Inorganic Chemistry
Article

Inorg. Chem. **2009**, *48*, 7159–7164 **7159**
DOI: 10.1021/ic900397r

Making a Robust Carbon−Cobalt(III) Bond

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Received February 26, 2009

The coordination ion with a well-characterized carbon−cobalt(III) bond, the (1,4,7-triazacyclononane)(1,6-diamino-3-thia-4-hexanido)cobalt(III) dication, $[Co(tacn)(C\text{-}aeaps)]^{2+}$ (aeaps, for aminoethylaminopropylsulfide), has been reacted with iodomethane, and the S-methyl thionium derivative has been isolated. The crystal structure of the resulting $[Co(tacn)(C\text{-}aeaps\text{-}SCH_3)]Br_3 \cdot 3H_2O$ at 122 K has been determined by X-ray diffraction techniques to verify the structure. The crystal structure determination shows that the carbon−cobalt bond length is even shorter (2.001(4) Å) than in $[Co(aeaps)(C\text{-}aeaps)]^{2+}$ (2.026(3) Å), while its trans elongating effect is less pronounced. The (1,4,7-triazacyclononane)(1,6-diamino-3-thia-4-hexanido)cobalt(III) dication $[Co(tacn)(C\text{-}aeaps)]^{2+}$ (aeaps, for aminoethylaminopropylsulfide) reacts relatively fast with acid, for example, with NH_4^+ to form a sulfur-bound aeaps ligand. The $[Co(tacn)(C\text{-}aeaps\text{-}SCH_3)]^{3+}$ ion is remarkably robust in strongly acidic aqueous solution in spite of the supposed high basicity of the carbon anion. However, with a large excess of iodide, the methyl group can be removed as iodomethane. The experimentally obtained distances around cobalt(III) for the three involved coordination ions are compared to those computed from DFT with different standard choices for functionals and basis sets. The agreements range from poor to modest depending of the choice of functionals. It is noteworthy, however, that a sulfur 3p orbital in $[Co(tacn)(C\text{-}aeaps)]^{2+}$ participates in bonding to cobalt(III), having implications for the transformation between the carbon- and sulfur-bound forms of the aeaps ligand.

Introduction

Monodentate thioether compounds of cobalt(III), for example, $[Co(NH_3)_5(S(CH_3)_2)]^{3+}$, undergo hydrolysis in basic solution to yield the corresponding hydroxo entity, that is, $[Co(NH_3)_5(OH)]^{2+}$, with release of the thioether.[1] Coordination compounds with 2-aminoethyl sulfides, $H_2NCH_2CH_2-S-R$, reacts similarly when R is a simple alkyl group. In this case, however, the ligand is retained singly coordinated at the cobalt(III) by the amino group (Figure 1).[2,3]

The positive activation entropies of the hydrolysis reactions are consistent with a dissociative process, in which the sulfur donor atom is detached from the cobalt(III) prior to the entering of the hydroxo ligand. The process was found to be reversible, with the thioether rechelating in acidic solution.[2]

From these studies on base hydrolysis, it was inferred that the acidity of the α-hydrogen atoms in the thioether is greatly increased upon coordination to cobalt(III), in that the thioether obtains some sulfonium character by coordination to the triply charged cation.[4] This opens possibilities within the area of metal-ion-promoted CH activation.

By tethering the thioether ligand with instead *two* 2-aminoethyl groups, that is, using bis(2-aminoethyl)sulphide, base hydrolysis was avoided, while the α-hydrogen atoms displayed a pronounced and stereospecific acidity, as studied by deuterium for hydrogen exchange.[5]

By extending the arm length of the aminoalkyl group to a 3-aminopropyl group, one gets the possibility of trapping the base form of the α-methylene group by coordination to cobalt (III) in a five-membered chelate ring. One suitable ligand with this property is 3-thia-hexane-1,6-diamine (aeaps, for aminoethylaminopropylsulfide), which is the mother ligand for the coordination compounds discussed in this paper. The C4 deprotonated form of this ligand, 1,6-diamino-3-thia-4-hexanide, is abbreviated C-aeaps. The first evidence for a cobalt−carbon bond with a ligand derived from aeaps came from the crystal structure of $[Co(aeaps)(C\text{-}aeaps)]S_2O_6$ obtained from $[Co(aeaps)_2]^{3+}$ reacting with a base.[6] In this

