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Formation and Crystal Structure of a Simple Carbanion Complex of Cobalt(III)

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The simple Werner-type coordination compound bis(2-aminoethyl 3-aminopropyl sulfide)cobalt(III) chloride consists of a number of isomers. It is shown that the unsymmetrically facial forms all react with strong base to form the same alkyl-cobalt(III) coordination compound, which has been crystallized as a dithionate salt. The structure of the dithionate has been determined by X-ray diffraction techniques using both Cu K α and Mo K α radiation. The crystals of bis(2-aminoethyl 3-aminopropyl sulfide)(1,8-diaza-4-thiaoct-5-yl)cobalt(III) dithionate, CoC₁₀H₂₇N₄S₄O₆, are monoclinic, space group *P*2₁, with the following cell parameters at 115 K: *a* = 9.463 (3) Å, *b* = 9.681 (3) Å, *c* = 11.097 (4) Å, β = 113.48 (3)°, *Z* = 2, *R* = 0.032 for 4298 unique reflections (Mo data). The reactions leading to the alkyl-cobalt(III) complex ion in 1 M sodium hydroxide have been followed by using spectrophotometry. It has been shown that the isolated compound is only one of several species present in an equilibrium mixture.

Introduction

The only naturally occurring metallorganic compounds of biological importance known presently are deoxyadenosylcobalamin (coenzyme B₁₂) and derivatives like methylcobalamin, which contain an alkyl-cobalt(III) bond.³ A large number of investigations have been performed on alkyl-cobalt compounds of natural corrin derivatives and of model compounds such as the cobaloximes.⁴ The approach for making alkyl-cobalt(III) compounds has been dominated by the idea that a plane of strongly coordinating ligand atoms would facilitate the formation of a carbon-cobalt bond in the axial direction. It might be tempting to suggest that the conjugate ligand systems found in cobalamins and cobaloximes are important to tune in the orbital energies to suit alkyl-cobalt bonding.⁵ However, also with the fully reduced macrocyclic amine 1,4,8,11-tetraazacyclotetradecane, an aquamethylcobalt(III) complex may be formed but in relatively low yield compared to the yields obtained with complexes of corresponding diene and tetraene complexes.⁶ These alkyl(amine)-cobalt(III) complexes were prepared by photochemical routes by Roche and Endicott, and once made, the compounds are robust under normal laboratory conditions toward air, light, acids, and bases. In fact these authors also predict that complexes like the (tetraamine)aquamethylcobalt(III) ion might be formed, but attempts to prepare such a complex using photolysis and methyl-transfer reactions were in vain.⁶ The carbon-cobalt bond in a methylcobalt(III) complex of a macrocyclic diene has been characterized in an X-ray diffraction study.⁷ The spectroscopic properties of the isolated methyl complexes indicate that CH₃⁻ is an innocent ligand with a position in the spectrochemical series near that of chloride.⁶

In this paper we describe the formation of an alkyl-cobalt(III) complex from a thioether-containing coordination compound. Thioether complexes of cobalt(III) have recently been subject to a number of studies,⁸⁻¹⁰ and it has been realized that the coordinated thioether behaves as a very weakly coordinating amine.⁸ The stability constant for bis[bis(aminoethyl) sulfide]cobalt(III), [Co(daes)₂]³⁺, has been shown to be only 10^{38.3} whereas the stability constant for the amine analogue bis(diethylenetri-

amine)cobalt(III) was measured to be 10^{48.8}.¹¹ In parallel with the low stability of the >S-Co^{III} bond it is observed that [Co(daes)₂]³⁺ is relatively labile as it is racemized with charcoal as a catalyst under weakly acid conditions down to pH 2.¹¹ Isomers of bis(2-aminoethyl 3-aminopropyl sulfide)cobalt(III), [Co(aeaps)₂]³⁺, have even less stability as they cannot be prepared from aqueous solution.⁸ Even without a catalyst [Co(aeaps)₂]³⁺ will slowly isomerize at pH above 6, and a pathway involving the intermediate formation of a hydroxocobalt(III) species with uncoordinated sulfur would explain this result. We therefore initiated a study of the reaction of [Co(aeaps)₂]³⁺ with base in the hope that it would lead to a characterization of the presumed intermediate. It is as a result of a study of this process that we have isolated the alkyl-cobalt(III) complex (2-aminoethyl 3-aminopropyl sulfide)(1,8-diaza-4-thiaoct-5-yl)cobalt(III) dithionate, [Co(aeaps)(diato)]S₂O₆. The products from three geometric isomers of [Co(aeaps)₂]³⁺ are identical, and the crystal structure of the dithionate salt has been determined by X-ray diffraction.

