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Article

NMR Spectroscopic and X-ray Crystallographic Study of Methylcobalt(III) Compounds with Saturated Amine Ligands

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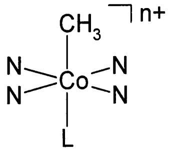
The ^{13}C chemical shifts of methylcobalt(III) compounds with saturated amine ligands in cis positions to the methyl group and a monodentate ligand, L = CN^-, NH_3, NO_2^-, N_3^-, H_2O, or OH^-, in the trans position are reported. The amine ligands used, 1,2-ethanediamine (en), 1,3-propanediamine (tn), *N*,*N*′-bis(2-aminoethyl)-1,3-propanediamine (2,3,2-tet), *N*,*N*′-bis(3-aminopropyl)-1,2-ethanediamine (3,2,3-tet), and 1,4,8,11-tetraazacyclotetradecane (cyclam), all exert an apparent cis influence on the ^{13}C resonance signal of the coordinated methyl group. In the *trans*-$[Co(en)_2(CH_3)(L)]^{n+}$ series the ^{15}N resonance frequency of the coordinated en has also been measured. The influence of L on the en ^{15}N chemical shifts is reverse the influence on the methyl ^{13}C chemical shifts except in the case of L = NO_2^-, which affects a further deshielding of the amine nitrogen nucleus. The methyl $^1J_{CH}$ coupling constants in the *trans*-$[Co(en)_2(CH_3)(L)]^{n+}$ series range from 128.09 Hz (L = CN^-) to 134.11 Hz (L = H_2O). The crystal structures of *trans*-$[Co(en)_2(CH_3)(ClZnCl_3)]$, *trans*-$[Co(3,2,3\text{-tet})(CH_3)(N_3)]ClO_4$, *trans*,*trans*-$[(CH_3)(en)_2Co(CN)Co(en)_2(CH_3)](PF_6)_3(CH_3CN)$, and *cis*-$[Co(en)_2(CH_3)(NH_3)]ZnCl_4$ were determined from low-temperature X-ray diffraction data.

Introduction

The properties of a carbanion coordinated to cobalt(III) are influenced by the other ligands in the coordination compound as described by trans and cis influences. This paper is concerned with methylcobalt(III) compounds having four nitrogen donor atoms in cis positions to the methyl group (Chart 1). Several such series have been reported in the literature during the last four decades. Most notable is the naturally occurring corrin-based methylcobalamin,[1] and the synthetically prepared series with, e.g., tetrapyrroles,[2] imines,[3] oximes,[4] mixed imines–oximes,[5] or amines,[6] have in many regards related properties. Literature data for the *trans*-$[Co(Hdmg)_2(CH_3)(L)]$ series (H_2dmg = dimethylglyoxime) reveal that the cobalt(III)–carbon bond distance,[7] the methyl ^{13}C chemical shift ($\delta(^{13}CH_3)$),[8] and the ^{59}Co–^{13}C one-bond

Chart 1. Representation of the Methylcobalt(III) Compounds in This Work[a]



[a] N denotes a nitrogen donor atom.

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coupling constant[8] are influenced by the trans ligand. The Co$-$C bond distances in a related series with the tetradentate ligand N^2,$N^{2\prime}$-propanediylbis(2,3-butanedione-2-imine-3-oxime) show similar dependencies.[7] Also in methylcobalamines and methylcobinamides the $\delta(^{13}CH_3)$ varies substantially with the trans ligand.[9] It is noteworthy that a related regularity was found in the *trans*-$[Co(en)_2(CH_3)(L)]^{n+}$ series.[6c]

The four in-plane nitrogen donor ligands (Chart 1) may exert cis influences. While several investigations have been devoted to cis influences on L, studies of cis influences upon the properties of the coordinated alkyl group are scarce. A comparison of Co$-CH_3$ bond lengths in oxime-based complexes with those of mixed imine$-$oxime-based complexes reveals only small differences.[7] Thus, $\delta(^{13}CH_3)$ chemical shifts in *trans*-$[Co(Hdmg)_2(py)(CH_3)]$ and *trans*-$[Co(Hchg)_2(py)(CH_3)]$ (H_2chg = 1,2-cyclohexanedioxime) differ by less than 0.5 ppm.[10] On the other hand, $\delta(^{13}CH_3)$ chemical shifts in complexes with different classes of in-plane nitrogen donor ligands may show a larger variation. For example, the $\delta(^{13}CH_3)$ chemical shifts in *trans*-$[Co(Hdmg)_2(H_2O)(CH_3)]$,[8] *trans*-$[Co(en)_2(CH_3)(H_2O)]^{2+}$,[6c] methylcobalamin at low pH,[9] and methylcobinamide[9] span a range of 9.5 ppm. The kinetics and thermodynamics of methyl group exchange between cobalt complexes with various tetraaza macrocyclic ligands show large variations.[3c] A related example of cis influence is the alkyl exchange between cobalt(III) complexes of different tetrapyrroles.[2c] Interestingly, it was found that the Co$-$C bond was stabilized by increasing the saturation of the tetrapyrrole macrocycle.[2c] It is also noteworthy that seemingly small modifications of the cis ligand may have a marked effect on reactivity.[11a,b] This has been exploited in organic synthesis using oxime-based complexes.[11c,d]

The saturated analogue to methylcobalamin model compounds, *trans*-$[Co(en)_2(CH_3)(NH_3)]^{2+}$, can be prepared[6c] by ligand exchange of $[Co(NH_3)_5(CH_3)]^{2+}$. In aqueous solution formation of the former has been proposed[12c] to proceed with *cis*-$[Co(en)_2(CH_3)(NH_3)]^{2+}$ as an intermediate. In this paper it is shown that the cis isomer can be obtained preparatively by replacing water with acetonitrile as a solvent for the exchange reaction. The *trans*-$[Co(en)_2(CH_3)(NH_3)]^{2+}$ cation benefits from being suitable for investigations of exchange reactions in the trans position to the methyl group, and the kinetics of substitutions with cyanide or azide in *trans*-$[Co(en)_2(CH_3)(H_2O)]^{2+}$ have been studied in detail by van Eldik and his group.[12a,b]

With the aim of investigating the influences of the in-plane nitrogen donor ligands on the structure, the NMR spectroscopic properties, and subsequently reactivity, we have prepared a series of compounds with saturated amines of varying chain length. The ^{13}C chemical shift data of the new compounds are discussed. For the series of *trans*-$[Co(en)_2(CH_3)(L)]^{n+}$ (L = CN^-, NH_3, NO_2^-, H_2O, or OH^-) methyl ^{13}C and 1,2-ethanediamine ^{15}N nuclear magnetic relaxation data were additionally obtained. Finally, the crystal structures of *trans*-$[Co(en)_2(CH_3)(ClZnCl_3)]$, *trans*-$[Co(3,2,3\text{-tet})(CH_3)(N_3)]ClO_4$, *trans*,*trans*-$[(CH_3)(en)_2Co(CN)Co(en)_2(CH_3)](PF_6)_3(CH_3CN)$, and *cis*-$[Co(en)_2(CH_3)(NH_3)]ZnCl_4$ are reported.

