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NMR Spectroscopic Characterization of Methylcobalt(III) Compounds with Classical Ligands. Crystal Structures of $[Co(NH_3)_5(CH_3)]S_2O_6$, *trans*-$[Co(en)_2(NH_3)(CH_3)]S_2O_6$ (en = 1,2-Ethanediamine), and $[Co(NH_3)_6]$-*mer,trans*-$[Co(NO_2)_3(NH_3)_2(CH_3)]_2$-*trans*-$[Co(NO_2)_4(NH_3)_2]$

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A series of methylcobalt(III) compounds with solely classical ligands such as NH_3, H_2O, NO_2^-, CN^-, and 1,2-ethanediamine (en) has been prepared by ligand substitution of the pentaamminemethylcobalt(III) cation. The new compounds have been characterized by ^1H, ^{13}C, and ^{59}Co nuclear magnetic resonance spectroscopy and by absorption spectroscopy. Single-crystal X-ray structure determinations at 122.0(5) K were performed on $[Co(NH_3)_5(CH_3)]S_2O_6$ (**1**), *trans*-$[Co(en)_2(NH_3)(CH_3)]S_2O_6$ (**2**), and $[Co(NH_3)_6]$-*mer,trans*-$[Co(NO_2)_3(NH_3)_2(CH_3)]_2$-*trans*-$[Co(NO_2)_4(NH_3)_2]$ (**3**). Compound **1** is monoclinic, $P2_1/n$, with cell dimensions $a = 6.4856(9)$ Å, $b = 18.0720(11)$ Å, $c = 9.7854(14)$ Å, and $\beta = 98.280(13)°$. Compound **2** is orthorhombic, $P2_12_12$, with cell dimensions $a = 12.211(3)$ Å, $b = 10.107(3)$ Å, and $c = 11.514(3)$ Å. Compound **3** is monoclinic, $P2_1/n$, with cell dimensions $a = 8.390(2)$ Å, $b = 8.970(3)$ Å, $c = 20.650(9)$ Å, and $\beta = 91.29(2)°$. Virtually identical Co−C distances in the range 1.980−1.984 Å are found in the three compounds. The methyl group exerts a strong *trans* influence. The largest relative elongation of the bond to the *trans* ligand is 0.170 Å in the *trans*-$[Co(en)_2(NH_3)(CH_3)]^{2+}$ cation. The structural *trans* influence appears to decrease with the overall charge of the coordination compound. Estimates of the scalar one-bond cobalt−carbon coupling constants, $^1J_{Co-C}$, in the pentacyanomethylcobalt(III) anion was obtained by line shape analysis, yielding values of 127, 95, and 62 Hz for the *cis* cyano groups, the *trans* cyano group, and the methyl group, respectively.

Introduction

The major part of organocobalt(III) chemistry, including coenzyme B_{12} mimetic chemistry, has been confined to organic solvents.[1] Many organocobalt(III) compounds are oxygen or moisture sensitive, the latter preventing an aqueous chemistry. Depending on the nature of the other ligands, the cobalt(III)−carbon σ-bond has, however, in a number of cases proven to be quite robust toward hydrolysis. The pentaamminemethylcobalt(III) cation is sufficiently robust in aqueous ammonia to allow for spectroscopic characterization,[2a] and a closely related methylcobalt(III) compound with the saturated macrocyclic ligand 1,4,8,11-tetraazacyclotetradecane even allows for precipitation with concentrated perchloric acid.[3a,b] The kinetics and thermodynamics of the protonation of a series of alkylcobalt(III) compounds with saturated amines containing a thioether group have been studied in detail in aqueous solution.[2d−g] Likewise, a dimethylcobalt(III) compound with unsaturated nitrogen donors, namely, the *cis*-$[Co(bipy)_2(CH_3)_2]^+$ cation (bipy = 2,2′-bipyridine), proved robust in neutral aqueous solution, although it like many alkylcobalt(III) compounds was found to be photolabile, yielding methane upon irradiation with UV light.[4]

Many alkylcobalt(III) compounds have been made with ligands such as dioximates, Schiffs bases, and β-diketonates in order to utilize the possible routes for forming cobalt(III)−carbon σ-bonds and, hence, producing compounds that are soluble in organic solvents, but sparingly soluble in water.[1] On the other hand, the alkyl group in a number of different pentacyanoalkylcobaltate(III) anions undergoes a *cis*-migration in aqueous solution to yield nitriles,[5a,b] in a reaction resembling the insertion reactions commonly studied in organic solvents.[1] It appears that an aqueous chemistry of alkylcobalt(III) compounds is not necessarily prohibited by the susceptibility of the cobalt(III)−carbon bond to hydrolysis, but has rather been limited by the choice of ligands.

In this paper we report a series of new water soluble methylcobalt(III) compounds prepared by ligand substitution of the pentaamminemethylcobalt(III) cation. This cation is isosteric with the classical hexaamminecobalt(III) cation. However, exchange of the ammine ligands occurs with much more ease

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in the pentaamminemethylcobalt(III) cation than in the hexaamminecobalt(III) cation, and methylcobalt(III) compounds with solely classical ligands such as NH_3, H_2O, NO_2^-, CN^-, and 1,2-ethanediamine (en) are readily obtained. The new compounds have been characterized by nuclear magnetic resonance (NMR) and absorption spectroscopy. The crystal structures of the starting material, $[Co(NH_3)_5(CH_3)]S_2O_6$, and two of the products, *trans*-$[Co(en)_2(NH_3)(CH_3)]S_2O_6$ and $[Co(NH_3)_6]$-*mer*,*trans*-$[Co(NO_2)_3(NH_3)_2(CH_3)]_2$-*trans*-$[Co(NO_2)_4(NH_3)_2]$, have been determined from low-temperature X-ray diffraction data.

Experimental Section

Caution! Perchlorate salts of coordination compounds with organic ligands are potentially explosive and were handled in quantities of less than 0.1 g.

Materials and Instrumentation. Pentaamminemethylcobalt(III) nitrate was prepared as previously reported.[2a] Hexaamminecobalt(III) chloride[6a] and potassium hexacyanocobaltate(III)[6b] were prepared according to literature methods. D_2O (99.8 at. % D), deuterated aqueous ammonia (26% in D_2O, 99+ at. % D), NaOD (40 wt % in D_2O, 99+ at. % D), acetonitrile-d_3 (99.5 at. % D), and potassium cyanide-^{13}C (99 at. % ^{13}C) were obtained from Sigma. Other chemicals were of the highest purity available.

NMR spectra were measured at 5.87 T on a Bruker AC 250 NMR spectrometer equipped with a 5 mm probe for ^1H and ^{13}C NMR measurements or a 10 mm broad-band tunable probe for ^{59}Co NMR measurements. Deuterated solvents were used to provide a deuterium lock. An additional line broadening of 1 Hz was employed for ^{13}C NMR spectra before Fourier transformation to improve the signal-to-noise ratio. ^1H and ^{13}C chemical shift values (δ) are reported in parts per million relative to the methyl group of internal sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) in aqueous solution or tetramethylsilane (TMS) in nonaqueous solution. ^{59}Co NMR spectra were measured using the RIDE (ring-down elimination) pulse sequence to suppress probe ringing.[7] With this pulse sequence the dead time could be reduced to 15 μs. ^{59}Co chemical shift values (δ) are reported in parts per million relative to an external D_2O solution of $K_3Co(CN)_6$ ($\delta = 0$ ppm), using replacement of the sample. Solutions for NMR were generally made up to be 0.2 M with respect to the coordination compound, except in cases of limited solubilities. UV−visible absorption spectra were recorded with a Cary 3 spectrophotometer.

Elemental analyses were made at the Microanalytical Laboratory at the Department of Chemistry, University of Copenhagen.

Pentaamminemethylcobalt(III) Bromide. A 2.0 g (7.06 mmol) amount of pentaamminemethylcobalt(III) nitrate was dissolved in *ca.* 6 M aqueous ammonia (50 mL) and addded to a saturated solution of sodium bromide (50 mL). The pink crystals were filtered off and washed with concentrated aqueous ammmonia followed by washing with acetone. The compound was air-dried and stored at 4 °C; yield, 1.66 g (63%). Anal. Calcd for $CoCH_{18}N_5Br_2$: C, 3.77; H, 5.69; N, 21.96. Found: C, 3.76; H, 5.60; N, 22.05.