The three [Co(aeaps)₂]³⁺ isomers used in this study are of the unsymmetrically facial type depicted in Figure 1. We have previously prepared and characterized the following isomers: Λ -*trans*-6,6-*u-fac*-[Co(*S*-aeaps)₂]³⁺ (I), Λ -*trans*-5,5-*u-fac*-[Co(*R*-aeaps)₂]³⁺ (II), Λ -*trans*-5,6-*u-fac*-[Co(*R*-aeaps)(*S*-aeaps)]³⁺ (III).⁸ The absolute configuration Λ is here a short notation for $\Lambda\Lambda\Lambda$, which is the total chirality of all pairs of skew lines representing the ligand rings.¹² In the following these isomers as racemates will be referred to by the Roman numbers shown in Figure 1. The coordinated sulfur atoms of unsymmetric thioethers become chiral, and in the above designations of the ligand this is reflected as *R* and *S*. Besides the isomers I-III, a fourth one, the meso form with the thioether sulfur atoms in *trans* positions, *s-fac*-[Co(*R*-aeaps)(*S*-aeaps)]³⁺, has also been characterized; however, it has only been obtained in small quantities.⁸ The reaction that I-III undergoes with 1 M aqueous sodium hydroxide is sketched in Figure 2.

Experimental Section

Materials and Instrumentation. Salts of the three different *u-fac* isomers of [Co(aeaps)₂]³⁺ were prepared as chloride salts as described earlier.⁸ All other chemicals were of analytical grade. Absorption spectra were measured on a Perkin-Elmer Lambda diode array spectrophotometer using a resolution of 1.5 nm and a scan time of 0.1 s per spectrum. The spectrophotometer was controlled by a P-E 7500 Professional computer and fitted with a thermostated cell holder.

Circular dichroism measurements were performed on a CNRS Roussel-Jouan Dichrographe III instrument.

Preparation. (2-Aminoethyl 3-aminopropyl sulfide)(1,8-diaza-4-thiaoct-5-yl)cobalt(III) Dithionate, [Co(aeaps)(diato)]S₂O₆. A solution of 0.5 g (1.11 mmol) of 6,6-[Co(aeaps)₂]Cl₃·H₂O in 1 M NaOH (12 mL)

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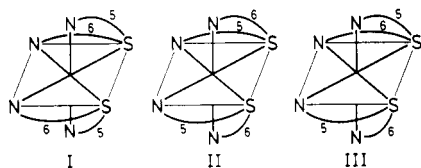


Figure 1. *u-fac* geometric isomers of $[\text{Co}(\text{aeaps})_2]^{3+}$ of Δ absolute configuration: (I) *trans*-6,6 isomer; (II) *trans*-5,5 isomer; (III) *trans*-5,6 isomer.

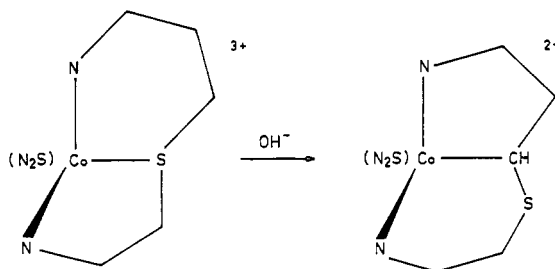


Figure 2. Geometric arrangement of the starting material, which can be any of the isomers I–III shown in Figure 1.

was kept at 25 °C for 8 min. The color of the solution changed from reddish to dark brown. A saturated solution of $\text{Na}_2\text{S}_2\text{O}_6$ (5 mL) was added, and a precipitate of yellow-brown crystals formed within 1 min. The mixture was stirred at room temperature for 8 min, and the crystals were then isolated by filtration. The sample was washed thoroughly with water, ethanol, and diethyl ether and was then dried in the air; yield 0.36 g (67%). Anal. Calcd for $\text{CoC}_{10}\text{H}_{27}\text{N}_4\text{S}_4\text{O}_6$: C, 24.69; H, 5.59; N, 11.52; S, 26.36. Found: C, 24.49; H, 5.65; N, 11.55; S, 26.12. Spectral data (0.1 M NaOH, 1 M LiCl; λ_{max} , nm (ϵ_{max} , $\text{M}^{-1}\text{cm}^{-1}$): 313 (8510), 225 (8700), 500 (sh, 167), 260 (sh, 5300).

The above procedure was also used in starting with the other two *u-fac* isomers. The products thus isolated were identical in the three cases as judged from X-ray powder diffraction patterns (and Weissenberg single-crystal investigations), which were analyzed and found compatible with the unit cell parameters obtained from the single-crystal study.

Material for single-crystal X-ray diffraction work was prepared as above, but the rate of precipitation was controlled in the following way: 1 mL of a saturated aqueous solution of $\text{Na}_2\text{S}_2\text{O}_6$ was placed in a small test tube. With minimum mixing was placed first a layer of 0.5 mL of 2 M NaOH and above that a layer of 2 mL of a solution of 0.1 g of a $[\text{Co}(\text{aeaps})_2]\text{Cl}_3$ isomer in 1 M NaOH. The test tube was kept at ca. 4 °C for several days, and during this time mixing and precipitation led to suitable crystals.

Kinetic Data. Pseudo-first-order rate constants, k_{obs} , and spectra at t_0 and t_{∞} were calculated from the absorbance, A , as a function of time by means of a nonlinear regression analysis using the expression $A = A_{\infty} + (A_0 - A_{\infty}) \exp(-k_{\text{obs}}t)$. These calculations were typically based upon absorbances measured at 200–470 different wavelengths in the region 190–900 nm. The values of k_{obs} given in the following are in each case the average of at least two determinations. In the cases of two consecutive first-order reactions it was always found that both the first and the second part of the reaction followed the expression above and gave the same well-defined calculated spectrum for the intermediate solution.