Experimental Section

Caution! Coordination compounds with organic ligands, azide, and perchlorate are potentially explosive and were handled in quantities of less than 0.1 g.

Materials. $[^{13}C]$Methyliodide (Sigma, 99 atom % ^{13}C), anhydrous hydrazine (Alfa Aesar), $[^{15}N]$ethanediamine (Icon Services Inc., 99 atom % ^{15}N), $K^{13}CN$ (Aldrich, 99 atom % ^{13}C), and $KC^{15}N$ (Aldrich, 98 atom % ^{15}N) were used as received. $[^{13}C]$Methylhydrazine was prepared from $[^{13}C]$methyl iodide and anhydrous hydrazine.[13]

Instrumentation. NMR spectra were measured at 14.1 T on a Varian Unity Inova 600 NMR spectrometer or at 7 T on a Varian Mercury 300 NMR spectrometer. ^{13}C, ^{15}N, and ^{59}Co spectra were measured on 5 or 10 mm broad-band tunable probes. Deuterium oxide was used as a solvent to provide a deuterium lock. ^{13}C chemical shift values (δ) are reported in parts per million relative to the peak for the methyl group of internal sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS). ^{15}N chemical shift values (δ) are reported relative to the peak for neat nitromethane ($\delta = 0$) in a coaxial NMR tube.[14] Spin$-$lattice relaxation times (T_1) were determined by inversion$-$recovery. Spin$-$spin relaxation times (T_2) were determined by the spin$-$echo technique. The relaxation times were obtained by fitting of an exponential function to the integrals of the peaks using the spectrometer system software. Solutions for NMR were usually 0.2 M with respect to the coordination compound when using samples with natural abundance ^{13}C. Elemental analyses were made at the Microanalytical Laboratory at the Department of Chemistry, University of Copenhagen.

Preparations. All methylcobalt(III) compounds used in this study were prepared by ligand substitution of the pentaamminemethylcobalt(III) cation as previously reported.[6c] The derivatives with an aqua ligand trans to the methyl group were used for further ligand substitutions in this position.[6c] All work was performed in dim light.

***trans*-Aquabis(1,2-ethanediamine)methylcobalt(III) Bromide.** A 0.5 g (1.57 mmol) amount of pentaamminemethylcobalt(III) bromide was added to a solution of 240 μL (3.59 mmol) of 1,2-ethanediamine in 10 mL of water. The mixture was stirred at room temperature for 72 h and then filtered. The filtrate was taken to dryness by rotary evaporation at 60 °C. The solid was dissolved in water (1 mL). Methanol (5 mL) followed by acetone (10 mL) was added, and the mixture was left overnight at 4 °C. The pink solid was collected by filtration, washed with acetone, and air-dried at

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20 °C. Recrystallization followed the same procedure. Yield: 0.48 g (82%). Anal. Calcd for $CoC_5H_{21}N_4OBr_2$: C, 16.14; H, 5.69; N, 15.06. Found: C, 16.62; H, 5.79; N, 15.62.

***trans*-Aquabis(1,3-propanediamine)methylcobalt(III) Bromide.** A 0.5 g (1.57 mmol) amount of pentaamminemethylcobalt(III) bromide was added to a solution of 300 μL (3.6 mmol) of 1,3-propanediamine in 20 mL of water. The mixture was stirred at room temperature for 72 h and then filtered. The filtrate was taken to almost dryness by rotary evaporation at 60 °C. The solid was dissolved in methanol (5 mL), ethyl acetate (45 mL) was added, and the mixture was left overnight at 4 °C. The pink solid was collected by filtration, washed with ethyl acetate followed by washing with diethyl ether, and air-dried at 20 °C. The product was recrystallized from methanol by addition of ethyl acetate. Yield: 0.22 g (35%). Anal. Calcd for $CoC_7H_{25}N_4OBr_2$: C, 21.02; H, 6.30; N, 14.01. Found: C, 21.20; H, 6.13; N, 14.05.

***trans*-Aqua(2,3,2-tet)methylcobalt(III) Bromide.** A 0.5 g (1.57 mmol) amount of pentaamminemethylcobalt(III) bromide was added to a solution of 290 μL (1.74 mmol) of *N*,*N*′-bis(2-aminoethyl)-1,3-propanediamine (2,3,2-tet) in 10 mL of water. The mixture was stirred at room temperature for 48 h and then filtered. The filtrate was taken to dryness by rotary evaporation at 60 °C. The solid was dissolved in methanol (25 mL), ethyl acetate (100 mL) was added, and the mixture was left overnight at 4 °C. The pink solid was collected by filtration, washed with ethyl acetate followed by washing with diethyl ether, and air-dried at 20 °C. The product was recrystallized from water (2 mL) by addition of tetrahydrofuran (20 mL). Yield: 0.40 g (62%). Anal. Calcd for $CoC_8H_{25}N_4OBr_2$: C, 23.32; H, 6.12; N, 13.60. Found: C, 23.82; H, 6.13; N, 13.80.