Pentaamminemethylcobalt(III) Chloride. A 1.0 g (3.53 mmol) amount of pentaamminemethylcobalt(III) nitrate was dissolved in *ca.* 6 M aqueous ammonia (25 mL) and added to a saturated solution of sodium chloride (40 mL). After cooling at 0 °C, the orange crystals were filtered off and washed with concentrated aqueous ammonia followed by washing with acetone. The compound was stored at 4 °C over dry silica gel; yield, 0.41 g (50%). Anal. Calcd for $CoCH_{18}N_5Cl_2$: C, 5.22; H, 7.89; N, 30.45. Found: C, 5.75; H, 7.36; N, 30.36.

Tetrabutylammonium *mer,trans*-Diamminemethyltrinitrocobaltate(III). A 0.566 g (2.0 mmol) amount of pentaamminemethylcobalt(III) nitrate was added to a solution of 3.0 g (43.5 mmol) of $NaNO_2$ in 10 mL of water. After being stirred at room temperature for 15 min, the suspension was slowly heated to 70 °C and kept at that temperature for 30 min. Upon cooling to 20 °C, the mixture was filtered and precipitated with a solution of 3 g of tetrabutylammonium chloride in 2 mL of water. The orange-yellow crystals were filtered off and washed with ice cold water. The compound was air-dried at 20 °C; yield, 0.8 g (82%). Anal. Calcd for $CoC_{17}H_{45}N_6O_6$: C, 41.79; H, 9.28; N, 17.20. Found: C, 41.97; H, 8.92; N, 17.11.

Tetraethylammonium Pentacyanomethylcobaltate(III). A 0.57 g (2 mmol) amount of pentaamminemethylcobalt(III) nitrate was added to a solution of 1.88 g (12 mmol) of tetraethylammonium cyanide in 3 mL of water at 0 °C. After the solution was stirred for 0.5 h at room temperature, the water was removed by rotary evaporation. The product was recrystallized three times from acetonitrile by addition of acetone and stored desiccated; yield, 1.08 g (91%). Anal. Calcd for $Co\ C_{30}\ H_{63}\ N_8$: C, 60.58; H, 10.68; N, 18.84. Found: C, 58.18; H, 10.43; N, 18.32.

***trans*-Amminebis(1,2-ethanediamine)methylcobalt(III) Bromide Hydrate.** A 0.50 g (1.57 mmol) amount of pentaamminemethylcobalt(III) bromide was added to a solution of 240 μL of 1,2-ethanediamine (3.59 mmol) in 3 mL of water. The suspension was stirred at 20 °C for 16 h. At the end of this period, concentrated aqueous ammonia (0.5 mL) was added, and the solution was stirred for another 0.5 h. After filtration, the bromide salt was precipitated by addition of 20 mL of acetone. The orange-brown crystals were filtered off, washed well with acetone, and air-dried at 20 °C; yield, 0.56 g (92%). Anal. Calcd for $CoC_5H_{24}N_5OBr_2$: C, 15.44; H, 6.22; N, 18.00. Found: C, 15.65; H, 6.05; N, 17.79.

***trans*-Aquabis(1,2-ethanediamine)methylcobalt(III) Dithionate.** A 1.28 g (3.45 mmol) amount of *trans*-amminebis(1,2-ethanediamine)-methylcobalt(III) dithionate in water (125 mL) was stirred at 60 °C for 2 h. Upon cooling to 4 °C, the solution was filtered, and to the filtrate was added acetone (200 mL) to precipitate *trans*-aquabis(1,2-ethanediamine)methylcobalt(III) dithionate as a pink powder; yield, 1.10 g (86%). Anal. Calcd for $CoC_5H_{21}N_4S_2O_7$: C, 16.13; H, 5.68; N, 15.05. Found: C, 16.24; H, 5.47; N, 14.99.

***trans*-Bis(1,2-ethanediamine)methylnitrocobalt(III) Perchlorate.** A 0.1 g (0.269 mmol) amount of *trans*-aquabis(1,2-ethanediamine)-methylcobalt(III) dithionate was dissolved in a saturated solution of sodium nitrite (1 mL) and stirred at room temperature for 15 min. After filtration, saturated sodium perchlorate (1 mL) was added to the filtrate. The yellow crystals were filtered off and washed with ice cold water, followed by washing with acetone; yield, 0.07 g (77%). Anal. Calcd for $CoC_5H_{19}N_5ClO_6$: C, 17.68; H, 5.64; N, 20.62. Found: C, 17.95; H, 5.41; N, 20.02.

***trans*-Cyanobis(1,2-ethanediamine)methylcobalt(III) Perchlorate.** A 0.1 g (0.269 mmol) amount of *trans*-aquabis(1,2-ethanediamine)-methylcobalt(III) dithionate was dissolved in a solution of 13.2 mg of NaCN (0.269 mmol) in water (1 mL) at 0 °C and stirred for 1 min. Upon filtration, the filtrate was added to a saturated solution of sodium perchlorate (1 mL). The yellow crystals were filtered off and washed with ice cold, water followed by washing with acetone; yield, 0.04 g (47%). Anal. Calcd for $CoC_6H_{19}N_5ClO_4$: C, 22.55; H, 5.99; N, 21.91. Found: C, 22.83; H, 5.27; N, 21.61.

X-ray Crystallography. Crystals of $[Co(NH_3)_5(CH_3)]S_2O_6$ (**1**) were grown by diffusion of a saturated solution of $[Co(NH_3)_5(CH_3)](NO_3)_2$ in a 6 M aqueous solution of ammonia into a saturated solution of $Na_2S_2O_6$.

Crystals of *trans*-$[Co(en)_2(NH_3)(CH_3)]S_2O_6$ (**2**) were grown by diffusion of a solution of *trans*-$[Co(en)_2(NH_3)(CH_3)]Br_2$ in a 14 M aqueous solution of ammonia into a saturated solution of $Na_2S_2O_6$.

Crystals of $[Co(NH_3)_6]$-*mer*,*trans*-$[Co(NO_2)_3(NH_3)_2(CH_3)]_2$-*trans*-$[Co(NO_2)_4(NH_3)_2]$ (**3**) were grown by diffusion of a saturated solution of $[Co(NH_3)_6]Cl_3$ into the reaction mixture obtained by heating $[Co(NH_3)_5(CH_3)](NO_3)_2$ in a $NaNO_2$ solution (see experimental procedure described above).

The crystal structure determinations were conducted in the same manner for the three Co(III) compounds. Low-temperature X-ray diffraction data were collected with CAD4 diffractometers using graphite monochromated Mo Kα radiation. The temperature was monitored with a thermocouple, adjusted by the tetragonal to orthorhombic phase transition of KH_2PO_4 at 122 K. The intensities of five standard reflections were recorded every 10 000 s. All three data sets showed a small systematic decrease in their intensity up to 8 (**1**), 3 (**2**), and 6% (**3**). The data sets were corrected for these variations using a polynominal fit up to third order. Table 1 lists the crystal data and

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Table 1. Crystal Data and Structure Refinement for $[Co(NH_3)_5(CH_3)]S_2O_6$ (**1**), *trans*-$[Co(en)_2(NH_3)(CH_3)]S_2O_6$ (**2**), and $[Co(NH_3)_6]$-*mer,trans*-$[Co(NO_2)_3(NH_3)_2(CH_3)]_2$-*trans*-$[Co(NO_2)_4(NH_3)_2]$ (**3**)

	1	2	3
empirical formula	$CH_{18}CoN_5O_6S_2$	$C_5H_{22}CoN_5O_6S_2$	$CH_{21}Co_2N_{11}O_{10}$
fw (g mol^{-1})	319.25	371.33	465.15
cryst syst	monoclinic	orthorhombic	monoclinic
space group	$P2_1/n$	$P2_12_12$	$P2_1/n$
a (Å)	6.4856(9)	12.211(3)	8.390(2)
b (Å)	18.0720(11)	10.107(3)	8.970(3)
c (Å)	9.7854(14)	11.514(3)	20.650(9)
β (deg)	98.280(13)	90	91.29(2)
vol (Å^3)	1135.0(2)	1421.0(7)	1553.7(9)
Z	4	4	4
temp (K)	122.0(5)	122.0(5)	122.0(5)
wavelength (Å)	0.710 73	0.710 73	0.710 73
density (calc) (Mg/m^3)	1.868	1.736	1.989
abs coeff (mm^{-1})	1.900	1.531	2.210
R indices[a]	$R_1 = 0.0391$ $R_{w2} = 0.0890$	$R_1 = 0.0175$ $R_{w2} = 0.0502$	$R_1 = 0.0438$ $R_{w2} = 0.1382$
range of transm factors	0.751−0.839	0.631−0.841	0.668−0.734

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $R_{w2} = [\sum w(F_o{}^2 - F_c{}^2)^2/\sum w(F_o{}^2)^2]^{1/2}$.

final refinement results. Data reduction performed with the DREADD programs[8a] included corrections for Lorentz, polarization, and absorption effects. The latter correction was performed using the Gaussian integration procedure. The space groups were deduced from the symmetry of the diffraction pattern and the systematically absent reflections. Averaging was performed for reflections related by the symmetry of the crystal class.

