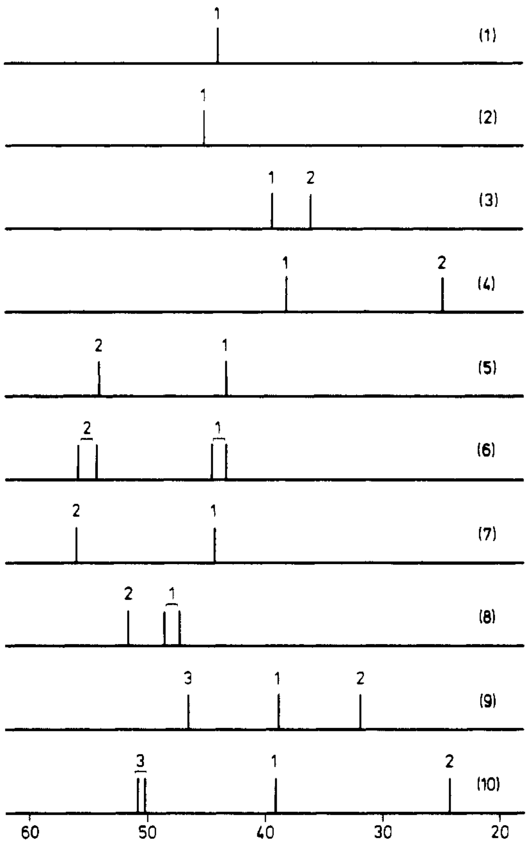

Figure 4. Proton-decoupled, schematic ^{13}C NMR spectra of free ligands and their cobalt(III) complexes: 1, en; 2, Co(en)$_3^{3+}$; 3, tn; 4, Co(tn)$_3^{3+}$; 5, dien; 6, *u-fac*-Co(dien)$_2^{3+}$; 7, *s-fac*-Co(dien)$_2^{3+}$;[23] 8, *mer*-Co(dien)$_2^{3+}$; 9, dpt; 10, Co(dpt)$_2^{3+}$.[24] The chemical shifts are measured for aqueous solutions (D$_2$O) relative to DSS.

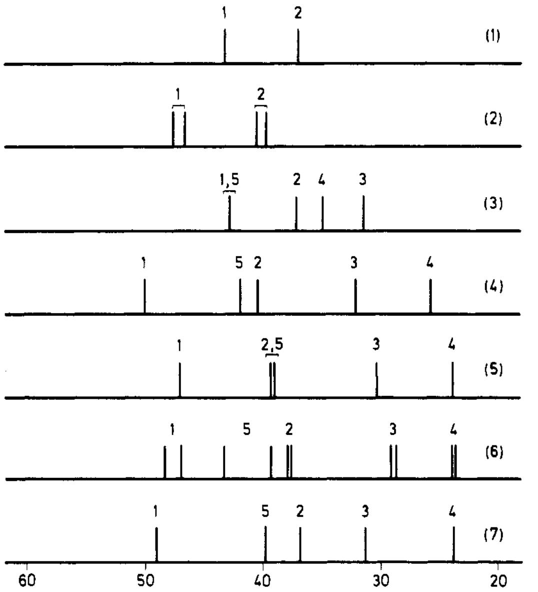

Figure 5. ^{13}C NMR chemical shifts in aqueous solutions (D$_2$O) relative to DSS of the free ligands daes and aeaps and of their cobalt(III) complexes: 1, daes; 2, *u-fac*-Co(daes)$_2^{3+}$; 3, aeaps; 4, *trans*-6,6-*u-fac*-Co(aeaps)$_2^{3+}$; 5, *trans*-5,5-*u-fac*-Co(aeaps)$_2^{3+}$; 6, *trans*-5,6-*u-fac*-Co(aeaps)$_2^{3+}$; 7, *trans*-6,6-*s-fac*-Co(aeaps)$_2^{3+}$.

membered chelate ring with cobalt(III).

(ii) ^{13}C chemical shifts of H$_2$NCH$_2$ groups are only slightly diminished when 1,3-propanediamine coordinates to cobalt(III), whereas the resonances for the middle carbon atoms shift considerably upfield.