***trans*-Aqua(3,2,3-tet)methylcobalt(III) Bromide.** A 0.5 g (1.57 mmol) amount of pentaamminemethylcobalt(III) bromide was added to a solution of 330 μL (1.8 mmol) of *N*,*N*′-bis(3-aminopropyl)-1,2-ethanediamine (3,2,3-tet) in 10 mL of water. The mixture was stirred at room temperature for 48 h and then filtered. The filtrate was taken to dryness by rotary evaporation at 60 °C. The solid was dissolved in methanol (25 mL), ethyl acetate (100 mL) was added, and the mixture was left for 48 h at 4 °C. The pink solid was collected by filtration, washed with ethyl acetate followed by washing with diethyl ether, and air-dried at 20 °C. The product was recrystallized from methanol by addition of ethyl acetate. Yield: 0.37 g (55%). Anal. Calcd for $CoC_9H_{27}N_4OBr_2$: C, 25.37; H, 6.39; N, 13.15. Found: C, 25.65; H, 6.33; N, 13.12.

***trans*-Aqua(1,4,8,11-tetraazacyclotetradecane)methylcobalt(III) Bromide.** A 0.5 g (1.57 mmol) amount of pentaamminemethylcobalt(III) bromide was added to a solution of 0.47 g (2.34 mmol) of 1,4,8,11-tetraazacyclotetradecane (cyclam) in 20 mL of water. The mixture was stirred at room temperature for 72 h and then filtered. The filtrate was taken to dryness by rotary evaporation at 60 °C. The solid was suspended in methanol (10 mL), collected by filtration, washed with methanol, and air-dried at 20 °C. Yield: 0.46 g (65%). Anal. Calcd for $CoC_{11}H_{29}N_4OBr_2$: C, 29.22; H, 6.47; N, 12.39. Found: C, 29.93, H, 6.59; N, 12.40.

***trans*,*trans*-*μ* -Cyanobis(bis(1,2-ethanediamine)methylcobalt(III)) Hexaflourophosphate.** A 0.9 g (3.18 mmol) amount of pentaamminemethylcobalt(III) nitrate was added to a solution of 470 μL (7.0 mmol) of 1,2-ethanediamine in 3 mL of water. The solution was stirred at 20 °C for 24 h. To the filtered solution was added 80 mg (1.6 mmol) of sodium cyanide in 1 mL of water, followed by 2.0 g (11.9 mmol) of sodium hexafluorophosphate in 3 mL of water, whereby $[(CH_3)(en)_2Co(CN)Co(en)_2(CH_3)](PF_6)_3$ precipitated. The mixture was left at 4 °C for 2 h. The yellow solid was collected by filtration, washed with ice-cold water, and air-dried. Recrystallization was performed from acetonitrile (10 mL) by addition of diethyl ether (90 mL). Yield: 0.65 g (48%). Anal. Calcd for $Co_2C_{11}H_{38}N_9P_3F_{18}$: C, 15.56; H, 4.51; N, 14.84. Found: C, 15.00; H, 4.36; N, 14.93.

***cis*-Amminebis(1,2-ethanediamine)methylcobalt(III) Hexaflourophosphate.** A 10.0 g (22.3 mmol) amount of pentaamminemethylcobalt(III) hexaflourophosphate was added to a solution of 3.4 mL of 1,2-ethanediamine (51 mmol) in 500 mL of acetonitrile. The suspension was stirred at 20 °C for 18 h. At the end of this period, the reaction mixture was filtered, and the filtrate was added to diethyl ether (2.5 L), whereby an orange oily precipitate formed. The supernatant was decanted off, and the oily precipitate was stirred overnight with 1,4-dioxane (500 mL), resulting in a solidification of the precipitate. The orange crystals were filtered off, washed well with 1,4-dioxane, and air-dried at 20 °C. Yield: 2.6 g (23%). Anal. Calcd for $CoC_5H_{22}N_5P_2F_{12}$: C, 11.98; H, 4.43; N, 13.98. Found: C, 12.03; H, 4.07; N, 13.90.

***cis*-Amminebis(1,2-ethanediamine)methylcobalt(III) Tetrachlorozincate.** A saturated solution of $Na_2[ZnCl_4]$ was added to a saturated solution of *cis*-amminebis(1,2-ethanediamine)methylcobalt(III) hexaflourophosphate in water, resulting in an immediate precipitation of *cis*-amminebis(1,2-ethanediamine)methylcobalt(III) tetrachlorozincate. Anal. Calcd for $CoC_5H_{22}N_5ZnCl_4$: C, 14.35; H, 5.30; N, 16.74. Found: C, 14.29; H, 5.07; N 16.67.

X-ray Crystallography. Crystals of *trans*,*trans*-$[(CH_3)(en)_2Co(CN)Co(en)_2(CH_3)](PF_6)_3(CH_3CN)$ (**1**) were grown by diffusion of diethyl ether into a saturated solution of **1** in acetonitrile. Crystals of *trans*-$[Co(en)_2(CH_3)(ZnCl_4)]$ (**2**) were grown by diffusion of an aqueous solution of *trans*-$[Co(en)_2(CH_3)(H_2O)](NO_3)_2$ into a solution of $Na_2[ZnCl_4]$. Crystals of *trans*-$[Co(3,2,3\text{-tet})(CH_3)(N_3)]ClO_4$ (**3**) were grown by diffusion of an aqueous solution of *trans*-$[Co(3,2,3\text{-tet})(CH_3)(H_2O)]SO_4$ in 1 M NaN_3 into a saturated solution of $NaClO_4$. Crystals of *cis*-$[Co(en)_2(CH_3)(NH_3)]ZnCl_4$ (**4**) were grown by diffusion of an aqueous solution of **4** into saturated NaCl.

Low-temperature X-ray diffraction data of **1** and **2** were collected with a CAD4 diffractometer using graphite (002) monochromated Mo Kα radiation. The temperature was set to 122 K, adjusted by the tetragonal to orthorhombic phase transition of KH_2PO_4 at this temperature. The cell dimensions were determined from 24 reflections in the θ range 19.20−22.37° for **1** and 19.37−22.52° for **2**. Data were collected for 11917 reflections (**1**) and 15064 reflections (**2**), including standards in the octants: $h, \pm k, \pm l$ ($1° < \theta < 30°$) for **1** and $h, k, \pm l$ ($1° < \theta < 35°$) for **2**. The intensities of five standard reflections were measured every 10000 s. The data set from **1** showed a small systematic decrease of 4%, for which it was corrected using a polynomial fit to third order. Table 1 lists the crystal data and the final refinement results. Data reduction, including corrections for Lorentz, polarization, and absorption effects, was done using the DREADD program suite.[15a] The absorption correction was performed with the Gaussian integration procedure. Both structures were determined by direct methods (SHELXS-86),[15b] and subsequently refined using SHELXL-97[15c] by minimizing $\sum w(|F_o|^2 - |F_c|^2)^2$. Totals of 9356 (**1**) and 6157 (**2**) unique reflections were used in the refinement of the 415 (**1**) and 193 (**2**) parameters. The conventional R_1 value was calculated from 7701 (**1**)/5049 (**2**) reflections with $|F_o| > 4\sigma(|F_o|)$.