The structure determinations were accomplished by a combination of Patterson and direct methods (SHELXS-86).[8b] The structures were refined by least squares minimizing $\sum w(|F_o|^2 - |F_c|^2)^2$ (SHELXL-93).[8c] The positions of the hydrogen atoms appeared clearly in the difference electron densities calculated after anisotropic atomic displacement parameters had been introduced for the non-hydrogen atoms.

The positional parameters of the hydrogen atoms were included in the refinement of all three structures. Their isotropic thermal parameters were refined in **1**, in **2** one common thermal parameter was refined for hydrogens bonded to N and another common parameter for hydrogens bonded to C, and in **3** the thermal parameters of the hydrogen atoms were made equal to U_{eq} of the parent C and N atoms multiplied by 1.2 and 1.5, respectively. The final difference electron densities were featureless, and the residual density could be associated with bonding and lone pair electrons.

It should be mentioned that it was not possible to refine the structure of **2** from an initial data set measured under equivalent conditions. Though this data set corresponds to identical cell dimensions, the data did not show any systematic absences. Introducing the model obtained from the second data set resulted in high *R*-values and unrealistic bond lengths and thermal parameters. This first batch of crystals was precipitated more rapidly, and therefore we assume that it could contain a disordered *meta*-stable form of **2** that gradually transforms to the stable modification.

Additional details for the three structure determinations are given in the following:

$[Co(NH_3)_5CH_3]S_2O_6$ (1). The cell dimensions were determined from 25 reflections with θ in the range 20−22°. Data were collected for 13 575 reflections, including standards in the octants $h,k,\pm l$ ($1° < \theta < 40°$) and $h,-k,\pm l$ ($1° < \theta < 35°$). Of the 6948 independent reflections, 6914 had intensities above $-3\sigma(|F|^2)$ and were used in the refinement of the 208 parameters. The conventional R_1-value was calculated from 5331 reflections with $|F_o| > 4\sigma(|F_o|)$.

***trans*-$[Co(en)_2(NH_3)(CH_3)]S_2O_6$ (2).** The cell dimensions were determined from the setting angles of 20 reflections within the θ-range of 22−23°. A complete data set including all octants was collected up to $\theta = 20°$, and a partial data set was collected between 20 and 25°. A set of 2501 independent reflections was measured, and 2251 reflections having $F_o{}^2 > -3\sigma(F_o{}^2)$ were used in the refinement of 238 parameters. The conventional R_1-value was calculated from 2205 reflections with $|F_o| > 4\sigma(|F_o|)$.

$[Co(NH_3)_6]$-*mer,trans*-$[Co(NO_2)_3(NH_3)_2(CH_3)]_2$-*trans*-$[Co(NO_2)_4(NH_3)_2]$ (3). The cell dimensions were determined from 20 reflections having θ between 18 and 21°. A complete data set was collected up to $\theta = 42°$ for $h,k,\pm l$, and a partial data set of symmetry related reflections was measured for $h,-k,\pm l$. Of the 4531 independent reflections 4419 reflections had $F_o{}^2 > -3\sigma(F_o{}^2)$. These were used in the refinement of 227 parameters. The conventional R_1-value was calculated from the 4212 reflections with $|F_o| > 4\sigma(|F_o|)$.

Results and Discussion

Syntheses. While the hexaamminecobalt(III) cation is exceptionally robust toward ligand exchange, the ammonia ligands of the isoelectronic pentaamminemethylcobalt(III) cation are readily exchanged with other simple inorganic ligands. This originates presumably from the well-established *trans* effect of an alkyl group.[9] It is evident from the X-ray crystal structures of the title compounds (*vide infra*) that the significant *trans* influence also is reflected in the bond lengths. Therefore the *trans* isomers of the bis(1,2-ethanediamine)methylcobalt(III) compounds are likely to be thermodynamically more stable than the corresponding *cis* isomers. It is plausible that substitution of ammonia with 1,2-ethanediamine occurs via the *trans* coordination site, although the detailed reaction mechanism(s) have yet to be determined.

According to ^1H and ^{13}C NMR measurements on the reaction mixture, the preparation of *mer,trans*-$[Co(NO_2)_3(NH_3)_2(CH_3)]^-$ gave only this methylcobalt(III) compound. Addition of a saturated solution of tetrabutylammonium chloride gave analytically pure (Bu_4N)-*mer,trans*$[Co(NO_2)_3(NH_3)_2(CH_3)]$. In our attempts to prepare crystals of the hexaamminecobalt(III) salt, another compound with the composition $[Co(NH_3)_6]$-*mer,trans*-$[Co(NO_2)_3(NH_3)_2(CH_3)]_2$-*trans*-$[Co(NO_2)_4(NH_3)_2]$ (*vide infra*) was obtained directly from the reaction mixture. It appears that the metal−carbon bond is disrupted to some extent during the preparation, yielding the *trans*-diamminetetranitrocobaltate(III) anion. Preliminary investigations indicate that *mer,trans*-$[Co(NO_2)_3(NH_3)_2(CH_3)]^-$ is robust under the conditions of its formation (see Experimental Section), implying that *trans*-$[Co(NO_2)_4(NH_3)_2]^-$ is not formed by decomposition of the former anion. Although an explanation for the disrupture of the cobalt−carbon bond has yet to be established, it is plausible that the nitrite ion to a minor extent acts as a reducing agent toward cobalt(III), thereby labilizing the Co−C bond.

The reaction between the pentaamminemethylcobalt(III) cation and cyanide is very fast and essentially quantitative, yielding the pentacyanomethylcobaltate(III) anion. This coordination compound was first prepared by reaction between methyl halides and pentacyanocobaltate(II).[5c] A large number of different pentacyanoorganocobalt(III) compounds has been prepared,[5d] and the X-ray crystal structure of $K_3[Co(CN)_5(CF_2CF_2H)]$ has been determined.[5e]

Description of the Crystal Structures. The structure determinations have enabled us to characterize three classical cobalt(III) coordination compounds that contain a methyl group. The bond lengths and angles are listed in Tables 2 and 3. The two closely related cations $[Co(NH_3)_5CH_3]^{2+}$ and *trans*-[Co-

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Table 2. Bond Distances (Å) and Bond Angles (deg) for the Cations in $[Co(NH_3)_5(CH_3)]S_2O_6$ and *trans*-$[Co(en)_2(NH_3)(CH_3)]S_2O_6$