X-ray Diffraction. Data Collection. An orange-brown, tabular crystal of $[\text{Co}(\text{aeaps})(\text{diato})]\text{S}_2\text{O}_6$ with dimensions of $0.10 \times 0.15 \times 0.30 \text{ mm}^3$ was mounted on a glass fiber in a random orientation. Preliminary examination and data collection were performed with Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) on an Enraf-Nonius CAD4 diffractometer¹³ equipped with a graphite-crystal, incident-beam monochromator.

Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range $14^\circ < \theta < 18^\circ$. The monoclinic cell parameters and the calculated unit cell volume are $a = 9.463(3) \text{ \AA}$, $b = 9.681(3) \text{ \AA}$, $c = 11.097(4) \text{ \AA}$, $\beta = 113.48(3)^\circ$, and $V = 932.49 \text{ \AA}^3$. For $Z = 2$ and $\text{fw} = 486.54$ the calculated density is 1.73 g/cm^3 . From the systematic absences of $0k0$ ($k = 2n + 1$), the space group was determined to be $P2_1$.

The data were collected at a temperature of 115 K by using the ω/θ scan technique. The scan rate varied from 1 to $7^\circ/\text{min}$ (in ω). Data were collected to a maximum 2θ value of 70.0° . The scan range was determined as $\omega = 1.0 + 0.350 \tan \theta$. The ratio of peak counting time to background counting time was 2:1.

To investigate the chirality of the compound, an additional data set was collected by using Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The same data collection parameters and temperature were used as for the molybdenum data set. Data were collected to $2\theta_{\text{max}} = 66^\circ$.

Data Reduction. Molybdenum Data Set. A total of 4501 reflections (hkl and $h\bar{k}l$) were collected, of which 4298 were unique. As a check on crystal and electronic stability 3 standard reflections were measured every 166 min. The intensities of these standards remained constant within experimental error throughout data collection. No decay correction was applied. However, Lorentz and polarization corrections were applied. $\mu = 13.8 \text{ cm}^{-1}$ for Mo $K\alpha$ radiation. No absorption correction was performed. $R_{\text{int}} = 0.025$ on the basis of intensities for the 300 reflections averaged.

Copper Data Set. A total data set of 1368 reflections (full sphere) was collected, 690 of which were unique. Three standard reflections were measured every 166 min. The intensities of these standards remained constant within experimental error throughout data collection. Thus, no decay correction was applied. Lorentz and polarization corrections were applied. $\mu = 240.7 \text{ cm}^{-1}$ for Cu $K\alpha$ radiation. Absorption correction using a semiempirical absorption curve based on 9 φ scans¹⁴ was applied (range of transmission 0.5052–0.9973 with an average value of 0.8154), giving $R_{\text{int}} = 0.019$ based on intensities for the 988 reflections averaged.

Structure Solution and Refinement. All calculations were performed by using the SDF programs.¹⁵ The structure was solved by using the Patterson heavy-atom method. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were located, and their positions were refined with least-squares methods; their isotropic thermal parameters were held fixed at 2.0 \AA^2 , and no correction for extinction was attempted. The structure was refined with full-matrix least-squares methods minimizing $\sum w(|F_o| - |F_c|)^2$, where $w^{-1} = \sigma^2(F)$, and $\sigma^2(F) = \sigma_{\text{counting}}^2(F) + (p/4)F^2$ with $p = 0.04$. Scattering factors were taken from Cromer and Waber.¹⁶ Only the 2972 reflections having $I/\sigma(I)$ greater than 3.0 were used in the refinements. The final cycle of refinement included 306 variable parameters and converged (largest shift/error 0.06) with $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.032$, $R_w = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2} = 0.034$, and $S = 1.07$. This was obtained by using $f'' = 0$ for all atoms. After this anomalous dispersion effects were included in F_c . The values for f' and f'' were those of Cromer.¹⁶ Refinements with signs of f'' corresponding to both enantiomeric forms gave less good agreement than did the refinement with $f'' = 0$, indicating a twinning of the crystal. The crystallites forming the twin should then be of different chirality. To investigate this in greater detail, the Cu data set was analyzed. Refinement with $f'' = 0$ gave $R = 0.040$, $R_w = 0.058$, and $S = 2.93$, with f'' signs corresponding to those of Cromer¹⁵ $R = 0.062$, $R_w = 0.101$, and $S = 5.07$, and with the f'' signs reversed $R = 0.072$, $R_w = 0.114$, and $S = 5.18$. These results seem to emphasize that the crystal does contain both enantiomeric forms of the alkyl-cobalt(III) complex ion. The parameters given below are all corresponding to the refinements on the molybdenum data set with $f'' = 0$.

The highest peak in the final difference Fourier had a height of $0.6(1) \text{ e/\AA}^3$ with the estimated error based on ΔF ; the minimum negative peak had a height of $-0.5(1) \text{ e/\AA}^3$.