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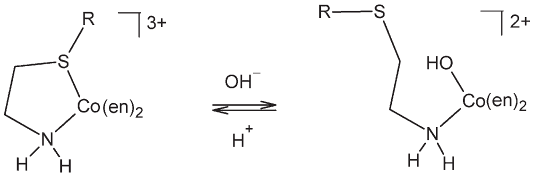

Figure 1. Base hydrolysis of cobalt(III) compounds with 2-aminoethyl sulphide ligands (en = 1,2-ethanediamine).[2]

cation, the C-aeaps ligand occupies an octahedral face coordinating two nitrogen atoms and one carbon atom, while the unreacted aeaps ligand occupies the other octahedral face coordinating two nitrogen atoms and one sulfur atom.

Subsequently, a series of cobalt(III) coordination compounds with C-aeaps has been studied, in which C-aeaps occupies one octahedral face, while the other face has been occupied by ligands like 1,4,7-triazacyclonane (tacn) or tris-(1-aminomethyl)ethane (tame) to simplify the observed reactions by avoiding different isomers. In these studies, it was shown that there is an equilibrium between the sulfur-bound form $[CoL(aeaps)]^{3+}$ and the carbon-bound form $[CoL(C\text{-}aeaps)]^{2+}$, and the structural, equilibrium, and kinetic parameters for the systems with L = tacn or L = tame have been determined.[7]

Similar base-induced transformations of thioether−cobalt (III) compounds with unsaturated N-donor ligands in methanol solution have also been reported.[8] To our knowledge, reversibility of the rearrangements have in these cases, however, not been demonstrated. In rare cases, a similar base-induced transformation of amine−cobalt(III) compounds has been observed. Thus, Jackson and co-workers studied the reversible formation of a cobalt(III)−carbon bond upon treatment of a tacn-derived cobalt(III) complex with an aqueous base.[9a] Deprotonation of an α-methylene group followed by coordination of the resulting carbanion yielded a four-membered C-bonded chelate ring.

Related examples of cyclometalation reactions upon cobalt (III)-promoted CH activation are the coordination of the γ-carbon atom of the 1,4-diazacyclononane ring in 1,4,8,11-tetraazabicyclo[9.5.2]octadecane to yield five-membered chelate rings (similar to tacn, but with a coordinated carbon instead of one of the nitrogen atoms)[9b] and the finding that a 1,5-diazaoctane-based ligand could undergo deprotonation of a β-methylene group to afford four-membered C-bonded chelate rings.[9c] It should be emphasized, however, that the latter two examples do not involve any rearrangement of a heteroatom (i.e., sulfur or nitrogen) bound to a carbon-bound form.

In the present paper, we discuss the reversibility of the cobalt(III)−carbon bond formation in the thioether-based carbanion−cobalt(III) compounds. We report the synthesis and structure of an equivalent coordination entity on which a methyl group has been attached to the sulfur atom and thus, supposedly, is preventing a bonding mode with sulfur as the donor atom. The preparation can be summarized schematically as given in Scheme 1.

The formation of I from II proceeds quantitatively in acidic solution. The mechanism for this reverse reaction deserves some attention, in that it might explain the robustness of II and the related Werner-type alkylcobalt(III) compounds. As organometallic compounds commonly decompose in aqueous solution by simple protonation, one might consider the possible intermediacy of an aqua complex, in which the coordinated carbanion is replaced by water. The tethered thioether ligand might subsequently (quickly) replace the coordinated water, driven by a chelate effect. This would be consistent with the early work on base hydrolysis of cobalt(III) compounds with 2-aminoethyl thioether ligands.[2−4] In this paper, we show that S-methylation of the coordinated C-aeaps not only prevents formation of the sulfur-bonded mode but even prevents the hydrogenolysis of the coordinated carbanion. An explanation for this is given in the form of a "sledge" mechanism picture, which is supported by DFT calculations.

Experimental Section

Preparations. The starting material $[Co(tacn)(C\text{-}aeaps)](ClO_4)_2$ was prepared as described earlier.[6] Acetonitrile and solutions of silver perchlorate in acetonitrile were dried using 4 Å molecular sieves.