	$[Co(NH_3)_5(CH_3)]^{2+}$	*trans*-$[Co(en)_2(NH_3)(CH_3)]^{2+}$
	Bond Distances	
Co−N2	1.9707(13)	1.957(2)
Co−N4	1.9708(13)	1.968(2)
Co−N3	1.9744(13)	1.968(2)
Co−N5	1.9779(13)	1.969(2)
Co−C1	1.980(2)	1.984(2)
Co−N6	2.1048(14)	2.127(2)
C4−N4		1.490(3)
C4−C5		1.513(3)
C5−N5		1.493(3)
C3−N3		1.490(3)
C3−C2		1.509(3)
N2−C2		1.490(3)
	Bond Angles	
N2−Co−N4	178.99(6)	179.18(8)
N2−Co−N3	92.19(6)	85.65(8)
N4−Co−N3	88.78(6)	94.26(8)
N2−Co−N5	89.34(6)	94.11(8)
N4−Co−N5	89.69(6)	85.98(8)
N3−Co−N5	178.35(6)	179.73(8)
N2−Co−C1	90.44(6)	88.34(9)
N4−Co−C1	89.79(7)	90.84(9)
N3−Co−C1	90.63(6)	90.90(9)
N5−Co−C1	88.76(7)	88.97(9)
N2−Co−N6	88.46(6)	91.47(8)
N4−Co−N6	91.32(6)	89.35(8)
N3−Co−N6	88.30(6)	89.10(8)
N5−Co−N6	92.33(6)	91.03(8)
C1−Co−N6	178.44(6)	179.81(9)
N4−C4−C5		107.2(2)
N5−C5−C4		107.8(2)
N3−C3−C2		106.7(2)
C5−N5−Co		109.21(14)
C2−N2−Co		109.51(14)
N2−C2−C3		106.6(2)
C3−N3−Co		108.89(13)
C4−N4−Co		109.47(14)

$(en)_2(NH_3)CH_3]^{2+}$ are shown in Figures 1 and 2, respectively. The anions in $[Co(NH_3)_6]$-*mer*,*trans*-$[Co(NO_2)_3(NH_3)_2(CH_3)]_2$-*trans*-$[Co(NO_2)_4(NH_3)_2]$ (**3**) are shown in Figure 3. $[Co(NH_3)_6]^{3+}$ and *trans*-$[Co(NO_2)_4(NH_3)_2]^-$ are found on crystallographic inversion centers. All of the cobalt(III) coordination compounds are ordered, and the positions of the protons could be established without any ambiguity. The crystal structures demonstrate that the CH_3 group behaves as a ligand which is equivalent to the isoelectronic NH_3.

In the three methylcobalt(III) compounds the Co−CH_3 distances are virtually identical, ranging from 1.980 to 1.984 Å. It is noteworthy that in amminecobalt(III) compounds the equivalent Co−NH_3 distances display much larger variations.[10] When the alkyl group is part of a tridentate saturated organic ligand, the Co−C distances are significantly longer.[2b,c,e] In six-coordinate bis(dimethylglyoximato)methylcobalt(III) compounds Co−C distances have been observed in the range 1.978−2.04 Å. This larger variation in bond lengths has been attributed to steric effects caused by the *trans* ligands.[11]

Another characteristic of these methylcobalt(III) compounds is the pronounced *trans* influence exerted by the Co−CH_3 group. The Co−NH_3 distance of the *trans* ammine group is significantly elongated up to 0.134 Å relative to the *cis* ammine groups in **1** and to 0.170 Å in **2** (Table 2). A distinct, albeit less pronounced, *trans* influence is also observed in *mer*,*trans*-$[Co(NO_2)_3(NH_3)_2(CH_3)]^-$, where the methyl group is *trans* to another negatively charged ligand (Table 3). A similar *trans* influence of the methyl group was observed in *cis*-$[Co(bipy)_2(CH_3)_2]^+$, where the Co−N bond *trans* to a methyl group on average is 0.093 Å longer than that *cis* to a methyl group.[4] It appears that the elongation of the cobalt(III)−ligand distance *trans* to the methyl group decreases with the overall charge of the complex.

It should be emphasized that the *trans* influence exerted by the CH_3 group is not only related to its formal negative charge as there is no sizable *trans* influence on the cobalt(III)−ammine bond lengths in pentaamminecobalt(III) compounds with other negatively charged ligands such as Cl^-, CN^-, and NO_2^-.[10b,c,e] The latter ligands are characterized by being more hydrophilic and therefore able to take part in hydrogen bond interactions. Therefore we suggest that the strong *trans* influence and the constancy in the Co−CH_3 bond lengths can be associated with the hydrophobic nature of the CH_3 group.

The geometry of the $[Co(NH_3)_6]^{3+}$ ion is in agreement with previous results for this cation.[12] The geometry of *trans*-$[Co(NO_2)_4(NH_3)_2]^-$ is at variance with those reported for the same anion in a NH_4^+ salt. In **3** the three independent Co−N distances are very similar, 1.945−1.965 Å, whereas they are reported to be significantly longer in the earlier study.[10a]

All complexes show an almost perfect octahedral coordination of cobalt(III). The octahedron is a bit more distorted in *trans*-$[Co(en)_2(NH_3)(CH_3)]^{2+}$ than in $[Co(NH_3)_5(CH_3)]^{2+}$. However, this is to be expected as the geometry of this compound is constrained by the bidentate 1,2-ethanediamine ligands.

The packing of **1** and **2** is dominated by short interatomic contacts between the dithionate oxygen atoms and the ammine group hydrogens of the cation. For **3** there is a mixture of short intra- and interatomic contacts.[8d] The ammine group hydrogens of $[Co(NH_3)_6]^{3+}$ hydrogen bond to the oxygens of the nitro groups of both the anions. There is, however, also many intracomplex contacts in *mer*,*trans*-$[Co(NO_2)_3(NH_3)_2(CH_3)]^-$ and in *trans*-$[Co(NO_2)_4(NH_3)_2]^-$ that correspond to hydrogen bonds between the hydrogen atoms of the ammine groups and the oxygen atoms of the nitro groups.

Absorption Spectra. The visible absorption spectra of the new series of methylcobalt(III) compounds are typical for cobalt(III) coordination compounds (Table 4).[13] An example is given in Figure 4. The position of the first absorption band is shifted to a slightly lower wavelength in *trans*-$[Co(en)_2(NH_3)(CH_3)]^{2+}$ ($\lambda_{max} = 464$ nm) as compared to $[Co(NH_3)_5(CH_3)]^{2+}$ ($\lambda_{max} = 481$ nm). However, ^1H NMR data (*vide infra*) in both cases unambigously demonstrate the coordination of a *trans* ammine ligand. The first absorption band of the *trans*-bis(1,2-ethanediamine)methylcobalt(III) compounds is very broad. The change of position upon change of the *trans* ligand is consistent with the spectrochemical series: $H_2O < NH_3 < CN^- \approx NO_2^-$. The absorption spectroscopic data for *trans*-$[Co(en)_2(OH_2)(CH_3)]^{2+}$ (Table 4) is not very different from those for *trans*-$[Co(Me_6[14]aneN_4)(OH_2)(CH_3)]^{2+}$ (λ_{max}, nm (ϵ_{max}, M^{-1} cm^{-1}): 384 (133), 498 (74)) ($Me_6[14]aneN_4$ = *C*-*meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane).[3a,c]

NMR Spectroscopic Characterization. The new compounds were characterized by ^1H and ^{13}C NMR spectroscopy

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Table 3. Bond Distances (Å) and Bond Angles (deg) of the Entities in $[Co(NH_3)_6]$-*mer,trans*-$[Co(NO_2)_3(NH_3)_2(CH_3)]_2$-*trans*-$[Co(NO_2)_4(NH_3)_2]^a$