Data collected with a Nonius KappaCCD diffractometer on a single crystal cooled to 122(1) K were used for the crystal structure determinations of **3** and **4**. The temperature was monitored as previously described. The COLLECT program[15d] was used for the data collection of the 51968 (**3**) and 91306 (**4**) reflections. Unit cell parameters were obtained by φ/χ scans[15e] and refined in DIRAX.[15f] The data were integrated with EvalCCD.[15g] Numerical absorption correction[15h] was performed in maXus.[15i] The structure

Table 1. Crystallographic Data for Complexes **1**−**4**

	1	**2**	**3**	**4**
empirical formula	$Co_2C_{13}H_{41}N_{10}P_3F_{18}$	$C_5H_{19}Cl_4CoN_4Zn$	$C_9H_{25}ClCoN_7O_4$	$C_5H_{22}Cl_4CoN_5Zn$
fw	890.33	401.34	389.74	418.38
temp (K)	122(2)	122(2)	122(2)	122(2)
wavelength (Å)	0.71073	0.71073	0.71073	0.71073
cryst syst, space group	monoclinic, $P2_1/n$	orthorhombic, *Pbca*	monoclinic, $P2_1/c$	orthorhombic, $P2_12_12_1$
unit cell dimens				
a (Å)	11.816(2)	9.406(2)	10.145(2)	7.654(2)
b (Å)	15.903(3)	12.070(3)	22.277(3)	13.368(2)
c (Å)	17.163(5)	24.719(5)	13.070(2)	14.662(2)
β (deg)	93.51(3)		146.55(3)	
vol (Å^3)	3219.0(12)	2806.4(11)	1628.3(6)	1500.2(5)
Z, density(calcd) (Mg/m^3)	4, 1.837	8, 1.900	4, 1.590	4, 1.852
abs coeff (mm^{-1})	1.208	3.629	1.247	3.400
no. of reflns collected/unique	11521/9356 [$R_{int} = 0.0275$]	13486/6157[$R_{int} = 0.0162$]	51968/3744[$R_{int} = 0.031$]	91306/12359[$R_{int} = 0.027$]
final *R* indices[a] [$I > 2\sigma(I)$]	$R_1 = 0.0583$, $R_w(F^2) = 0.1642$	$R_1 = 0.0318$, $R_w(F^2) = 0.0601$	$R_1 = 0.0575$, $R_w(F^2) = 0.2037$	$R_1 = 0.0306$, $R_w(F^2) = 0.1253$
R indices (all data)	$R_1 = 0.0734$, $R_w(F^2) = 0.1788$	$R_1 = 0.0450$, $R_w(F^2) = 0.0623$	$R_1 = 0.0667$, $R_w(F^2) = 0.2235$	$R_1 = 0.0405$, $R_w(F^2) = 0.1506$

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

was solved with SIR97[15j] and refined by full-matrix least-squares on F^2 in SHELXL-97.[15c] Totals of 3744 (**3**) and 12359 (**4**) unique reflections were used in the refinement of the 199 (**3**) and 146 (**4**) parameters. The conventional R_1 value was calculated from 3459 (**3**)/11668 (**4**) reflections with $|F_o| > 4\sigma(|F_o|)$. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms (except for the hydrogen atoms in the acetonitrile molecule in **1**) could be identified in the difference electron density maps. In structures **1**, **3**, and **4** these hydrogen atoms were introduced on ideal positions riding on the parent atom. In **2** the positional parameters of the hydrogen atoms were included in the refinement. The thermal parameters were made equal to U_{eq} of the parent C or N atom multiplied by 1.2 or 1.5, respectively. Details of the crystal data and refinement are given in Table 1.

Results and Discussion

Syntheses. In aqueous solution exchange of the ammine ligands in the pentaamminemethylcobalt(III) cation with tn, 2,3,2-tet, 3,2,3-tet, and cyclam invariably yields the trans isomers in accordance with the previously reported[6c] exchange with en. Subsequent exchange of the trans aqua ligand with stronger ligands occurs with conservation of the stereochemistry for complexes with en, 2,3,2-tet, and cyclam. Addition of cyanide, nitrite, or strong base results according to ^{13}C NMR measurements in further substitution reactions or isomerizations for complexes with tn or 3,2,3-tet. These have yet to be elucidated.

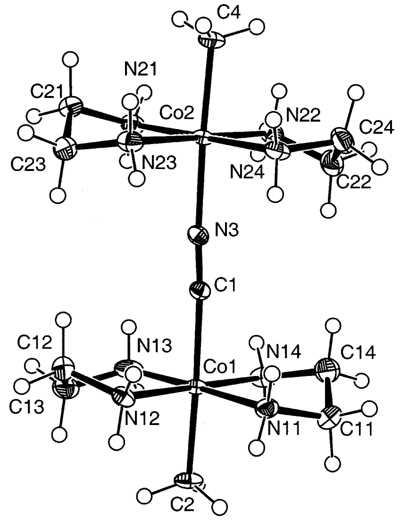

Figure 1. Ortep(II)[15k] 50% probability plots of the cation in **1**.

Whereas organocobalt(III) compounds with open chain amine ligands are relatively new, cyclam-based compounds have been in the literature for three decades. The preparation of *trans*-[Co(cyclam)(CH_3)(OH_2)]$^{2+}$ was first carried out using *trans*-[Co(cyclam)(OH_2)$_2$]$^{2+}$ as a trap for methyl radicals,[6a] which in turn were produced by photolysis of [Co(NH_3)$_5$(O_2CH_3)]$^{2+}$. Subsequently, preparative procedures employing *trans*-[Co(Hdmg)$_2$(H_2O)(CH_3)][6b] or methylhydrazine[6d] as methylating agents have been published. Although ligand substitution of the pentamminemethylcobalt(III) cation indirectly makes use of methylhydrazine, the present method benefits from the simple workup procedure.