$[Co(tacn)(C\text{-}aeaps\text{-}SCH_3](ClO_4)_3$. To a filtered solution of 1.94 g (3.93 mmol) $[Co(tacn)(C\text{-}aeaps)](ClO_4)_2$ in 80 mL of acetonitrile was added 5 mL (79 mmol) of methyliodide. To this solution was added a solution of 3.11 g (15 mmol) $AgClO_4$ in 10 mL of acetonitrile. The mixture was stirred for 4 h at room temperature. During this time, silver iodide precipitated. After filtration, the red filtrate was evaporated under reduced pressure at room temperature until precipitation commenced. The crystallization was completed by the addition of ca. 250 mL of 1,2-dichloroethane and cooling in an ice bath. Orange-brown crystals of $[Co(tacn)(C\text{-}aeaps\text{-}SCH_3)](ClO_4)_3$ were filtered off and washed with 3 times 10 mL of $CH_3CN/ClCH_2CH_2Cl$ (1:5) and dried in the air. Yield: 2.11 g (89%). The ion exchange high-performance liquid chromatography (IE-HPLC) of the crude product showed the presence of two minor impurities, namely, the starting material (1.8%) and $[Co(tacn)_2](ClO_4)_3$ (2.3%). Recrystallization was performed by dissolving 0.1 g of the crude product in 10 mL of CH_3CN and stirring for 5 min. A slurry was obtained after the addition of ca. 0.1 g of finely powdered NaCl. The stirring was continued 10 min after the addition of 10 mL of CH_2Cl_2. The solid content of NaCl and $[Co(tacn)_2]Cl_3$ was filtered off, and to the filtrate was added another 10 mL of CH_2Cl_2. After stirring for 15 min at room temperature, 0.07 g $[Co(tacn)(C\text{-}aeaps\text{-}SCH_3)]$ $(ClO_4)_3$ was isolated. This product gave a negative test for chloride ions with silver nitrate solution, and the IE-HPLC showed only one component.

Analytical Data. Calculated for $C_{12}H_{31}N_5O_{12}SCl_3Co$: C, 22.71%; H, 4.92%; N, 11.03%; S, 5.05%; Cl, 16.75%. Found: C, 21.95%; H, 4.71%; N, 10.95; S, 4.71; Cl, 15.60.

$[Co(tacn)(C\text{-}aeaps\text{-}SCH_3)]Br_3 \cdot 3H_2O$ was obtained from 0.20 g of the perchlorate by ion exchange on a strong cation exchanger (BIO-REX 70, 50−100 mesh, Na^+ form). After application on the column and washing first with water and then with 0.5 M HBr, the cation was eluted with 6 M HBr. The eluent was concentrated by evaporation and kept in a desiccator with an open container with ethanol to obtain a yield of 0.17 g of crystals suited for single-crystal X-ray diffraction work.

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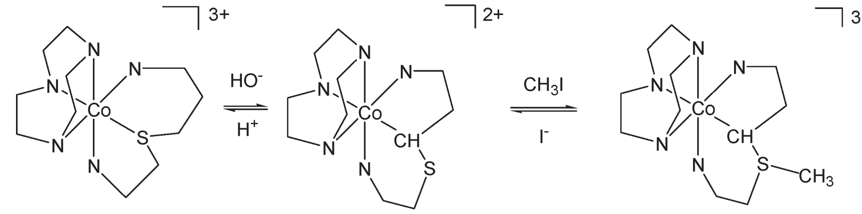
Scheme 1



$[Co(tacn)(aeaps)]^{3+}$ $[Co(tacn)(C\text{-}aeaps)]^{2+}$ $[Co(tacn)(C\text{-}aeaps\text{-}SCH_3)]^{3+}$

I II III

Spectral Measurements. Absorption spectra were recorded on a Spectronic 1201.

IE-HPLC was performed using a Waters HPLC system connected to a diode array detector and fitted with a SP-5PW cation exchanger. The eluent used was 0.20 M Na_2SO_4 with a flow rate of 1 mL/min.

NMR spectra were measured at 5.87 T on a Bruker AC 250 NMR spectrometer. All measurements were performed at 25 °C. ^{13}C DEPT NMR was used to distinguish between CH, CH_2, and CH_3 groups. ^{13}C chemical shift values (δ) are reported in parts per million relative to internal 2,2-dimethyl-2-silapentane-5-sulfonate ($\delta = 0$, 17.66, 21.74, and 57.02 ppm).