mer,trans-$[Co(NO_2)_3(NH_3)_2(CH_3)]^-$		$[Co(NH_3)_6]^{3+}$		*trans*-$[Co(NO_2)_4(NH_3)_2]^-$	
		Bond Distances			
Co1−N15	1.919(2)	Co2−N21	1.957(2)	Co3−N31	1.945(2)
Co1−N12	1.937(2)	Co2−N22	1.966(2)	Co3−N32	1.956(2)
Co1−N14	1.951(2)	Co2−N23	1.971(2)	Co3−N33	1.965(2)
Co1−N13	1.951(2)			N32−O322	1.232(3)
Co1−C11	1.981(3)			N32−O321	1.235(3)
Co1−N16	2.027(2)			N33−O332	1.228(4)
N16−O161	1.243(3)			N33−O331	1.243(4)
N16−O162	1.245(3)				
N12−O121	1.244(3)				
N12−O122	1.247(3)				
N15−O152	1.231(3)				
N15−O151	1.245(3)				
		Bond Angles			
N15−Co1−N12	177.57(9)	N21−Co2−N22′	91.12(9)	N31−Co3−N32″	89.57(10)
N15−Co1−N14	90.83(9)	N21−Co2−N22	88.89(9)	N31−Co3−N32	90.43(10)
N12−Co1−N14	90.13(9)	N21−Co2−N23′	88.50(10)	N31−Co3−N33	89.58(10)
N15−Co1−N13	89.00(9)	N22−Co2−N23′	91.08(9)	N32−Co3−N33	92.75(11)
N12−Co1−N13	90.10(9)	N21−Co2−N23	91.50(10)	N31−Co3−N33″	90.42(10)
N14−Co1−N13	178.61(9)	N22−Co2−N23	88.92(9)	N32−Co3−N33″	87.25(11)
N15−Co1−C11	88.89(11)			O322−N32−O321	119.0(3)
N12−Co1−C11	88.87(11)			O322−N32−Co3	120.0(2)
N14−Co1−C11	90.24(9)			O321−N32−Co3	120.7(2)
N13−Co1−C11	91.13(9)			O332−N33−O331	117.7(3)
N15−Co1−N16	89.77(9)			O332−N33−Co3	120.7(2)
N12−Co1−N16	92.47(10)			O331−N33−Co3	120.5(2)
N14−Co1−N16	89.77(9)				
N13−Co1−N16	88.85(9)				
C11−Co1−N16	178.66(10)				
O161−N16−O162	117.3(2)				
O161−N16−Co1	121.4(2)				
O162−N16−Co1	121.4(2)				
O121−N12−O122	116.3(2)				
O121−N12−Co1	121.4(2)				
O122−N12−Co1	122.0(2)				
O152−N15−O151	118.1(2)				
O152−N15−Co1	121.4(2)				
O151−N15−Co1	120.4(2)				

[a] Symmetry transformations used to generate equivalent atoms: (1) $-x, -y, -z$; (2) $-x + 1, -y + 1, -z$.

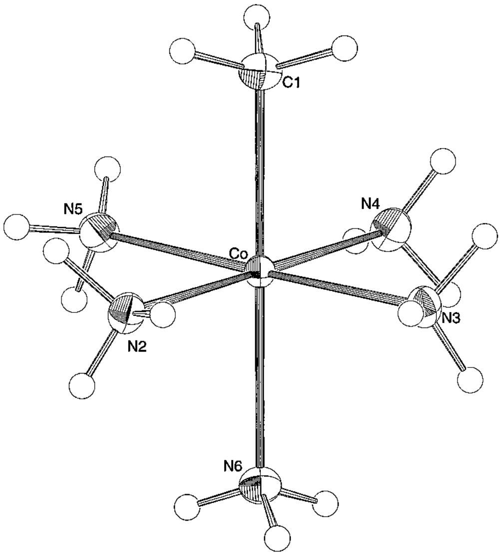

Figure 1. Crystal structure of the cation in $[Co(NH_3)_5(CH_3)]S_2O_6$.

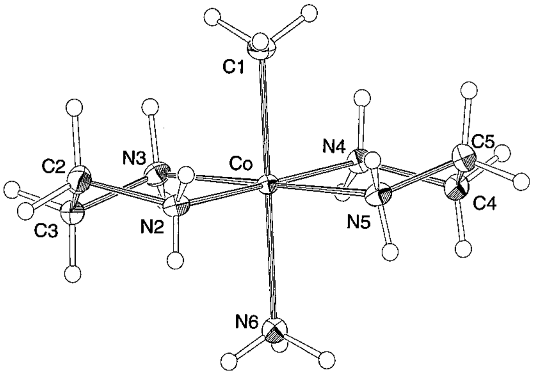

Figure 2. Crystal structure of the cation in $[Co(en)_2(NH_3)(CH_3)]S_2O_6$.

(Table 5). ^{59}Co NMR was applied whenever detection of a resonance signal was possible. The ^{1}H NMR resonance signals of ammine and amine protons were observed in aqueous solution (H_2O) but were absent in D_2O, which together with integration established a basis for their assignment. There is furthermore an isotope shift toward lower frequency of both ^{1}H and ^{13}C resonance signals upon exchange of amine protons with deuterons. It is common that substitution with a heavier nucleus gives an increased shielding.[14]

The resonance signals of the ligand nuclei in cobalt(III) coordination compounds are in many cases broad due to scalar coupling between the ^{59}Co nucleus (spin $I = {}^{7}/_{2}$, 100% natural abundance) and the ligand nuclei. The broadening is most pronounced for the nucleus of a coordinating atom, *i.e.*, the methyl or cyano ^{13}C nuclei ($I = {}^{1}/_{2}$) in the present cases. For the ^{59}Co spin−lattice relaxation rate being much larger than the scalar coupling constant, *i.e.*, $1/T_{1A} \gg J_{AX}$, the coupling contributes to the spin−spin relaxation rate of the ^{13}C nucleus

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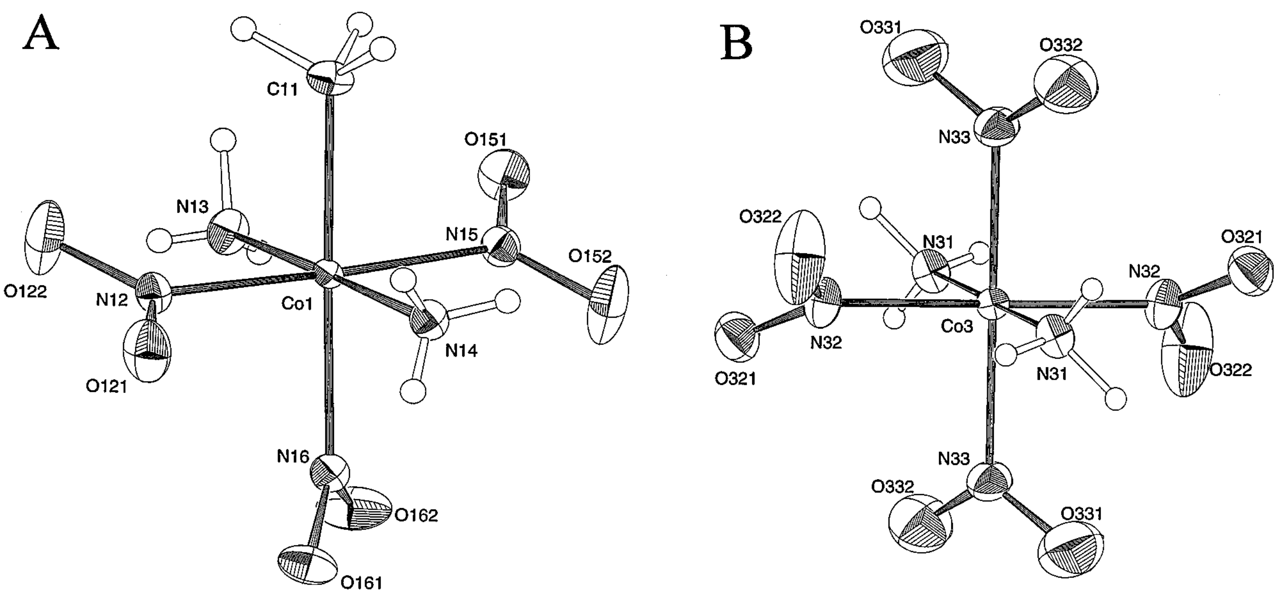

Figure 3. Crystal structures of (A) *mer,trans*-$[Co(NO_2)_3(NH_3)_2(CH_3)]^-$ and (B) *trans*-$[Co(NO_2)_4(NH_3)_2]^-$ in **3**.

Table 4. Absorption Spectroscopic Data for Methylcobalt(III) Compounds at 20 °C[a]

compound	λ_{max} (nm) (ϵ_{max} (M^{-1} cm^{-1}))		
$[Co(NH_3)_5(CH_3)]Cl_2$[b]	306 (111)	358 (123)	481 (50)
(Bu_4N)-*mer,trans*-$[Co(NO_2)_3(NH_3)_2(CH_3)]$[c]		322 (2055) (sh)	420 (159) (sh)
trans-$[Co(en)_2(CN)(CH_3)]ClO_4$[d]		332 (218)	445 (53)
trans-$[Co(en)_2(NH_3)(CH_3)]Br_2$[b]	289 (156) (sh)	355 (133)	464 (56)
trans-$[Co(en)_2(NO_2)(CH_3)]ClO_4$[e]			442 (64)
trans-$[Co(en)_2(NO_2)(CH_3)]ClO_4$[c]		337 (478)	444 (70)
trans-$[Co(en)_2(OH_2)(CH_3)]S_2O_6$[d]		365 (137)	472 (74)

[a] sh = shoulder. [b] In 5.0 M aqueous ammonia. [c] In acetonitrile. [d] In water. [e] In 1.0 M $NaNO_2$.