Results

Formation of an Alkyl-Cobalt(III) Bond. Each of the three *u-fac* isomers of $[\text{Co}(\text{aeaps})_2]^{3+}$ react within minutes in 1 M sodium hydroxide. The reactions are readily followed visually since the color of the solution changes from orange-red to gray-brown for each of the three isomers. Addition of an excess of a saturated, aqueous solution of sodium dithionate to the product solutions gave almost quantitative crystallization of orange-brown crystals, which were analyzed as $[\text{Co}(\text{C}_{10}\text{H}_{27}\text{N}_4\text{S}_2)]\text{S}_2\text{O}_6$. X-ray diffraction analyses showed that the crystals obtained from each of the three isomers of $[\text{Co}(\text{aeaps})_2]^{3+}$ were identical, and a single-crystal analysis showed that the isolated crystals contained an alkylcobalt(III) complex as described in the following.

The reaction of each of the three isomers of $[\text{Co}(\text{aeaps})_2]^{3+}$ in 1 M sodium hydroxide was followed spectrophotometrically in the wavelength region 190–900 nm. The spectra changed drastically and became constant after about 2 h at 1.0 °C and after 10 min at 25.0 °C. The spectra of the final product solutions were

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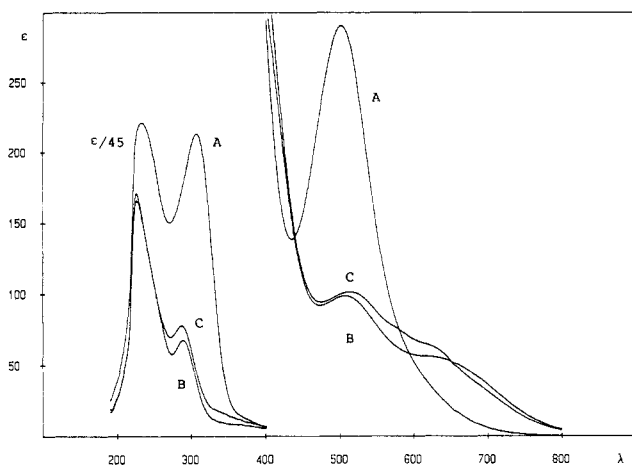


Figure 3. Absorption spectra of the solution extrapolated back to the time of dissolution (A), of the intermediate solution (B), and of the product solution (C) for the reaction of 6,6-[Co(aeaps)₂]³⁺ in 1 M NaOH at 1.0 °C.

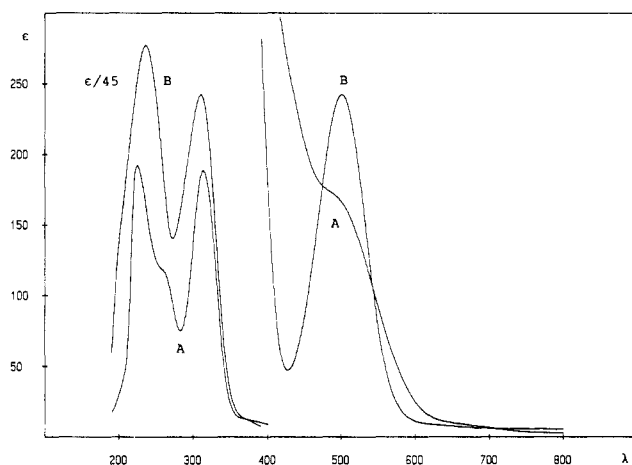


Figure 4. Absorption spectra of the alkyl-cobalt(III) dithionate in 0.1 M NaOH and 1 M LiCl at 1.0 °C extrapolated back to the time of dissolution (A) and of 6,6-[Co(aeaps)₂]₃·H₂O in 1 M NaClO₄ at 1.0 °C (B).

identical for all three isomers. For each isomer the change of absorbance with time showed the presence of at least two reaction phases, which has been interpreted as a fast reaction followed by a slow reaction. The observed pseudo-first-order rate constants at 1.0 °C for the reactions of the 6,6-isomer I are $k_1 = 8.1 \times 10^{-3} \text{ s}^{-1}$ and $k_2 = 4.9 \times 10^{-4} \text{ s}^{-1}$. Similar values were found for the two other isomers. The spectrum extrapolated back to the time of dissolution and the spectra of the intermediate solution and of the product solution for the reaction of 6,6-[Co(aeaps)₂]³⁺ in 1 M NaOH are shown in Figure 3. The spectra of 6,6-[Co(aeaps)₂]₃·H₂O in 1 M NaClO₄ (Figure 4) and in 1 M NaOH (extrapolated back to the time of dissolution, Figure 3) are very similar. The differences in absorbances are believed to be due to ion-pair formation, and it is concluded, therefore, that no fast reaction between 6,6-[Co(aeaps)₂]³⁺ and hydroxide takes place prior to the time at which the first spectrum is recorded ($t \approx 10 \text{ s}$).

The circular dichroism spectra of each of the three isomers I–III dissolved in base change with time. The CD spectra in 0.01 M NaOH have been followed through several hours. All three geometrical isomers of the Δ absolute configuration produced after about 20 min at room temperature intermediate, maximum-intensity circular dichroism spectra with the same overall shape but with different sign and intensity. The subsequent changes of the CD spectra indicated a slow "racemization" with $t_{1/2} \approx 2 \text{ h}$.