Electrochemical Measurements. Cyclic voltammetry of the ions I−III in 0.1 M NBu_4PF_6 solutions in DMF was performed with a three-electrode cell using a glassy carbon working electrode and a Ag/AgCl reference electrode. An *Autolab* system from ECO Chemie, B.V., Utrecht, Holland, was used in combination with a PC as the potentiostat and digital recorder. The formal potentials reported are all relative to the normal hydrogen electrode.

X-Ray Crystallography. Diffraction data were collected on a Nonius KappaCCD diffractometer with graphite monochromated Mo Kα radiation. The temperature was kept at 122.4(5) K using an Oxford Cryosystems low-temperature liquid-nitrogen cooling device. The data reduction was performed using the Nonius Collect suite of programs.[10] A numerical absorption correction was applied on the basis of the crystal shape. The structure was obtained by direct methods using SIR97[11] and refined by full-matrix least-squares against F2 using the SHELXL-97 program.[12] Positions and anisotropic displacement parameters were refined for all non-hydrogen atoms. Hydrogen atoms were visible in difference Fourier maps, but were not refinable, and were therefore kept at idealized positions using SHELXL AFIX and constrained isotropic displacement parameters.[12] Crystallographic data are summarized in Table 1. Two water molecules were disordered and modeled with two sites and isotropic displacement parameters. No hydrogen atoms could be located for these water molecules.

As it was not possible to define the polarity of the crystal with certainty, it was attempted to refine it as a racemic twin, and this gave a better description. The refined twin parameter is 0.65(1). The final residuals are listed in Table 1. The largest peaks in the final difference Fourier map were found close to Br. Further details have been included in a crystallographic information file, which is available in the Supporting Information or from the CCDC with refcode CCDC 719358, which contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. $[Co(tacn)(C\text{-}aeaps\text{-}SCH_3)]Br_3 \cdot 3H_2O$ Crystal Data and a Summary of Data Reduction and Structure Refinement

formula	$CoBr_3C_{12}H_{33}N_5O_3S$
formula mass/g mol^{-1}	626.13
space group	$Pna2_1$
cell dimensions at 122 K	
a/Å	8.1480(13)
b/Å	15.0310(10)
c/Å	18.1150(11)
V/Å^3	2218.6(8)
z	4
D_c/g cm^{-3}	1.890
μ (Mo Kα)/cm^{-1}	6.3
octants measured	*hkl*
θ-range/deg	1−35
no. of measured refl.	69985
unique reflns used in refinement ($I > -3\sigma)(I)$)	9706
no. of variables	228
GOF	1.06
w^{-1}	$\sigma^2(\lvert F_o\rvert^2) + (0.0494p)^2 + 4.21p$
$p =$	$\max(\lvert F^o\rvert^2,0) + 2\ \lvert F_c\rvert^2)/3$
$R_2(w)$	0.1120
R_1, ($\lvert F_o\rvert$) > $4\sigma(\lvert F_o\rvert)$	0.0461

DFT Computations. The program package Gaussian03, revision E for Windows and version 98 for Linux, was used for density functional computations.[13] Standard convergence criteria were used, and for all calculations, standard functionals and standard basis sets were employed.

Results and Discussions

The S-methylthionium derivative, III, of $[Co(tacn)(C\text{-}aeaps)]^{2+}$, II, has now been prepared, and although this is satisfying, its existence is not so surprising, while some of its properties are. The absorption spectra of II and III are summarized in Table 2. The data demonstrate that the two ions have the first spin-allowed d−d band at nearly the same energy. A tail from a carbon-to-cobalt charge-transfer band with a maximum at 302 nm in $[Co(tacn)(C\text{-}aeaps)]^{2+}$

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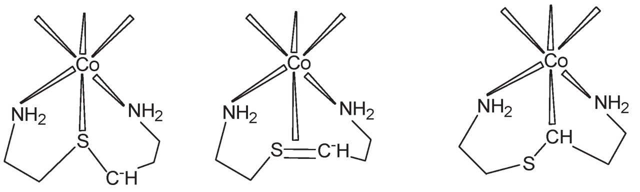
Table 2. Vis and UV Absorption Spectra

coordination ion	$[Co(tacn)(C\text{-}aeaps\text{-}SCH_3)]^{3+}$		$[Co(tacn)(C\text{-}aeaps)]^{2+}$	
Assignment	λ/nm	ε_{max}/M^{-1} cm^{-1}	λ/nm	ε_{max}/M^{-1} cm^{-1}
d−d ($^1T_{1g} \leftarrow {}^1A_{1g}$)	460	93.9	464	95.4 sh
d−d ($^1T_{2g} \leftarrow {}^1A_{1g}$)	348	171 sh	356	491 sh
C to Co CT	258	14352	302	10512
N to Co CT	214	13478	209	12419