It is interesting that formation of each of the two isomers of the [Co(en)$_2$(CH_3)(NH_3)]$^{2+}$ cation can be controlled alone by the choice of solvent. As expected,[12c] *cis*-[Co(en)$_2$(CH_3)(NH_3)]$^{2+}$ isomerizes and hydrolyzes to *trans*-[Co(en)$_2$(CH_3)(H_2O)]$^{2+}$ in aqueous solution upon standing at room temperature for a prolonged period.

Description of the Crystal Structures. The structures of the cations in **1**−**4** are shown in Figures 1−4. In all four structures the cobalt(III) ion is six-coordinated with ap-

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(15) (a) Blessing, B. *Crystallogr. Rev.* **1987**, *1*, 3−58. (b) Sheldrick, G. M. *SHELXS-86. Program for Crystal Structure Determination*; University of Göttingen: Göttingen, Germany, 1986. (c) Sheldrick, G. M. *SHELXL97. Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997. (d) Nonius BV. *"Collect" data collection software*; Delft, The Netherlands, 1999. (e) Duisenberg, A. J. M.; Hooft, R. W. W.; Schreurs, A. M. M.; Kroon, J. *J. Appl. Crystallogr.* **2000**, *33*, 893−898. (f) Duisenberg, A. J. M. *J. Appl. Crystallogr.* **1992**, *25*, 92−96. (g) Duisenberg, A. J. M. Reflections in area detectors. Ph.D. Thesis, University of Utrecht, The Netherlands, 1998. (h) Coppens, P. In *Crystallographic Computing*; Agmed, F. R., Hall, S. R., Huber, C. P., Eds.; Munksgaard: Copenhagen, Denmark, 1970; pp 255−270. (i) Mackay, S.; Gilmore, C. J.; Edwards, C.; Tremayne, M.; Stuart, N.; Shankland. K. *MaXus: a computer program for the solution and refinement of crystal structure diffraction data*; University of Glasgow: Glasgow, Scotland, U.K.; Nonius BV: Delft, The Netherlands; MacScience Co. Ltd.: Yokohama, Japan, 1998. (j) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115−119. (k) Johnson, C. K. *ORTEPII*; Technical Report-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976. (l) Cambridge Crystallographic Data Center (CCDC), Cambridge, U.K.

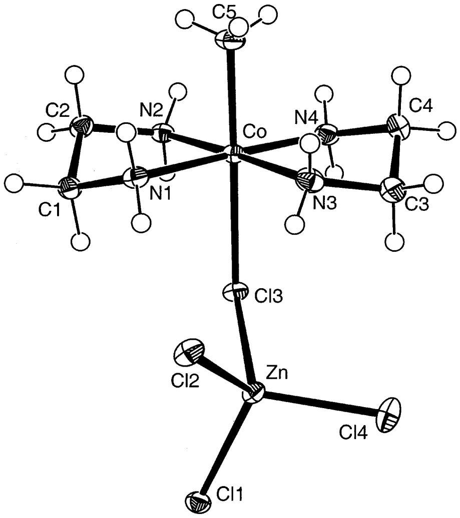

Figure 2. Ortep(II)[15k] 50% probability plots of **2**.

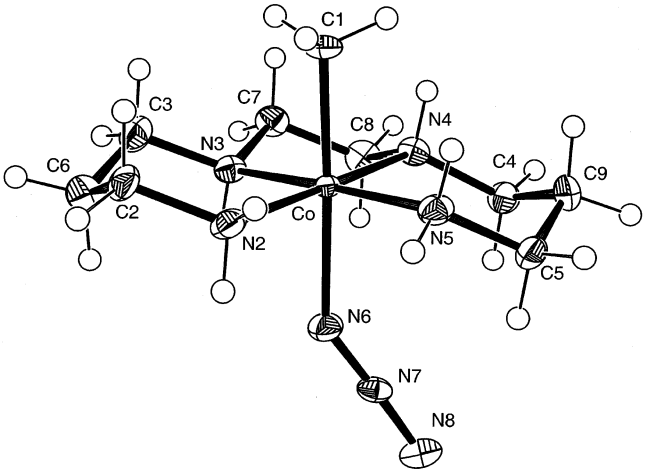

Figure 3. Ortep(II)[15k] 50% probability plots of the cation in **3**.

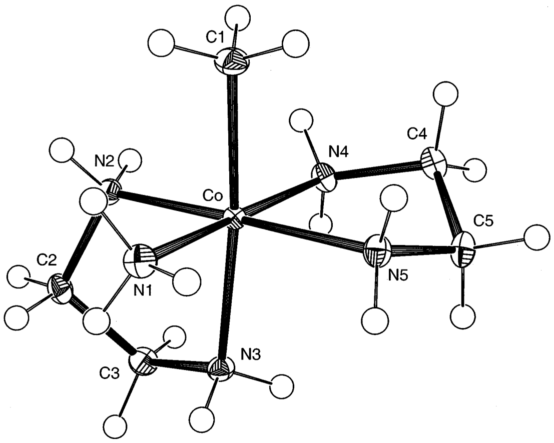

Figure 4. Ortep(II)[15k] 50% probability plots of the cation in **4**.

proximately octahedral geometry. The Co−CH_3 bond length is between 1.972(3) and 1.9804(18) Å (Table 2), which is close to that found for related compounds.[6c] The cobalt−nitrogen bond distances of the cis amine nitrogen donor atoms are typical for aminecobalt(III) compounds, and the most prominent structural feature is the elongation of the bond trans to the methyl group.