(iii) The ^{13}C chemical shift of the NHCH$_2$ of 1,5,9-triazanonane is found to be augmented in *mer*-Co(dpt)$_2^{3+}$ relative to the ligand, whereas NH$_2$–CH$_2$ is nearly unaffected by the coordination and the CH$_2$ groups surrounded by CH has smaller shifts, as observed for Co(tn)$_3^{3+}$. The influence of the sulfur atom in daes and *u-fac*-Co(daes)$_2^{3+}$ is evident when the spectra of these molecules are compared with the spectra of dien and its three cobalt(III) complexes. The changes in ^{13}C chemical shifts occurring when daes coordinates the cobalt(III), forming five-membered chelate rings, is larger than for 1,2-ethanediamine and for 1,3,7-triazaheptane. The effect is probably steric in origin, caused by the long cobalt–sulfur bond, which introduces pronounced puckering in the five-membered ring. In a six-membered ring, such as in one of the chelate rings of Co(aeaps)(H$_2$O)$_3^{3+}$, we should expect much less pronounced changes in ^{13}C chemical shifts, for which even the sign will be unpredictable. Guided by these considerations, we arrive at the assignments given in Figure 5. The results seem to indicate that a quantitative correlation between ^{13}C chemical shifts and structure is not possible. However, assignments are often possible as shown in this case. The NMR spectra show that one of the isomers, d, which has not been studied by X-ray

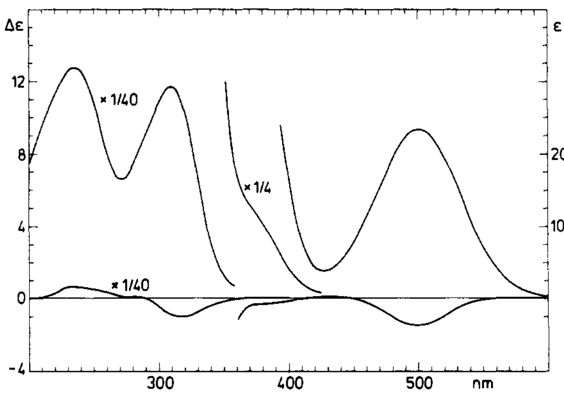

Figure 6. Absorption and CD spectra of the (−)$_{589}$-Λ-*trans*-6,6-*u-fac*-Co(aeaps)$_2^{3+}$ isomer (I of Figure 1).

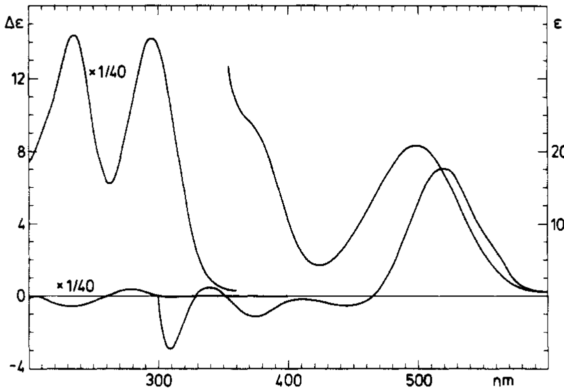

Figure 7. Absorption and CD spectra of the (+)$_{589}$-Λ-*trans*-5,5-*u-fac*-Co(aeaps)$_2^{3+}$ isomer (II of Figure 1).

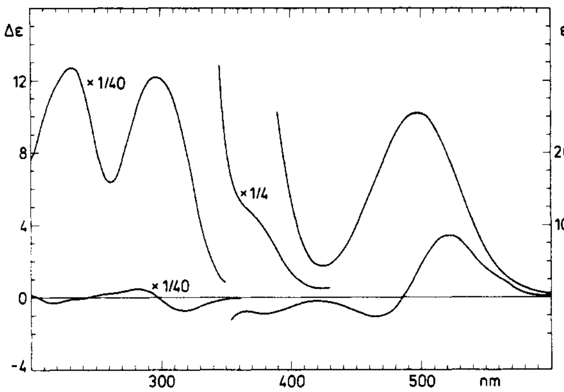

Figure 8. Absorption and CD spectra of the (+)$_{589}$-Λ-*trans*-5,6-*u-fac*-Co(aeaps)$_2^{3+}$ isomer (III of Figure 1).

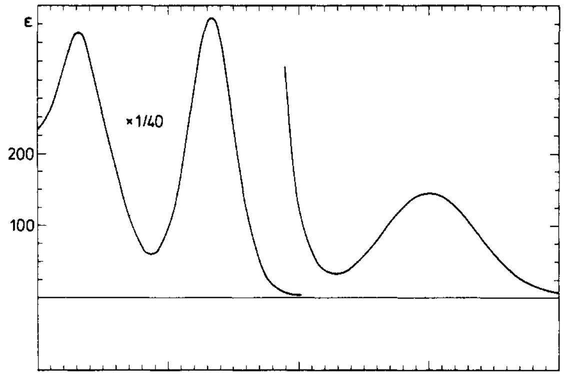

Figure 9. Absorption spectrum of the *trans*-5,6-*s*-*fac*-Co(aeaps)$_2^{3+}$ isomer (V of Figure 1).

diffraction, lacks symmetry elements. The UV–vis absorption spectrum indicates that isomer d has the sulfur atoms cis and it must therefore have the structure *trans*-5,6-*u*-*fac*-Co(aeaps)$_2^{3+}$.