Scheme 2



broadens the low-intensity bands of the d−d transitions. The corresponding charge transfer in $[Co(tacn)(C\text{-}aeaps\text{-}SCH_3)]^{3+}$ is found to have a maximum at a much lower wavelength, 258 nm, in agreement with common intuition considering the more localized electronic structure in III. However, some of the properties noted for the new coordination ion are opposite to those of common intuition vide infra.

Reactivity. The first property we find especially noteworthy is the robustness of the ion. It is possible to boil the compound with concentrated hydrochloric acid for hours without a trace of decomposition. This is contrary to the complete decomposition caused by a similar treatment of both $[Co(tacn)(aeaps)]^{3+}$ and $[Co(tacn)(C\text{-}aeaps)]^{2+}$. It is proposed for the equilibrium of the latter two ions that the binding π orbital composed of p_π atomic orbitals from sulfur and carbon in the ylide ligand could act as a σ donor to a 3d orbital on cobalt(III). Such a bonding mode may account for the relatively fast transformation from one to the other. This means that the unusually facile transformation from the sulfur-bound form to the coordinated carbon anion is highly dependent on the formation of a coordinated ylide, that is, the anion of aeaps. In this coordinated ylide, a π bond between the formally positively charged sulfur atom and the carbanion could not only be the stabilizing element but the electron density could also act as a "sledge" allowing a σ bond to cobalt to exist during the transformation. We thus envisage a weak bond due to overlap between the doubly occupied p orbitals on sulfur and carbon and an empty e_g orbital on cobalt(III) as well as the empty cobalt orbitals with $n = 4$. This is shown schematically in Scheme 2.

The facile and stereospecific H-to-D exchange in D_2O already described for $[Co(tacn)(aeaps)]^{3+}$ is a very strong advocate for this explanation.[7] In the methylated cation, III, this transformation is not possible. However, the carbanion must have a very high affinity to hydrogen ions and ought to decompose. We interpret the observed lack of decomposition not as being due to high stability but being due to a very high activation energy, giving rise to a pronounced degree of robustness.

In connection with calorimetric measurement on cobalt (III) compounds, we have noticed that cation III does not react with sulfide ions to form cobalt sulfide. This is highly unusual since, to our knowledge, only $[Co(CN)_6]^{3-}$ behaves similarly among Werner-type cobalt (III) complexes. We interpret this as a very strong resistance against an inner-sphere reaction between cobalt (III) and an attacking reagent. The ligands in $[Co(tacn)(C\text{-}aeaps\text{-}SCH_3)]^{3+}$ simply act as a cage.

Table 3. ^{13}C NMR δ Values, with Dimethylsulfoxide-d_6 as a Solvent and D_20 for $[Co(tacn)(aeaps)]^{3+}$

compound	$[Co(tacn)(C\text{-}aeaps\text{-}SCH_3)]^{3+}$	$[Co(tacn)(C\text{-}aeaps)]^{2+}$	$[Co(tacn)(aeaps)]^{3+}$
tacn	51.1	50.8	57.1
	50.8	49.0	56.9
	49.8	48.9	56.7
	49.5	48.7	51.5
	48.9	48.5	51.2
	48.0	46.3	50.7
L^a Numbering of Atoms			
1	37.4	37.7	40.5
2	27.9	24.6	25.0
4	27.2	38.1	31.8
5	33.1	36.7	38.5
6	43.4	42.9	48.4
7	22.9		

[a] L ligand is here numbered N−C1−C2−S(C7)−C4−C5−C6−N.