Structural Results. The results of the diffraction studies are summarized in Table I, which gives the positional and thermal parameters for all the atoms in [Co(aeaps)(diato)]S₂O₆. Bond

Table I. Positional and Thermal Parameters for the Alkyl-Cobalt(III) Complex Derived from [Co(aeaps)₂]S₂O₆^a

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> /Å ²
Co	0.78371 (4)	0.773	0.74648 (4)	0.533 (5)
N1	0.7733 (3)	0.8968 (3)	0.5979 (3)	0.84 (5)
C2	0.8897 (4)	1.0044 (4)	0.6095 (3)	1.04 (6)
C3	1.0472 (4)	0.9435 (4)	0.6400 (3)	1.11 (6)
S4	1.13410 (9)	0.8715 (1)	0.80327 (8)	1.02 (1)
C5	1.0084 (3)	0.7288 (4)	0.7919 (3)	0.81 (5)
C6	1.0138 (4)	0.6169 (4)	0.6959 (3)	0.94 (5)
C7	0.8800 (4)	0.5191 (4)	0.6701 (3)	0.94 (5)
N8	0.7403 (3)	0.6070 (3)	0.6332 (2)	0.75 (4)
N11	0.8331 (3)	0.9323 (3)	0.8673 (3)	0.85 (5)
C12	0.8001 (4)	0.9099 (4)	0.9866 (3)	1.00 (5)
C13	0.8656 (3)	0.7721 (4)	1.0457 (3)	1.01 (5)
S14	0.80756 (8)	0.63899 (9)	0.91926 (7)	0.75 (1)
C15	0.6243 (4)	0.5786 (4)	0.9137 (3)	0.97 (5)
C16	0.4844 (4)	0.6727 (4)	0.8533 (3)	1.04 (5)
C17	0.4406 (3)	0.7040 (4)	0.7087 (3)	0.89 (5)
N18	0.5454 (3)	0.8070 (3)	0.6868 (3)	0.80 (5)
H011	0.706 (7)	0.935 (7)	0.587 (5)	2.0
H012	0.761 (7)	0.834 (7)	0.523 (5)	2.0
H021	0.898 (7)	1.073 (7)	0.688 (5)	2.0
H022	0.854 (7)	1.052 (7)	0.525 (5)	2.0
H031	1.038 (6)	0.881 (8)	0.571 (5)	2.0
H032	1.112 (7)	1.003 (7)	0.640 (5)	2.0
H051	1.055 (7)	0.683 (7)	0.888 (5)	2.0
H061	1.004 (7)	0.667 (7)	0.610 (5)	2.0
H062	1.093 (7)	0.572 (7)	0.730 (5)	2.0
H071	0.893 (7)	0.461 (7)	0.751 (6)	2.0
H072	0.864 (7)	0.460 (7)	0.597 (5)	2.0
H081	0.719 (7)	0.626 (7)	0.555 (5)	2.0
H082	0.657 (7)	0.557 (7)	0.629 (5)	2.0
H111	0.947 (7)	0.962 (8)	0.895 (5)	2.0
H112	0.784 (7)	1.007 (7)	0.831 (5)	2.0
H121	0.685 (7)	0.914 (7)	0.958 (5)	2.0
H122	0.846 (7)	0.977 (7)	1.057 (6)	2.0
H131	0.826 (7)	0.736 (7)	1.100 (5)	2.0
H132	0.967 (6)	0.771 (8)	1.079 (5)	2.0
H151	0.639 (7)	0.555 (7)	1.006 (5)	2.0
H152	0.606 (7)	0.497 (7)	0.862 (5)	2.0
H161	0.498 (6)	0.756 (8)	0.898 (5)	2.0
H162	0.405 (6)	0.625 (7)	0.857 (5)	2.0
H171	0.321 (6)	0.749 (7)	0.661 (5)	2.0
H172	0.440 (7)	0.618 (7)	0.658 (5)	2.0
H181	0.513 (6)	0.815 (7)	0.594 (5)	2.0
H182	0.524 (7)	0.884 (7)	0.710 (5)	2.0
S1	0.58669 (8)	1.23715 (8)	0.68578 (7)	0.70 (1)
S2	0.40453 (9)	1.19978 (9)	0.74882 (7)	0.78 (1)
O1	0.7295 (3)	1.2344 (3)	0.8030 (2)	1.27 (4)
O2	0.5500 (3)	1.3709 (3)	0.6195 (2)	1.02 (4)
O3	0.5710 (3)	1.1236 (3)	0.5951 (2)	1.17 (4)
O4	0.4111 (3)	1.3075 (3)	0.8403 (2)	1.29 (4)
O5	0.4371 (3)	1.0612 (3)	0.8040 (2)	1.33 (5)
O6	0.2681 (3)	1.2065 (3)	0.6253 (2)	1.11 (4)

^a Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $B_{eq} = \frac{1}{3}(a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23})$.

distances and angles are presented in Table II while the hydrogen bonds are described in Table III. The labeling of the atoms in the coordination ion is shown in Figure 5.