Table 2. Selected Bond Distances (Å) and Angles (deg) for the Cations in **1**−**4**

	Complex **1**		
Co1−C2	1.974(3)	Co2−C4	1.972(3)
Co1−C1	2.023(3)	Co2−N3	2.020(3)
Co1−N11	1.964(2)	Co2−N21	1.969(2)
Co1−N12	1.970(3)	Co2−N22	1.967(3)
Co1−N13	1.962(3)	Co2−N23	1.967(3)
Co1−N14	1.967(3)	Co2−N24	1.965(2)
C1−N3	1.155(4)		
C2−Co1−C1	178.10(12)	C4−Co2−N3	177.68(12)
Co1−C1−N3	175.9(2)	Co2−N3−C1	175.6(2)
	Complex **2**		
Co−C5	1.9804(18)	Co−Cl3	2.5225(6)
Co−N1	1.9545(16)	Co−N2	1.9690(15)
Co−N3	1.9628(16)	Co−N4	1.9696(16)
Zn−Cl1	2.2777(6)	Zn−Cl2	2.2496(7)
Zn−Cl3	2.3203(6)	Zn−Cl4	2.2394(6)
C5−Co−Cl3	178.37(6)	Co−Cl3−Zn	115.42(2)
	Complex **3**		
Co−C1	1.980(3)	Co−N6	2.098(3)
Co−N2	1.980(3)	Co−N3	1.996(3)
Co−N4	1.987(3)	Co−N5	1.967(3)
N6−N7	1.173(4)	N7−N8	1.178(5)
Co−N6−N7	142.5(3)	N6−N7−N8	177.6(4)
	Complex **4**		
Co−C1	1.978(2)	Co−N1	1.985(2)
Co−N2	1.964(2)	Co−N3	2.092(2)
Co−N4	1.975(2)	Co−N5	1.982(2)
C1−Co−N3	173.61(8)	C1−Co−N1	88.36(8)

It is difficult to distinguish the C and the N atoms in the cyano bridge of **1**. Therefore, this compound is likely to be disordered with respect to this bond. This can explain why we cannot distinguish the Co2−N3 bond length of 2.020(3) Å and the Co1−C1 bond length of 2.023(3) Å. This does not, however, change the observation that, in **1**, the cobalt−cyanide distances of 2.023(3) and 2.020(3) Å to C and N, respectively, are significantly longer than observed in related cyano-bridged compounds. In pentacyanocobalt(III)−μ-cyanopentaamminecobalt(III) monohydrate[16a] the two distances are only 1.886 and 1.921 Å, respectively. The bridging C≡N distance of 1.152(5) Å in the latter complex is, however, not significantly different from that in **1** (Table 2). The Co−C−N and Co−N−C angles are on the other hand significantly larger in **1** (175.9(2)° and 175.6(2)°, respectively) than in pentacyanocobalt(III)−μ-cyanoopentaamminecobalt(III) monohydrate (172.4(3)° and 159.8(3)°, respectively). In the related cubic $[(tacn)_8Co_8(CN)_{12}]^{12+}$ (tacn = 1,4,7-triazacyclononane) the corresponding[16b] angle is 177(2)°, thereby demonstrating some flexibility of this structural motif.

A search in the Cambridge Structural Database[15l] revealed no preceding reports on X-ray crystal structures of tetrachlorozincate(II) coordinated to cobalt(III). In **2**, the distance between the cobalt atom and the bridging chloro ligand of 2.5225(6) Å is very long compared to, e.g., the Co−Cl distance of 2.325(9) Å in μ-chloro-μ-amidooctaamminedicobalt tetrachloride tetrahydrate.[17a] The Zn−Cl distance of the bridging chloro ligand is significantly elongated com-

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Table 3. ^{13}C Chemical Shift Data[a]

compound	$\delta(^{13}CH_3)$ (ppm)	$\delta(^{13}CH_2)$ (ppm) (number of C nuclei)
trans-$[Co(en)_2(CH_3)(N_3)]^{+}$[j]	1.6	44.5 (4C)
trans-$[(CH_3)(en)_2Co(CN)Co(en)_2(CH_3)]^{3+}$[h,i]	5.1	46.5 (4C), 46.2 (4C)
	13.1	
trans-$[Co(tn)_2(CH_3)(OH_2)]^{2+}$	−4.2	40.2 (4C), 28.3 (2C)
trans-$[Co(2,3,2\text{-tet})(CH_3)(CN)]^{+}$[b,c]	11.0	57.1 (2C), 53.6 (2C), 42.9 (2C), 30.0 (1C)
trans-$[Co(2,3,2\text{-tet})(CH_3)(NH_3)]^{2+}$	5.8	55.7 (2C), 51.1 (2C), 42.8 (2C), 29.7 (1C)
trans-$[Co(2,3,2\text{-tet})(CH_3)(NO_2)]^{+}$	3.6	55.5 (2C), 50.8 (2C), 43.4 (2C), 30.0 (1C)
trans-$[Co(2,3,2\text{-tet})(CH_3)(N_3)]^{+}$[j]	2.3	56.0 (2C), 51.9 (2C), 43.5 (2C), 30.1 (1C)
trans-$[Co(2,3,2\text{-tet})(CH_3)(OH_2)]^{2+}$	0.1	55.7 (2C), 51.3 (2C), 43.4 (2C), 29.9 (1C)
trans-$[Co(2,3,2\text{-tet})(CH_3)(OH)]^{+}$[d]	−0.5	55.1 (2C), 50.8 (2C), 43.1 (2C), 29.9 (1C).
trans-$[Co(cyclam)(CH_3)(CN)]^{+}$[e,f]	7.0	55.0 (2C), 53.5 (2C), 52.1 (2C), 48.6 (2C), 29.6 (1C), 29.5 (1C)
trans-$[Co(cyclam)(CH_3)(NH_3)]^{2+}$	5.4	53.5 (2C), 52.7 (2C), 50.8 (2C), 48.5 (2C), 29.4 (1C), 29.2 (1C)
trans-$[Co(cyclam)(CH_3)(NO_2)]^{+}$	4.7	53.2 (2C), 53.1 (2C), 50.9 (2C), 48.7 (2C), 29.5 (1C), 29.4 (1C)
trans-$[Co(cyclam)(CH_3)(N_3)]^{+}$[j]	2.8	53.9 (2C), 53.1 (2C), 51.4 (2C), 48.6 (2C), 29.5 (1C), 29.4 (1C)
trans-$[Co(cyclam)(CH_3)(OH_2)]^{2+}$	1.8	53.7 (2C), 53.1 (2C), 51.4 (2C), 48.6 (2C), 29.5 (1C), 29.4 (1C)
trans-$[Co(cyclam)(CH_3)(OH)]^{+}$[d]	0.3	53.2 (2C), 53.0 (2C), 50.9 (2C), 48.7 (2C), 29.7 (1C), 29.5 (1C)
trans-$[Co(3,2,3\text{-tet})(CH_3)(N_3)]^{+}$[g]	−0.4	52.1 (1C), 51.9 (1C), 50.1 (1C), 47.3 (1C), 40.6 (1C), 38.8 (1C), 27.8 (1C9, 27.6 (1C)
cis-$[Co(en)_2(CH_3)(NH_3)]^{2+}$	1.6	47.0 (1C), 45.9 (1C), 45.7 (1C), 44.5 (1C)