Table 4. Cyclic Voltammetry Results Obtained from 0.1 M NBu_4PF_6 in Dimethylformamide

compounds	$E_{1/2SHE}$/V	ΔE/mV	I_{pc}/I_{pa}
$[Co(tacn)((aeaps)]Cl_3$	−0.11	82	1.49
$[Co(tacn)(C\text{-}aeaps)](ClO_4)_2$	−1.16	87	1.03
$[Co(tacn)(C\text{-}aeaps\text{-}SCH_3)](ClO_4)_3$	−0.69	74	1.68

The ^{13}C NMR spectra of 0.2 M solutions of $[Co(tacn)(C\text{-}aeaps\text{-}SCH_3)]^{3+}$ and $[Co(tacn)(C\text{-}aeaps)]^{2+}$ were obtained in DMSO, and the δ values are reported in Table 3. The spectrum of $[Co(tacn)(C\text{-}aeaps)]^{2+}$ was assigned previously.[7] In the spectrum of $[Co(tacn)(C\text{-}aeaps\text{-}SCH_3)]^{3+}$, the signals at 27.2 ppm and 22.9 ppm were assigned to the CH group and the CH_3 group, respectively, by use of the DEPT technique. The remaining signals from the aeaps-derived ligand in $[Co(tacn)(C\text{-}aeaps\text{-}SCH_3)]^{3+}$ were assigned similarly to $[Co(tacn)(C\text{-}aeaps)]^{2+}$.

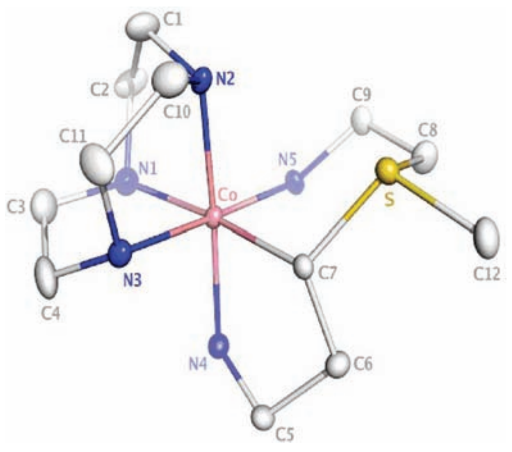


Figure 2. Cation III with atomic labeling. The thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms have been omitted for the sake of clarity.

Table 5. Experimentally Observed and Computed Distances around Cobalt(III)[a]

		experimental values					
distance/Å	$[Co(tacn)(aeaps)]^{3+}$	A	B	C	D	E	F
Co−N1	1.965(4)	2.014	2.004	1.950	1.976	1.990	2.008
Co−N2	1.960(4)	2.002	2.015	1.939	1.941	1.980	1.990
Co−N3	1.984(3)	2.051	2.050	1.930	1.953	1.071	1.978
Co−N4	2.004(4)	2.048	2.053	1.961	1.963	2.027	2.024
Co−N5	1.994(4)	2.048	2.053	1.960	1.967	2.023	2.024
Co−X	2.243(1)	2.401	2.324	2.282	2.189	2.359	2.294
R/%		1.6	0.8	0.4	0.3	0.7	0.3
distance/Å	$[Co(tacn)(C\text{-}aeaps)]^{2+}$	A	B	C	D	E	F
Co−N1	2.047(10)	2.135	2.168	2.017	2.048	2.085	2.123
Co−N2	1.951(9)	1.976	2.022	2.017	1.936	1.982	1.980
Co−N3	1.966(9)	2.003	2.006	1.924	1.927	1.974	1.986
Co−N4	1.992(11)	2.032	2.038	1.955	1.952	2.033	2.011
Co−N5	1.992(11)	2.055	2.057	1.953	1.959	2.016	2.036
Co−X	2.05(2)	1.979	2.012	1.923	1.957	1.956	1.980
R/%		1.0	1.4	1.3	0.7	0.7	0.7
distance/Å	$[Co(tacn)(C\text{-}aeaps\text{-}SCH_3)]^{3+}$	A	B	C	D	E	F
Co−N1	2.002(4)	2.071	2.168	2.071	2.002	2.042	2.050
Co−N2	1.966(3)	2.007	2.022	2.007	1.940	1.984	1.989
Co−N3	1.983(3)	2.008	2.006	2.008	1.942	1.985	1.989
Co−N4	1.986(4)	2.038	2.048	2.038	1.955	2.014	2.011
Co−N5	2.006(3)	2.073	2.066	2.073	1.970	2.046	2.038
Co−X	2.001(4)	2.014	2.012	2.014	1.976	1.994	2.023
R/%		0.6	1.7	0.6	0.3	0.2	0.2

[a] For numbering, see Figure 2. The computed bond distances are obtained using DFT with the functional B3LYP and the basis sets 6-31g (A) and 6-311g++(2d,2p) (B), the functional LSDA, and the basis sets 6-31g (C) and 6-311g++(d,p) (D). Finally, the functional MPW1PW91 and the basis sets 6-31g (E) and 6-311++g(d,p) (F) were used. $R = 100(d_{exp} - d_{calcd})^2/d_{exp}$ is used as a measure of the goodness of the fit.