Properties of the Alkyl-Cobalt(III) Coordination Compound.

The dithionate salt of the alkyl-cobalt(III) complex decomposes almost instantaneously in neutral or acid aqueous solution. It is sparingly soluble in basic aqueous solvents such as 1 M NaOH or 1 M LiOH, and it is also unstable in basic solutions. It is insoluble in organic solvents such as dimethylformamide and dimethyl sulfoxide. These properties made it difficult to study further solution properties of the new compound. However, we have found that the dithionate salt is moderately soluble in basic solutions of aqueous lithium chloride. Such solutions could be used for a spectrophotometric study of the solution properties. In 0.1 M NaOH and 1 M LiCl the first reaction is so slow at 1.0 °C ($t_{1/2} \approx 4 \text{ min}$) that a reliable extrapolation of the spectra back to the time of dissolution could be made (Figure 4). The same

Table II. Bond Distances (Å) and Angles (deg) for the Alkyl-Cobalt(III) Complex Derived from $[\text{Co}(\text{aeaps})_2]\text{S}_2\text{O}_6$

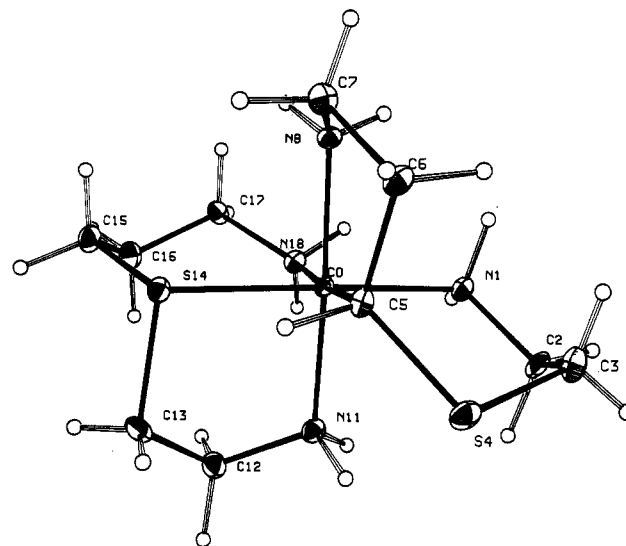
Co-N1	2.011 (3)	C3-H032	0.84 (7)
Co-C5	2.026 (3)	C5-H051	1.07 (6)
Co-N8	1.976 (3)	C6-H061	1.04 (6)
Co-N11	1.977 (3)	C6-H062	0.82 (6)
Co-S14	2.2482 (9)	C7-H071	1.02 (6)
Co-N18	2.110 (3)	C7-H072	0.96 (6)
N1-C2	1.484 (5)	N8-H081	0.83 (6)
C2-C3	1.510 (5)	N8-H082	0.91 (7)
C3-S4	1.805 (3)	N11-H111	1.04 (6)
S4-C5	1.794 (4)	N11-H112	0.87 (6)
C5-C6	1.535 (5)	C12-H121	1.01 (6)
C6-C7	1.514 (5)	C12-H122	0.98 (6)
C7-N8	1.487 (4)	C13-H131	0.90 (7)
N1-C12	1.492 (5)	C13-H132	0.88 (5)
C12-C13	1.507 (5)	C15-H151	1.01 (6)
C13-S14	1.822 (4)	C15-H152	0.95 (6)
S14-C15	1.808 (4)	C16-H161	0.90 (7)
C16-C17	1.520 (4)	C17-H171	1.13 (6)
C17-N18	1.493 (5)	C17-H172	1.00 (7)
N1-H011	0.71 (7)	N18-H181	0.95 (6)
N1-H012	1.00 (6)	N18-H182	0.84 (7)
C2-H021	1.07 (7)	S1-O1	1.456 (2)
C2-H022	0.98 (6)	S1-O2	1.461 (3)
C3-H031	0.96 (6)	S1-O3	1.457 (3)
S2-O4	1.439 (3)	S2-O6	1.463 (2)
S2-O5	1.456 (3)	S1-S2	2.1335 (13)
N1-Co-C5	92.0 (1)	C13-S14-C15	104.3 (2)
N1-Co-N8	92.0 (1)	S14-C15-C16	118.4 (3)
N1-Co-N11	90.5 (1)	C15-C16-C17	114.0 (3)
N1-Co-S14	176.91 (7)	C16-C17-N18	112.7 (2)
N1-Co-N18	87.2 (1)	H011-N1-H012	113 (5)
C5-Co-N8	85.4 (1)	H021-C2-H022	112 (5)
C5-Co-N11	93.1 (1)	H031-C3-H032	105 (6)
C5-Co-S14	85.9 (1)	H061-C6-H062	114 (6)
C5-Co-N18	175.5 (1)	H071-C7-H072	110 (6)
N8-Co-N11	177.1 (1)	H081-N8-H082	103 (5)
N8-Co-S14	90.02 (8)	H111-N11-H112	102 (6)
N8-Co-N18	90.2 (1)	H121-C12-H122	108 (5)
N11-Co-S14	87.45 (9)	H131-C13-H132	113 (5)
N11-Co-N18	91.4 (1)	H151-C15-H152	110 (6)
S14-Co-N18	95.20 (8)	H161-C16-H162	112 (6)
N1-C2-C3	112.2 (3)	H171-C17-H172	106 (4)
C2-C3-S4	113.0 (3)	H181-N18-H182	105 (6)
C3-S4-C5	101.7 (1)	O1-S1-O2	114.6 (1)
S4-C5-C6	112.8 (3)	O1-S1-O3	114.0 (1)
C5-C6-C7	108.4 (3)	O2-S1-O3	112.5 (1)
C6-C7-N8	106.3 (3)	O4-S2-O5	115.4 (2)
N11-C12-C13	108.6 (3)	O4-S2-O6	113.7 (1)
C12-C13-S14	110.3 (2)	O5-S2-O6	113.3 (1)