Circular Dichroism and Absorption. The electronic absorption spectra of the four geometric of Co(aeaps)$_2^{3+}$ are shown in Figures 6–9. The absorption spectra exhibit three distinct features: (1) a weak absorption maximum near 500 nm and a shoulder near 370 nm assignable to the d–d transitions of the type $^1T_{1g} \leftarrow {}^1A_{1g}$ and $^1T_{2g} \leftarrow {}^1A_{1g}$, respectively; (2) near 300 nm an intense absorption assigned to S → Co charge-transer transitions; (3) an equally intense band at approximately 230 nm considered to arise from N → Co charge-transfer transitions. All three types of transitions have circular dichroism associated with absorption bands in the three optically active complexes.

The CD associated with absorption of $^1T_{1g} \leftarrow {}^1A_{1g}$ octahedral parentage in optically active cobalt(III) complexes has often been used to assign the absolute configuration. A number of investigations have found empirical correlations between the sign of the CD and the absolute configuration, and quantum-mechanical models used for the calculation of the net rotatory strength associated with this absorption band appear to provide support for the validity of such correlations.[25] Among *cis*-CoN$_4$S$_2$ complexes the absolute configurations of Δ-(−)$_{589}$-*u*-*fac*-Co(daes)$_2^{3+}$ and Λ-(−)$_{589}$-*trans*-6,6-*u*-*fac*-Co(aeaps)$_2^{3+}$ from isomer c have been established from X-ray diffraction studies.[26,18] The former complex ion has CD extrema from the $^1T_{1g} \leftarrow {}^1A_{1g}$ band at 512 ($\Delta\epsilon = -3.35$) and 457 nm ($\Delta\epsilon = 1.18$), whereas the latter complex ion has only one CD component at 498 nm ($\Delta\epsilon = -1.57$). As mentioned earlier, the first absorption band is split and in the *u*-*fac* complexes the holohedrized component $E_g \leftarrow A_{1g}$ has higher energy than the $A_{2g} \leftarrow A_{1g}$ component. In this enantiomer of isomer c the two sulfur atoms have the absolute configuration (*R*), and the resulting negative sign of the rotatory strength under the $^1T_{1g} \leftarrow {}^1A_{1g}$ band is a result of both the chiral sulfur atoms and the chiral distribution of the chelate rings. The CD maximum is displaced slightly toward higher energy relative to the absorption maximum, and this is taken as evidence that the holohedrized component $^1E_g \leftarrow {}^1A_{1g}$ has more (negative) rotatory strength than the (positive) $^1A_{2g} \leftarrow {}^1A_{1g}$ component. This is analogous to the situation for Δ-*u*-*fac*-Co(daes)$_2^{3+}$.

On the basis of the CD curves the (+)$_{589}$ enantiomers of isomers b and d can be assigned the absolute configurations Λ. In both cases there are two distinct CD bands of $^1T_{1g} \leftarrow {}^1A_{1g}$ parentage, and the rotational strength for the component $^1A_{2g} \leftarrow {}^1A_{1g}$ is positive for both isomers, as is also the case for the Λ-(−)$_{589}$ enantiomer of isomer c.

The above assignments are also supported by a semiquantitative partition of the total rotatory strength of $^1T_{1g} \leftarrow {}^1A_{1g}$ as a sum of contributions from the chiral distribution of chelate rings and from chiral sulfur atoms. There are three such relations and only two parameters and a reasonable self-consistency is found. Taking $\Delta\epsilon_{\max}$ values as proportional to the rotatory strengths, the three relations are

$$\begin{array}{lll} \text{isomer c:} & \Delta\epsilon_\Lambda - 2\Delta\epsilon_R = -1.6 & \Delta\epsilon_R = -\Delta\epsilon_S \\ \text{isomer b:} & \Delta\epsilon_\Lambda + 2\Delta\epsilon_R = 6.4 & \\ \text{isomer d:} & \Delta\epsilon_\Lambda + \Delta\epsilon_R + \Delta\epsilon_S = 2.5 & \end{array}$$

These equations give $\Delta\epsilon_\Lambda = 2.4$ and $\Delta\epsilon_R = 2.0$. If these values are compared with the CD of Δ-*u*-*fac*-Co(daes)$_2^{3+}$, it is evident that the total rotatory strength expressed as $\Delta\epsilon_{\text{exptl}} = -2.1$ is dominated by the contribution from the configuration ($\Delta\epsilon_\Delta = -2.4$) while the sulfur atoms contribute so little ($\Delta\epsilon_R \approx 0.3$) that they can be considered nearly achiral.