Cyclic Voltammetry. Cyclic voltammetry (CV) results of the three coordination ions, I−III, are shown in Table 4. It is remarkable that the voltammograms appear nearly reversible with peak separations at 74−87 mV in DMF because cobalt(II) coordination ions of amine ligands are expected to dissociate very fast in aqueous solution and also in other coordinating solvents like dimethylformamide. When the CV shows a peak separation near 60 mV, the experiment demonstrates complete electrochemical reversibility, and for the $[Co(tacn)(C\text{-}aeaps\text{-}SCH_3)]^{2+,3+}$ system, we have come surprisingly close to this situation.

The results indicate that the stability of the cobalt(III) coordination ions relative to the stability of the same cobalt(II) species vary for the three such that the stability of the cobalt(III) entity in the series is increasing as $[Co(tacn)(C\text{-}aeaps)]^{2+} < [Co(tacn)(C\text{-}aeaps\text{-}SCH_3)]^{3+} < [Co(tacn)(aeaps)]^{3+}$. This indicates that the introduction of a positive charge next to the ligating carbanion seems to have a strong destabilizing effect on the cobalt(III) relative to the effect for cobalt(II).

Description of the Structure. A drawing of the cation as it is found in the structure is shown in Figure 2, which also illustrates the atomic labeling. The molecular geometry is apparent from the bond lengths and angles listed in Table 5. The crystal structure determination verified that substitution had occurred on the sulfur atom. The tacn ligand appears to be slightly disordered, as indicated by the shape of the thermal ellipsoids for some carbon atoms (C3 and C4) and the relatively short C3−C4 distance. Otherwise, this coordination of the tacn ligand is virtually identical to the one observed in the crystal structures containing the $[Co(tacn)(aeaps)]^{3+}$ and $[Co(tacn)(C\text{-}aeaps)]^{2+}$ cations.[7]

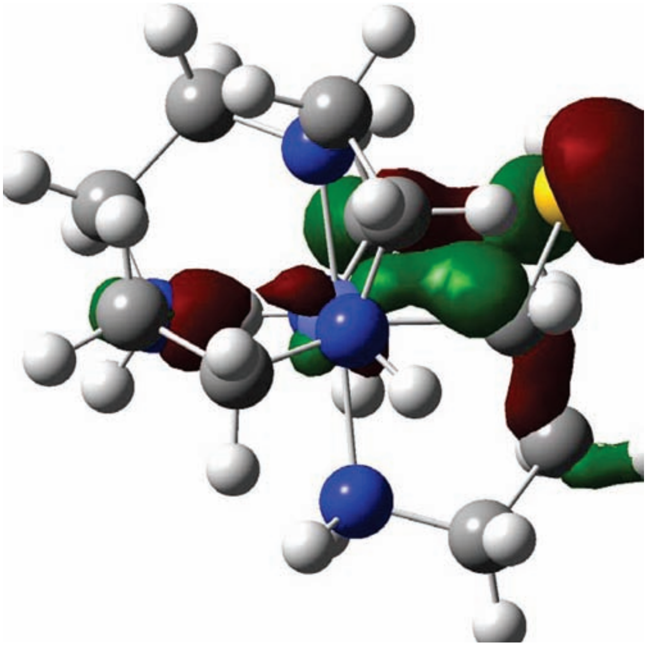


Figure 3. Electron density in MO no. 80 using isovalue 0.060 and density 0.00040 for DFT computation on $[Co(tacn)(C\text{-}aeaps)]^{2+}$ (E). The view is approximately along N3−Co−N5 from Figure 2.

Likewise, the overall coordination of the (C-aeaps-SCH_3) ligand is similar to the coordination of unsubstituted C-aeaps found in the crystal structure of $[Co(tacn)(C\text{-}aeaps)](ClO_4)_2$.[7] However, the methyl substitution on

S seems to have caused some distinct differences between this structure and the one of related cations in terms of much higher robustness.