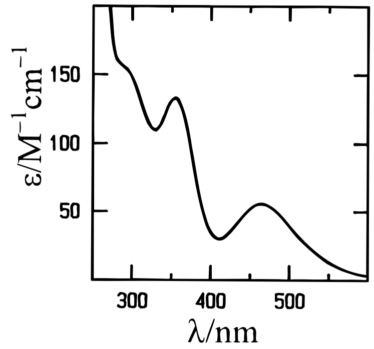

Figure 4. Absorption spectrum of *trans*-$[Co(en)_2(NH_3)(CH_3)]Br_2$ in 5 M aqueous ammonia.

according to eq 1 with X = ^{13}C, A = ^{59}Co, and $I = {}^7/_2$.[15]

$$\frac{1}{T_{2X}} = \frac{4\pi^2 {J_{AX}}^2}{3} I(I+1)\left\{\frac{T_{2A}}{1+(\omega_X-\omega_A)^2 {T_{2A}}^2} + T_{1A}\right\} \tag{1}$$

The other symbols have their usual meaning.

If both T_{1A} and T_{2X} are well-determined under identical conditions, it is possible to obtain an estimate for J_{AX} despite the absence of a splitting of the ^{13}C resonance signal. Since $T_1 = T_2$ for quadrupole relaxation in the limit of rapid molecular reorientation,[15] the ^{59}Co spin−lattice relaxation time can reasonably well be determined from the ^{59}Co resonance line width (Table 5).

Of particular interest is also the coordination shift of the CH_3 group. The ^{13}C resonance frequency of this group is seen to be strongly dependent on the nature of the other ligands, with the chemical shift ranging from 12.6 ppm in the *trans*-cyanobis(1,2-ethanediamine)methylcobalt(III) cation to −3.0 ppm in the pentacyanomethylcobaltate(III) anion in aqueous solution (Table 5).

^{1}H NMR. The ^1H NMR spectrum of $[Co(NH_3)_5(CH_3)](NO_3)_2$ in 1 M aqueous ammonia (H_2O) is shown in Figure 5A. The broad signals at 4.03 and 1.51 ppm, integrating in the ratio 1:4, have been assigned to the *trans* ammine group and the four *cis* ammine groups, respectively. The signal at 2.83 ppm is assigned to the methyl group. The ^1H NMR spectrum of $[Co(NH_3)_5(CH_3)](PF_6)_2$ in acetonitrile-d_3 is shown in Figure 5B. The signals at 3.73 and 1.04 ppm have been assigned to the *trans* ammine group and the four *cis* ammine groups, respectively. These signals are absent in a solution of $[Co(ND_3)_5(CH_3)](PF_6)_2$ in acetonitrile (not shown). The signal at 2.91 ppm is assigned to the methyl group.

The ^1H NMR spectra of the pentaamminemethylcobalt(III) cation show that the *cis* and *trans* ammine groups are distinctively different, and this also manifests itself in the crystal structure (Figure 1, Table 2). The *trans* ammine group in six-coordinate pentaamminecobalt(III) compounds may have ^1H resonances at either higher or lower frequency than the *cis* ammine groups, depending on the nature of the sixth ligand.[16] For example, in the pentaamminecyanocobalt(III) cation the *trans* ammine group has $\delta = 3.96$ and the *cis* ammine groups have $\delta = 3.05$.[16d] The methyl carbanion is thus grouping with the cyanide ion in this respect, although the former is causing

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Table 5. ^{1}H, ^{13}C, and ^{59}Co NMR Data for Methylcobalt(III) Compounds at 300 K[a]

compound	$\delta(C\mathrm{H_3})$ (ppm)	$\delta(C\mathrm{H_2})$ (ppm)	$\delta(\mathrm{C}H_3)$ (ppm)	$\Delta\nu_{1/2}(\mathrm{C}H_3)$ (Hz)	$\delta(\mathrm{C}H_2)$ (ppm)	$\delta(\mathrm{C}N)$ (ppm)	$\Delta\nu_{1/2}(\mathrm{C}N)$ (Hz)	δ(Co) (ppm)	$\Delta\nu_{1/2}$(Co) (kHz)
$[\mathrm{Co(NH_3)_5(CH_3)}]^{2+}$ [b]	2.76		3.2[c]	18.4[c]				7370[c]	13.2[c]
mer,trans-$[\mathrm{Co(NO_2)_3(NH_3)_2(CH_3)}]^-$ [d]	1.84		3.6	22.1				5520	5.6
$[\mathrm{Co(CN)_5(CH_3)}]^{3-}$ [e]	0.61		−3.0	18.5		161.3 (*trans*) 159.4 (*cis*)		−203	3.4
$[\mathrm{Co(CN)_5(CH_3)}]^{3-}$ [d]	0.16		−5.7	10.5		154.1 (*trans*) 151.7 (*cis*)	24.5 (*trans*) 43.4 (*cis*)	−39	7.8
trans-$[\mathrm{Co(en)_2(^{13}CN)(CH_3)}]^+$ [e]	2.05 [f]	2.49 (m) 2.35 (m)	12.6[g]	4.0	46.1	168.1	6.9	nd	nd
trans-$[\mathrm{Co(en)_2(CN)(CH_3)}]^+$ [d]	1.98	2.45 (m) 2.24 (m)	10.9	1.4	44.6	162.2	2.4	nd	nd
trans-$[\mathrm{Co(en)_2(NH_3)(CH_3)}]^{2+}$ [b]	2.06	2.40 (s,b)	5.2	13.9	45.1			6400	15
trans-$[\mathrm{Co(en)_2(NO_2)(CH_3)}]^+$ [h]	1.96	2.30 (m)	4.3	19.0	45.3			5820	15
trans-$[\mathrm{Co(en)_2(OH_2)(CH_3)}]^{2+}$ [e]	2.02	2.52 (m) 2.41 (m)	0	very broad	45.5			6630	2.2
trans-$[\mathrm{Co(en)_2(OH)(CH_3)}]^+$ [i]	1.58	2.46 (m) 2.34 (m)	−1.5	12.5	45.0			nd	nd

[a] s = singlet, m = multiplet, b = broad, nd = not determined. [b] In *ca.* 6 M $\mathrm{ND_3}$ ($\mathrm{D_2O}$). [c] From ref 2a. [d] In acetonitrile-d_3. [e] In $\mathrm{D_2O}$. [f] $^3J_{\mathrm{CH}}(trans)$ = 1.2 Hz. [g] $^2J_{\mathrm{CC}}(trans)$ = 25.1 Hz. [h] In 1 M $\mathrm{NaNO_2}$ ($\mathrm{D_2O}$). [i] In 5 M KOD.

a somewhat larger chemical shift difference. The ^{1}H chemical shift differences between the *trans* and *cis* ammine groups in six-coordinate pentaamminecobalt(III) compounds have been interpreted in terms of the magnetic anisotropy of the cobalt(III) ion.[16a,b]

The ^{1}H NMR spectrum of *trans*-$[\mathrm{Co(en)_2(NH_3)(CH_3)}]\mathrm{Br_2}$ in 1 M $\mathrm{NH_3}$ ($\mathrm{H_2O}$) is shown in Figure 5C, which also indicates the assignments. Figure 5D shows the ^{1}H NMR spectrum of $(\mathrm{Bu_4N})$-*mer*,*trans*-$[\mathrm{Co(NO_2)_3(NH_3)_2(CH_3)}]$ in acetonitrile-d_3. The broad signal at 2.48 ppm, integrating for six ^{1}H nuclei, is assigned to the two ammonia ligands. The fact that only one resonance frequency is observed from the ammonia ligands suggests that this coordination compound is either the *mer*,*trans* isomer or the *fac*,*cis* isomer. The *mer*,*cis* isomer would be expected to have different ^{1}H resonance frequencies for the two ammonia ligands. Crystal structure analysis (Figure 3A, Table 3) reveal that this coordination compound is the *mer*,*trans* isomer.