Table III. Hydrogen Bond Lengths (Å) and Angles (deg) in the Alkyl-Cobalt(III) Complex Derived from $[\text{Co}(\text{aeaps})_2]\text{S}_2\text{O}_6$ ^a

H011...O3	2.24 (7)	H112...O1	2.25 (6)
H012...O6 ¹	1.98 (6)	H181...O2 ¹	2.26 (6)
H081...O6 ¹	2.19 (5)	H182...O5	2.31 (6)
H082...O2 ²	2.04 (6)		
O3...H011-N1	155 (6)	O1...H112-N11	158 (6)
O6 ¹ ...H012-N1	178 (6)	O2 ¹ ...H181-N18	170 (6)
O6 ¹ ...H081-N8	162 (5)	O5...H182-N18	165 (5)
O2 ² ...H082-N8	150 (7)		

^aSuperscripts indicate atoms that have been symmetry-transformed: (1) $1-x, y-1/2, 1-z$; (2) $x, y-1, z$.

spectrum was obtained for 0.2 M NaOH and 1.0 M LiCl ($t_{1/2} \approx 3$ min). It is seen that the spectrum of the alkyl-cobalt(III) coordination compound is very different from that of the final product solution for the reaction of $[\text{Co}(\text{aeaps})_2]^{3+}$ in 1 M NaOH (Figures 3 and 4). The reaction of the alkyl-cobalt(III) complex in 1 M NaOH at 1 °C was followed spectrophotometrically. A well-defined isosbestic point at $\lambda = 556$ nm was observed during the initial stage of the reaction, but it vanished completely toward the end of the reaction. This shows that at least three species are involved in this reaction. The absorption spectrum became constant after about 30 min, and this final spectrum was nearly

**Figure 5.** ORTEP drawing of the alkyl-cobalt(III) complex ion showing the coordinated carbanion ligand and the numbering scheme for the cation.

identical with that of the product solution for the reaction of $[\text{Co}(\text{aeaps})_2]^{3+}$ in 1 M NaOH.

$[\text{Co}(\text{aeaps})_2(\text{diato})]^{2+}$ is unstable in acidic solution. When excess hydrochloric acid was added to a solution of the dithionate salt in 0.1 M NaOH and 1 M LiCl at 0 °C, the color of the acidified ($[\text{H}^+] \approx 1.0$ M) solution within 1 min changed from orange-brown to reddish purple and then became colorless within 30 min. The final colorless solution contained cobalt(II) as indicated by its reaction with SCN^- .

Discussion

The most striking feature of the structural determination is the presence of the cobalt-carbon bond, Co-C5. The bond distance (2.026 (3) Å) is only slightly longer than the average distance of the four Co-N bonds (2.019 Å). However, the Co-N18 bond (2.110 (3) Å), trans to the Co-C5 bond, is dramatically longer than usual amine-cobalt(III) bonds and thus much longer than the average of the remaining three Co-N distances (1.988 Å). The length of the Co-N18 bond suggests that the bond is relatively weak and probably also labile.

The other bond lengths and angles in the coordination compound are similar to those found for *s-fac*- and *u-fac*- $[\text{Co}(\text{aeaps})_2]\text{Cl}_3$.¹⁰ The six-membered chelate rings both have chair conformations, and the five-membered rings take the puckered conformation λ (aeaps) and δ (diato) when the configuration of the chelate rings are $\Delta\Delta\Delta$. Very recently¹⁷ a crystal structure was determined of a coordination compound with an alkyl-cobalt(III) bond similar to the one described above. However, in that case the coordination of carbon leads to the formation of two four-membered chelate rings resulting in substantial strain in this part of the ligand, which is derived from 1,5-diazacyclooctane-*N,N'*-diacetate (dacoda). In the alkyl complex $\text{Co}(\text{dacoda-H})(\text{H}_2\text{O})$ with the aqua ligand trans to the coordinated carbon the Co-OH₂ bond is as long as 2.15 Å. In view of this and our result for the Co-N18 distance it seems that an alkyl ligand in general has a strong trans influence in Werner-type alkyl-cobalt(III) complexes.