First, we note the short Co−C distance of 2.001(4) Å, which is the shortest Co−C distance so far observed in Co C-aeaps complexes. In the related cations [Co(aeaps)(C-aeaps)]$^{2+}$ and [Co(tacn)(C-aeaps)]$^{2+}$, the equivalent distances are 2.026(3) Å and 2.05(2) Å, respectively. In [Co(tame)(C-aeaps)]$^{2+}$, the corresponding Co−C bond length is 2.049(7) Å.[9]

The trans effect of C7 is not so pronounced in the present structure, where the Co−N1 distance, 2.002(4) Å, is slightly larger than the equivalent Co−N2 and Co−N3 distances and much less than the distance, 2.047(10), found in [Co(tacn)(C-aeaps)](ClO$_4$)$_2$.

The C−S distances display significant differences: the C8−S distance of 1.809(4) Å corresponds to a normal thioether bond, but both S−C7 (1.793(4) Å) and S−C12 (1.796(5) Å) are shorter. The short C7−S bond length supports the ylide sledge mechanism proposed here.

The packing in the crystal is influenced by hydrogen bonding between the cation and the bromide ions. Only two of the water molecules appear to be hydrogen-bonded to the bromide; they fill cavities between the ions. The lack of interactions for the water molecules may explain why it was impossible to localize their hydrogen atoms.

Density Functional Theory. Density functional theoretical computations of structural data for the three cations I−III are summarized in Table 5, where the common structural features for the three structures oriented as shown in Figure 2 are reported. The experimental crystal data are somewhat better for I and III than for II, where disorder of the crystal causes inaccuracy. DFT and especially time-dependent DFT have been very successful in recent years, and even second-order spectroscopic effects like natural and magnetic circular dichroism have been computed with good agreement with experimentally measured spectra.[14−16] Spin-crossover calculations for pseudotetrahedral cobalt(III) complexes are also successful,[17] like relativistic DFT calculating ^{13}C and ^{59}Co NMR parameters for complexes of the type [Co(en)$_2$(CH$_3$)(X)] where en = 1,2-ethanediamine and X = CN$^-$, N$_3$$^-$, NH$_3$, NO$_2$$^-$, or H$_2$O.[18]

Also, DFT-computed distances are generally close to the experimental ones. However, for Werner-type cobalt(III) coordination compounds, difficulties seem to arise, and the usually very successful B3LYP functional has been claimed to be less successful than, for instance, the local density functional, LSDA.[19] More recently, DFT functionals and molecular geometries were studied for organic molecules. Even for these molecules, there were variations, and B3LYP performed rather well.[20,21] Most of the recent very successful DFT results are in fact made with functionals containing better approximations than LSDA and B3LYP functionals.[22] Since Co−S and Co−C distances are less often met, it was interesting to see how well the coordination ions I, II, and III are modeled by three standard functionals and a simple and a large basis set. The chosen hybrid functionals are B3LYP, LSDA, and B3PW91, and the results vary so much that there is basis for choosing in this case the functional MPW1PW91 as the best, as judged from the R values calculated as 100 $(d_{\mathrm{exp}} - d_{\mathrm{calcd}})^2/d_{\mathrm{exp}}$. It is also satisfying here that a better basis set seems to produce better agreements with the experimental results.

For [Co(tacn)(C-aeaps)]$^{2+}$, orbital number 80 shows reminiscences from the postulated intermediate ylide state depicted in Scheme 2, thus supporting the idea. As seen from Figure 3, sulfur (yellow) has an orbital derived from its 3p orbitals oriented roughly parallel to the view and now participating both in a σ bond to the carbon atom (C8) and in a σ bond to cobalt (green loop). The carbon atom (gray) bound to cobalt(III) (light blue) has a distorted π orbital where the green loop binds with σ symmetry to cobalt and the red loop forms the σ bond to the next carbon atom in the five-membered chelate ring (C6).

In conclusion, the proposed sledge mechanism is corroborated both by the fact that S-methylation acts as a lock against the reversal to the acid form of the α-methylene group in the aeaps ligand and by the participation of sulfur 3p orbitals in bonding to cobalt(III) in [Co(tacn)(C-aeaps)]$^{2+}$, as elucidated by DFT calculations.

Acknowledgment. The authors thank Mr. Flemming Hansen for help during the crystallographic data collection. Support from The Danish Research Council to E.L. is gratefully acknowledged.

Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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