The ^{1}H resonance frequency of the methyl group is seen to depend significantly on the nature of the other ligands (Table 5). It is noted that the methyl ^{1}H nuclei in the pentacyanomethylcobaltate(III) anion is considerably more shielded (δ = 0.61 ppm) than in the corresponding compound with ammonia (δ = 2.76 ppm). This does not seem only to be due to a *trans* influence of the cyano group, since a similar large effect is not seen on the methyl ^{1}H resonance frequency of the bis(1,2-ethanediamine)methylcobalt(III) compounds upon exchange of the *trans* ammine group with cyanide (Table 5). It is possible that the magnetic anisotropy of the triple bonds of the *cis* cyano groups causes an increased shielding of the methyl ^{1}H nuclei in the pentacyanomethylcobaltate(III) anion, but this effect is likely to be small due to the actual angle and distance between the CN triple bond and the methyl protons. In analogy with the shielding of the ^{1}H nuclei of coordinated ammine groups,[16a,b] the ^{1}H resonance frequency of the coordinated methyl group may be influenced by differences in magnetic anisotropy of the cobalt(III) ion, and this could possibly account for the chemical shift differences observed through the series of methylcobalt(III) compounds.

The ^{1}H nuclei in the methyl group in $[\mathrm{Co(^{13}CN)_5(CH_3)}]^{3-}$ (δ = 0.61 ppm) are more shielded than that in $[\mathrm{Co(^{12}CN)_5(CH_3)}]^{3-}$ (δ = 0.65 ppm). This is an isotope effect of ^{13}CN versus ^{12}CN. Furthermore, while the latter ^{1}H resonance signal is a singlet, the former resonance signal is a doublet of a pentet due to scalar coupling to the ^{13}C nuclei of the cyano groups (Figure 6A). The resonance line pattern shows

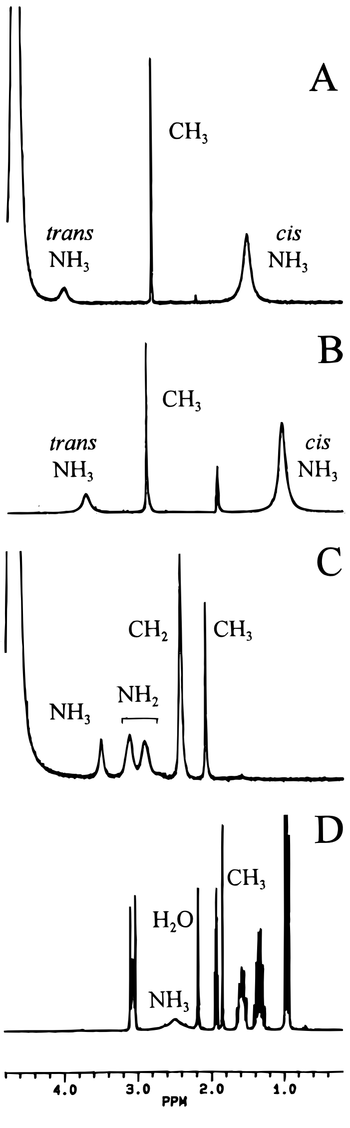

Figure 5. ^{1}H NMR spectra at 300 K of saturated solutions of (A) $[\mathrm{Co(NH_3)_5(CH_3)}](\mathrm{NO_3})_2$ in 1 M aqueous ammonia ($\mathrm{H_2O}$). (B) $[\mathrm{Co(NH_3)_5(CH_3)}](\mathrm{PF_6})_2$ in acetonitrile-d_3. The pentet at 1.93 ppm is due to $\mathrm{NCCD_2H}$. (C) *trans*-$[\mathrm{Co(en)_2(NH_3)(CH_3)}]\mathrm{Br_2}$ in 1 M aqueous ammonia ($\mathrm{H_2O}$). (D) $(\mathrm{Bu_4N})$-*mer*,*trans*-$[\mathrm{Co(NO_2)_3(NH_3)_2(CH_3)}]$ in acetonitrile-d_3. The signal at 2.2 ppm is assigned to water (has varying position and intensity in different solutions). The remaining four resonance signals are from the butyl groups.

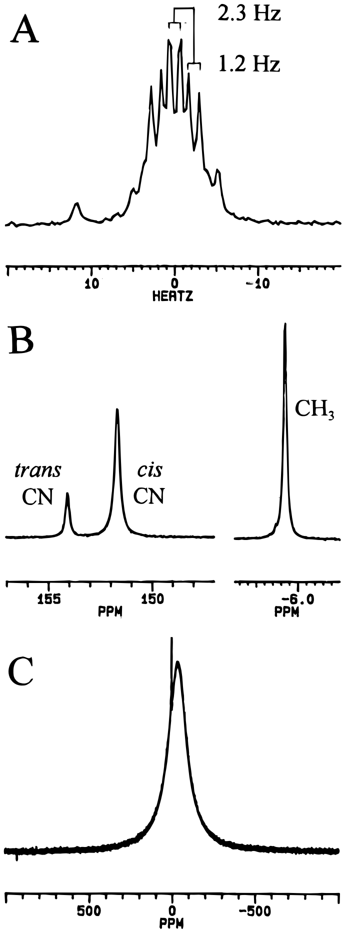

Figure 6. (A) ^1H NMR spectrum of $[Co(^{13}CN)_5(CH_3)]^{3-}$ in D_2O. The signal at 12 Hz (0.65 ppm from DSS) is from the corresponding anion with cyanide-^{12}C. (B) ^1H decoupled ^{13}C NMR spectrum of $(Et_4N)_3[Co(CN)_5(CH_3)]$ in acetonitrile-d_3. (C) ^{59}Co NMR spectrum of 0.2 M $(Et_4N)_3[Co(CN)_5(CH_3)]$ in acetonitrile. The sharp signal at 0 ppm is assigned to the hexacyanocobaltate(III) anion. All spectra were measured at 300 K.

one coupling constant to the four *cis* cyano groups of $^3J_{CH}(cis) = 2.3$ Hz and one smaller coupling, assigned to the *trans* cyano group, of $^3J_{CH}(trans) = 1.2$ Hz. A computer simulation of the resonance line pattern confirmed this interpretation, which indicates that there is a *trans* influence of the methyl group on the bonding between cobalt(III) and the cyano group. The crystal structure of $[Co(CN)_5(CF_2CF_2H)]^{3-}$ showed, however, that the cobalt−carbon bond length of the *trans* cyano group (1.927 Å) was only a little longer than that of the *cis* cyano groups (1.894 Å).[5e]

The ^1H resonance signal of the methylene protons in the coordinated 1,2-ethanediamine shows one or two broad multiplets (Table 5), as is typical for cobalt(III) coordination compounds with this ligand. An example is given in Figure 7A. The individual signals of the AA′BB′ spin system may be additionally broadened by scalar coupling to ^{14}N and ^{59}Co.[17a,b]

^{13}C NMR. In the bis(1,2-ethanediamine)methylcobalt(III) compounds reported here, only one ^{13}C resonance signal is in all cases detected from the coordinated 1,2-ethanediamine. An example is given in Figure 7B. This finding is consistent with these coordination compounds being *trans* isomers. The *cis* isomer is expected to have four different resonance signals from the coordinated 1,2-ethanediamine. In the case of the *trans*-amminebis(1,2-ethanediamine)methylcobalt(III) cation this assignment is confirmed by crystal structure determination (Figure 2).