The dithionate anion has a staggered conformation, and the hydrogen bonding between the oxygen atoms of this anion and the hydrogen atoms of the four nitrogen atoms seems to greatly stabilize the crystal as is also implied by the high calculated density of 1.73 g/cm³. Only one nitrogen-bound hydrogen atom (on N11) does not participate in the hydrogen bonding. The reason may simply be found in the steric hindrance imposed by the sulfur atom

(17) Kanamori, K.; Broderick, W. E.; Jordan, R. F.; Willett, R. D.; Legg, J. I. *J. Am. Chem. Soc.* **1986**, *108*, 7122.

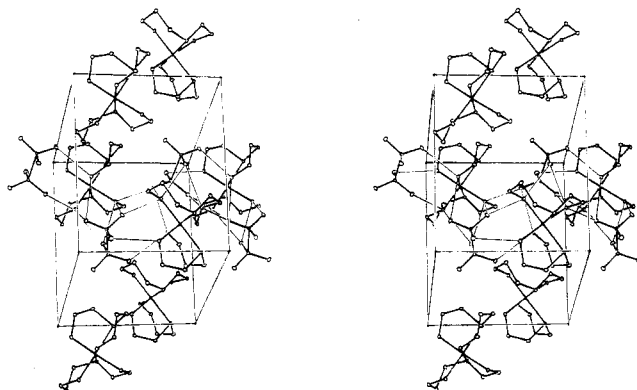


Figure 6. ORTEP stereoscopic drawing of the unit cell, with the *a* axis approximately orthogonal to the plane of the paper, the *b* axis horizontal, and the *c* axis vertical. The intermolecular distances shorter than 3.25 Å are shown as thin lines. These are the hydrogen bonds and one non-bonding interaction between N1 and O2.

S4 displaced only 2.52 (7) Å away. The stereoscopic packing diagram in Figure 6 shows this packing, and it is also evident from this figure that almost all the hydrogen bonds are directed along the *b* axis, which also is the crystal growth axis.

On the basis of the spectrophotometric and synthetic results mentioned above, some qualitative conclusions can be drawn with respect to the reactions leading to the alkyl-cobalt(III) complex. The three geometric isomers I–III of $[\text{Co}(\text{aeaps})_2]^{3+}$ react with 1 M NaOH to form product solutions from which only one isomer of an alkyl-cobalt(III) complex has been isolated in high yields. This suggests that the reactions in each case yield the same products. This is strongly supported by the observation that the absorption spectra of the product solutions are the same for the three geometric isomers. This conclusion is further supported by the similarities in the CD spectra of the three isomers developed with time in 0.01 M NaOH. These results are not understood in detail at present, but the CD curves are detailed enough to ensure that they must be the result of the same distribution of optically active species.

The product solution in 1 M base contains more than one species since it has a spectrum which is completely different from that of the salt which has been isolated from this solution. However, since the isolated dithionate crystallizes in high yield from the product solutions within a few minutes at room temperature, we conclude that the species in this solution must be in a rapidly established equilibrium. This is further supported by the ob-

servation that the alkyl-cobalt(III) coordination compound in 1 M NaOH re-forms the product solution from which it is isolated. The spectral changes of this reaction show that at least three species are present in the equilibrium solution. It is therefore concluded that the reaction of each of the three *u-fac* isomers of $[\text{Co}(\text{aeaps})_2]^{3+}$ in 1 M NaOH, via at least two consecutive reactions, leads to the same equilibrium mixture. This equilibrium mixture contains at least three species, one of which is the isolated alkyl-cobalt(III) complex. The remaining species in the solution might include isomers of the isolated cation as well as dialkyl-cobalt(III) or N-deprotonated species. Also hydroxo-cobalt(III) species containing uncoordinated sulfur are possible products in this equilibrium mixture. These issues are now being pursued, but so far attempts to crystallize other products from the equilibrium mixture have been unsuccessful.

Though the alkyl-cobalt(III) coordination compound is formed in strong base, it is unstable in this medium, and this might indicate a kinetically controlled reaction. From the discussion above it follows, however, that it is a thermodynamically controlled process and that the isolation of the new compound is a result of low solubility of the dithionate salt. From preliminary experiments we estimate that the equilibrium solution contains at least 20% of the alkyl compound. The alkyl-cobalt(III) moiety must accordingly be of high stability. The formation of the Co–C bond must involve a deprotonation of the methylene group, which is a very weak acid. The coexistence of the Co–S- and the Co–C-bonded species indicate a strong Co–C bond, which probably gives the driving force to the formation of the alkyl-cobalt(III) compound. The findings of Kamanori et al.¹⁷ together with the results reported here indicate that alkyl-cobalt(III) bonds may be abundant in basic solutions of cobalt(III) coordination compounds of large chelates.

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Registry No. [I]Cl₃, 100164-53-2; [II]Cl₃, 100164-52-1; [III]Cl₃, 116747-07-0; $[\text{Co}(\text{aeaps})(\text{diato})]\text{S}_2\text{O}_6$, 116747-06-9.

Supplementary Material Available: Tables of general displacement parameters and torsion angles for the cation and the anion (4 pages); lists of observed and calculated structure factors for molybdenum and copper data (37 pages). Ordering information is given on any current masthead page.