[a] The solutions were 0.2 M in D_2O and measured at 300 K. [b] $^2J_{CC}$(trans) = 23.7 Hz. [c] $\delta(CN)$ = 167.1 ppm. [d] In 5 M NaOD. [e] $^2J_{CC}$(trans) = 22.2 Hz. [f] $\delta(CN)$ = 165.3 ppm. [g] In acetonitrile-d_3. [h] $^2J_{CC}$(trans) = 25.7 Hz. [i] $\delta(CN)$ = 171.7 ppm. [j] In 1 M NaN_3.

pared to the remaining Zn−Cl distances. This has also been observed, e.g., in a structure of a copper(II) complex.[17b] If we calculate a least-squares plane created by the four amine groups, the Co atom seems to be pushed out of this plane by the bulky tetrachlorozincate(II) ligand by 0.031(1) Å. This has apparently no influence on the cobalt−methyl distance, which is 1.980(2) Å.

The Co−N distance of 2.098(3) Å to the azido ligand in **3** is similarly considerably larger than that[18a] of $[Co(NH_3)_5(N_3)](N_3)_2$ (1.943(5) Å). The two N−N distances in the azido ligand are within uncertainty identical (Table 2). This is also in contrast to the coordinated azide in $[Co(NH_3)_5(N_3)](N_3)_2$, where the two bond distances are significantly different[18a] as is also found in hydrazoic acid[18b] and in methyl azide.[18c] The fact that the structure of the azido ligand resembles that of uncoordinated azide is probably a manifestation of the trans influence of the methyl group.

The structure of the cation in **4**, *cis*-amminebis(1,2-ethanediamine)methylcobalt(III), may be compared with the previously reported[6c] structure of the trans isomer. The Co−C distances of 1.975(2) and 1.984(2) Å, respectively, are similar. However, while the cobalt−ammine bond distance of 1.985(2) Å in **4** is typical for amminecobalt(III) compounds, the cobalt−ammine distance in the trans isomer is significantly longer, namely, 2.127(2) Å.[6c] Conversely, in **4** the Co−N distance to the trans amine ligand is 2.092(2) Å, which is 0.118(9) Å longer than the average of 1.974(9) Å of the three cis amine groups.

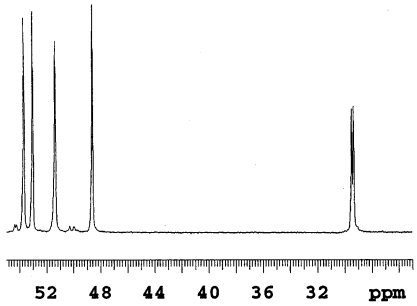

Figure 5. CH_2 region of the ^{13}C NMR spectrum of *trans*-aqua(1,4,8,11-tetraazacyclotetradecane)methylcobalt(III) bromide in D_2O. The spectrum is consistent with the coordinated cyclam adopting the 1*R*,2*R*,3*S*,4*S* isomer among the five configurational trans isomers.

NMR Spectroscopic Characterization. The geometric isomers resulting from the exchange reactions with saturated amines can in most of the present cases be deduced from the number of ^{13}C resonance signals from the coordinated amine (Table 3). Thus, the coordinated en, tn, and 2,3,2-tet show one, two, and four ^{13}C signals, respectively, in the trans isomers. The coordinated cyclam shows six ^{13}C signals consistent with the 1*R*,2*R*,3*S*,4*S* isomer (Figure 5). The coordinated 3,2,3-tet shows eight signals because this tetraaza ligand coordinates as the 2*S*,3*S* isomer whereby all carbon nuclei are differently shielded. The coordinated 3,2,3-tet thus adopts the same geometry as cyclam except that one $-CH_2-CH_2-$ bridge is lacking in the former. Complexes with one of the nitrogen donor atoms in a trans position to the methyl group would, however, also give eight signals. X-ray crystallography of *trans*-$[Co(3,2,3\text{-tet})(CH_3)(N_3)]ClO_4$ (above) shows that it is the trans isomer which is obtained from aqueous solution.

Addition of a less than stoichiometric amount of CN^- to *trans*-$[Co(en)_2(CH_3)(H_2O)]^{2+}$ yields an equilibrium mixture of the mononuclear aqua complex, the dinuclear *trans*,*trans*-$[(CH_3)(en)_2Co(CN)Co(en)_2(CH_3)]^{3+}$cation, and the *trans*-$[Co(en)_2(CH_3)(CN)]^+$ cation as evidenced by ^{13}C NMR. The ^{13}C NMR spectrum of the doubly ^{13}C enriched *trans*,*trans*-$[(^{13}CH_3)(en)_2Co(^{13}CN)Co(en)_2(^{13}CH_3)](PF_6)_3$ (Figure 6) shows the coexistence of the three entities. The doublet at 13.1 ppm ($^2J_{CC}$ = 25.7 Hz) is assigned to the methyl group at the cyano-C-bonded cobalt(III) ion, while the singlet at 5.1 ppm is assigned to the methyl group at the cyano-N-bonded metal ion. The latter resonance signal is split into a doublet ($^2J_{C-N}$

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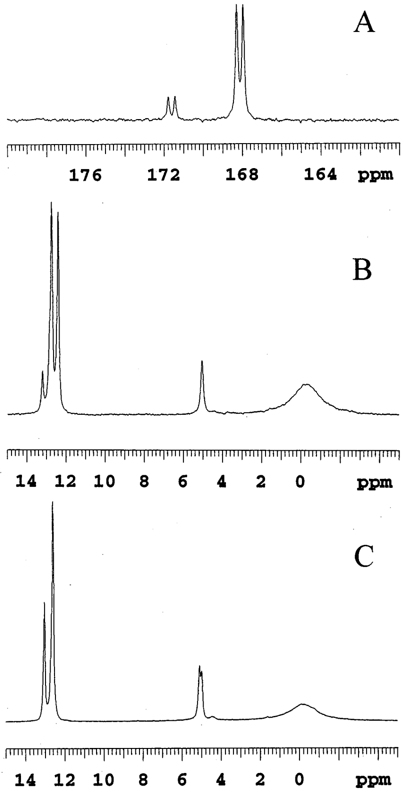

Figure 6. Cyano region (A) and methyl region (B) of the ^{13}C NMR spectrum of a saturated solution of the doubly ^{13}C enriched *trans,trans*-[($^{13}CH_3$)(en)$_2$Co(^{13}CN)Co(en)$_2$($^{13}CH_3$)](PF$_6$)$_3$ in D_2O. (C) Methyl region of a saturated solution of *trans,trans*-[($^{13}CH_3$)(en)$_2$Co(C^{15}N)Co(en)$_2$($^{13}CH_3$)](PF$_6$)$_3$ in D_2O.