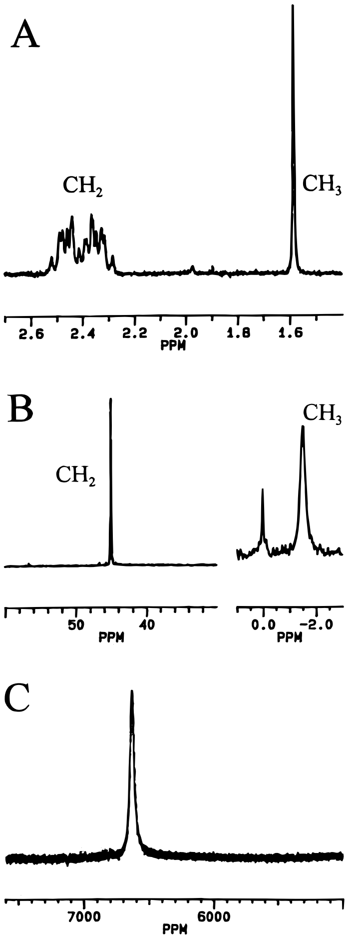

Figure 7. (A) ^1H NMR spectrum of *trans*-$[Co(en)_2(OH)(CH_3)]^+$ in 5 M KOD. (B) ^1H decoupled ^{13}C NMR spectrum of *trans*-$[Co(en)_2(OH)(CH_3)]^+$ in 5 M KOD. The signal at 0 ppm is DSS. (C) ^{59}Co NMR spectrum of a saturated solution of *trans*-$[Co(en)_2(OH_2)(CH_3)]S_2O_6$ in H_2O.

The magnetic shielding of the methyl group in the *trans*-bis(1,2-ethanediamine)methylcobalt(III) cations increases through the series $CN^- < NH_3 \approx NO_2^- < OH^-$, that is, from a softer to a harder ligand. A parallel trend in coordination shifts upon exchange of the *trans* ligand has been observed with various coenzyme B_{12} derivatives.[18] This *trans* influence may originate from the π-acceptor properties of the cyanide ion versus the σ-donor properties of the hydroxide ion. However, the ^{13}C chemical shift differences of the coordinated methyl group might also be due to differences in the magnetic anisotropy of the cobalt(III) ion. This has previously been discussed for the ^{14}N and ^{15}N chemical shift differences of the coordinated ammine groups in six-coordinate pentaamminecobalt(III) compounds.[16b,c]

The ^{13}C NMR spectrum of tetraethylammonium pentacyanomethylcobaltate(III) in acetonitrile-d_3 shows a clear distinction between the *trans* cyano group ($\delta = 154.1$ ppm) and the *cis* cyano groups ($\delta = 151.7$ ppm), integrating in the ratio 1:4 (Figure 6B). For comparison the ^{13}C chemical shift of the cyanide ion in a solution of tetraethylammonium cyanide in acetonitrile is $\delta = 166.4$ ppm. In aqueous solution the ^{13}C resonance signals of the *cis* and *trans* cyano groups are partly overlapping. The pentacyanomethylcobaltate(III) anion was

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found to be robust in aqueous solution in the precence of excess cyanide as revealed by NMR spectroscopy. This is in agreement with earlier observations on other pentacyanoalkylcobaltate(III) anions.[5b] Formation of the hexacyanocobaltate(III) anion (which would give a characteristic octet centered at 140.1 ppm)[19a,b] could not be detected by ^{13}C NMR, even when using potassium cyanide-^{13}C (99 at. % ^{13}C) for the preparation. However, a sharp signal assigned to the hexacyanocobaltate(III) anion was found at 0 ppm in the ^{59}Co NMR spectra both in aqueous and in acetonitrile solution (Figure 6C). An attempt to estimate the amount of hexacyanocobaltate(III) by integration of the ^{59}Co NMR signals indicated that the impurity was less than 1%.

It is seen in Figure 6B and Table 5 that the ^{13}C resonance signals are all very broad. We interpret this as originating from scalar coupling to the ^{59}Co nucleus according to eq 1. For the pentacyanomethylcobaltate(III) anion (prepared with cyanide containing natural abundance (1.1%) ^{13}C) $^{13}C-^{13}C$ scalar coupling is insignificant, and with T_{2X} obtained from a fit of a Lorentzian to the ^{13}C resonance signal, application of eq 1 gives the one-bond cobalt−carbon coupling constants $^1J_{Co-C}(cis) = 127$ Hz, $^1J_{Co-C}(trans) = 95$ Hz, and $^1J_{Co-C}(CH_3) = 62$ Hz from the measurements in acetonitrile (Figure 6). The uncertainty of the calculated coupling constants was estimated to be ±5 Hz.

The ^{59}Co resonance line width of tetraethylammonium pentacyanomethylcobaltate(III) in acetonitrile solution is strongly dependent on the concentration, resulting in increased line widths at higher concentrations, with a concominant decrease of the ^{13}C resonance line widths at higher concentrations. To avoid any uncertainty in the estimation of the scalar coupling constants due to concentration dependency of the line widths, the data given in Table 5 for tetraethylammonium pentacyanomethylcobaltate(III) in acetonitrile solution were obtained using measurements at the same solution (0.2 M). The concentration dependency is likely to be caused by ion pair formation in acetonitrile solution.

The scalar coupling constant of the *cis* cyano groups in the pentacyanomethylcobalte(III) anion is strikingly similar to that of the hexacyanocobaltate(III) anion ($^1J_{Co-C} = 126.5$ Hz).[19b] The scalar coupling constant of the *trans* cyano group is significantly smaller, indicating a *trans* influence of the methyl group. It is also apparent that the cobalt−carbon coupling constant for the methyl group in the pentacyanomethylcobaltate(III) anion ($^1J_{Co-C}(CH_3) = 62$ Hz) is significantly smaller than the one found for the pentaamminemethylcobalt(III) cation ($^1J_{Co-C}(CH_3) = 105$ Hz),[2a] showing that this parameter is strongly dependent on the nature of the other ligands.

It must be emphasized that this estimation of scalar cobalt−carbon coupling constants, using line widths, neglects other contributions to the spin−spin relaxation rates of the ^{13}C nuclei, such as scalar coupling to the ^{14}N nuclei in the cyano groups. However, if the spin−lattice relaxation rate of the ^{14}N nuclei is rapid, the contribution of scalar coupling between ^{14}N and ^{13}C to the ^{13}C resonance line width is insignificant, and, for example, it was not found necessary to consider such a contribution in order to obtain a good fit of a calculated line shape to the observed ^{13}C NMR spectrum of the hexacyanocobaltate(III) anion.[19c]

^{59}Co NMR. Table 5 reports the ^{59}Co chemical shifts for some of the new compounds. The paramagnetic contribution to ^{59}Co chemical shifts of low-spin cobalt(III) compounds is related to the temperature independent paramagnetism, which in turn is related to ligand-field parameters.[20] In general, strong-field ligands give a higher magnetic shielding of the ^{59}Co nucleus than weak-field ligands. For example, the ^{59}Co chemical shift of $[Co(CN)_5(CH_3)]^{3-}$ is $\delta = -203$ ppm, while that of $[Co(NH_3)_5(CH_3)]^{2+}$ is $\delta = 7370$ ppm in aqueous solution.

We were unsuccessful in determining any resonance signal from *trans*-$[Co(en)_2(CN)(CH_3)]^+$. This is presumably due to rapid relaxation, which may be caused by a large quadrupole coupling. A small ^{59}Co spin−lattice relaxation time in this compound is also inferred from the relatively narrow ^{13}C resonance signals of the methyl and cyano groups (Table 5).

For *trans*-$[Co(en)_2(NH_3)(CH_3)]^{2+}$ and *trans*-$[Co(en)_2(NO_2)(CH_3)]^+$ the ^{59}Co resonance signals are very broad and could be detected only with difficulty. All of the detected ^{59}Co resonance signals are within the typical range of chemical shifts. It is noteworthy that the ^{59}Co nucleus is more shielded in the pentacyanomethylcobaltate(III) anion ($\delta = -203$ ppm) than in the hexacyanocobaltate(III) anion ($\delta = 0$ ppm) when measured in aqueous solution (Table 5). In acetonitrile solution the chemical shifts of the two anions are almost identical (Figure 6C).

In conlusion, the pentaamminemethylcobalt(III) cation is a versatile starting material for the preparation of simple water soluble methylcobalt(III) compounds. X-ray crystal structure determinations of the title compounds show that the methyl group exerts a pronounced *trans* influence. It is plausible that this is the origin of the relative lability of these cobalt(III) compounds. For the series of *trans*-bis(1,2-ethanediamine)-methylcobalt(III) compounds the resonance frequency of the methyl ^{13}C nucleus is strongly dependent of the nature of the *trans* ligand.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for complexes **1**−**3** are available on the Internet only. Access information is given on any current masthead page.

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