The assignments of the absolute configurations are supported by the chromatographic elution behavior of the isomers determined with sodium bis(μ-(*R*,*R*)-tartrato(4−))diantimonate(III). The above mentioned enantiomers were all eluted as the slowest moving enantiomers.

The CD associated with S → Co charge-transfer transitions indicate that there are two components. In (−)$_{589}$-Λ-*trans*-6,6-*u*-*fac*-Co(aeaps)$_2^{3+}$ ((*S*)-sulfur) the absorption maximum is at 309 nm, while the CD has its extremum at 318 nm with $\Delta\epsilon = -42.8$. For (+)$_{589}$-*trans*-5,5- and (+)$_{589}$-*trans*-5,6-*u*-*fac*-Co(aeaps)$_2^{3+}$, both CD components are observed. The former isomer ((*R*)-sulfur) has an absorption maximum at 294 nm and CD extrema at 310 ($\Delta\epsilon = -3$) and 280 nm ($\Delta\epsilon = 13.6$), while the latter isomer ((*R*)- and (*S*)-sulfur) has an absorption maximum at 296 nm and CD extrema at 316 ($\Delta\epsilon = -29.1$) and 283 nm ($\Delta\epsilon = 19.4$). In (−)$_{589}$-Δ-*u*-*fac*-Co(daes)$_2^{3+}$, absorption (279 nm) and CD (276 nm, $\Delta\epsilon = 24.3$) data are nearly coincident, and the magnitude of the CD shows that the sulfur atoms have become effectively chiral although the two adjacent chelate rings are both five-membered. Detailed assignments of these charge-transer transitions seem possible only after numerical computations, but the magnitude of the dipole strengths and the rotatory strengths indicate that the transitions have both considerable electric and magnetic dipole moments. This suggests an electronic transition from a carbon–sulfur σ* orbital (having π-symmetry with respect to the Co–S bond direction) to a cobalt 3d$_{\sigma^*}$ orbital.

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Registry No. aeaps, 56973-49-0; daes, 871-76-1; dien, 111-40-0; en, 107-15-3; tn, 109-76-2; dpt, 72879-17-5; *trans*-5,5-*s*-*fac*-Co(aeaps)$_2$Cl$_3$, 100164-51-0; *trans*-5,5-*u*-*fac*-Co(aeaps)$_2$Cl$_3$, 100164-52-1; (+)$_{589}$-Λ-*trans*-5,5-*u*-*fac*-Co(aeaps)$_2$(ClO$_4$)$_2$Cl, 100164-61-2; (−)$_{589}$-Δ-*trans*-5,5-*u*-*fac*-Co(aeaps)$_2$(ClO$_4$)$_2$Cl, 100164-59-8; *trans*-6,6-*u*-*fac*-Co(aeaps)$_2$Cl$_3$, 100164-53-2; *trans*-6,6-*u*-*fac*-Co(aeaps)$_2$(ClO$_4$)$_2$Cl, 100164-57-6; (−)$_{589}$-Λ-*trans*-6,6-*u*-*fac*-Co(aeaps)$_2$Cl$_3$, 100164-64-5; (+)$_{589}$-Δ-*trans*-6,6-*u*-*fac*-Co(aeaps)$_2$Cl$_3$, 100164-62-3; *trans*-5,6-*u*-*fac*-Co(aeaps)$_2$(ClO$_4$)$_3$, 100164-55-4; (+)$_{589}$-Λ-*trans*-5,6-*u*-*fac*-Co(aeaps)$_2^{3+}$, 100164-65-6; (−)$_{589}$-Δ-*trans*-5,6-*u*-*fac*-Co(aeaps)$_2$Cl$_3$, 100164-63-4; Co(en)$_3^{3+}$, 14878-41-2; Co(tn)$_3^{3+}$, 16786-53-1; *u*-*fac*-Co(dien)$_2^{3+}$, 38318-04-6; *mer*-Co(dien)$_2^{3+}$, 38318-06-8; *u*-*fac*-Co(daes)$_2^{3+}$, 59366-63-1; aeaps·2HCl, 60115-93-7; trichlorotris(pyridine)cobalt(III), 100164-02-1; 2-aminoethanethiol, 60-23-1; 1-amino-3-chloropropane hydrochloride, 6276-54-6.

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