= 8.1 Hz) in the ^{15}N-enriched *trans*,*trans*-[($^{13}CH_3$)(en)$_2$Co(C^{15}N)Co(en)$_2$($^{13}CH_3$)]$^{3+}$. It may be noted that the two methyl ^{13}C resonance signals in *trans*,*trans*-[(CH$_3$)(en)$_2$Co(CN)Co(en)$_2$(CH$_3$)]$^{3+}$ are typical for methyl groups trans to C and N, respectively (Table 3). The ^{15}N spectrum (Figure 7C) of a saturated solution of *trans*,*trans*-[($^{13}CH_3$)(en)$_2$Co(C^{15}N)Co(en)$_2$($^{13}CH_3$)](PF$_6$)$_3$ shows a major singlet from the *trans*-[Co(en)$_2$(CH$_3$)(C^{15}N)]$^{+}$ cation and a minor poorly resolved doublet which by virtue of its 8.1 Hz splitting is assigned to the bridging cyano group in the dinuclear entity. The two ^{15}N signals (Figure 7B) in a saturated solution of *trans*,*trans*-[(CH$_3$)([^{15}N]en)$_2$Co(C^{15}N)Co([^{15}N]en)$_2$(CH$_3$)](PF$_6$)$_3$ are assigned to the two mononuclear entities by comparison with the spectra of the latter two compounds (Figure 7A, Table 4). The two [^{15}N]en resonance signals from the dinuclear entity are not resolved from the mononuclear entities probably due to the broad resonance lines caused by unresolved scalar coupling to the ^{59}Co nucleus ($I = {}^{7}/_{2}$) in combination with the smaller chemical shift range of the cis [^{15}N]en compared to $\delta(^{13}CH_3)$. The formation of a cyano-bridged dimer is confirmed by crystal structure analysis (above).

If the trans ligand L is ordered according to its influence on $\delta(^{13}CH_3)$, the series L = CN$^-$ > NH$_3$ > NO$_2^-$ > N$_3^-$ > H$_2$O > OH$^-$ is obtained irrespective of the actual cis amine ligand for complexes with en, 2,3,2-tet, and cyclam. Related series were found for methylcobinamides[9] (CN$^-$ > pyridine > H$_2$O) and *trans*-[Co(Hdmg)$_2$(L)(CH$_3$)][8] (P(OCH$_3$)$_3$ ≈ P(OCH$_2$CH$_3$)$_3$ ≈ P(C$_6$H$_5$)$_3$ > *N*-methylimidazole ≈ pyridine > H$_2$O). It appears that a strong-field ligand results in a relative deshielding of the methyl ^{13}C nucleus. Related trans influences in cobalamins have been explained by cobalt(III) magnetic anisotropy.[19] The ^{13}C NMR chemical shifts of the benzimidazole moiety in various cobalamins were thus used to determine the cobalt(III) magnetic anisotropy in each derivative. Comparison of the $\delta(^{13}CH_3)$ for the complexes with en, 2,3,2-tet, and cyclam reveals that the major difference is the *span* of the chemical shifts, whereas the overall position on the chemical shift scale is practically unaltered. If the cis ligand is ordered according to its apparent cis influence on $\delta(^{13}CH_3)$, the series en > 2,3,2-tet > cyclam is obtained for L = CN$^-$, whereas the order is reversed for L = N$_3^-$, H$_2$O, and OH$^-$. If the differences in chemical shifts

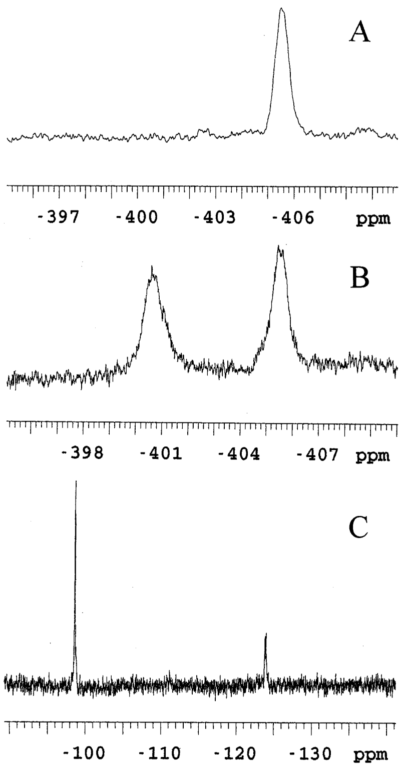

Figure 7. ^{15}N NMR spectra in D$_2$O: (A) *trans*-[Co([^{15}N]en)$_2$(CH$_3$)(CN)](PF$_6$); (B) saturated solution of *trans,trans*-[(CH$_3$)([^{15}N]en)$_2$Co(CN)Co([^{15}N]en)$_2$(CH$_3$)]Br; (C) saturated solution of *trans,trans*-[(CH$_3$)(en)$_2$Co(C^{15}N)Co(en)$_2$ (CH$_3$)]Br$_3$.

Table 4. NMR Data for 0.2 M *trans*-[Co(en)$_2$(CH$_3$)(L)]$^{n+}$ in D$_2$O at 300 K

L	$^1J_{CH}$-(CH$_3$) (Hz)	$T_1(^{13}CH_3)$ (s)	$T_2(^{13}CH_3)$ (ms)	δ-([^{15}N]en)	T_1([^{15}N]en) (s)	T_2([^{15}N]en) (ms)
CN$^-$	128.09	5.53 ± 0.11	106.2 ± 5.3	−405.5	20.84 ± 0.44	176.2 ± 21.4
NH$_3$	131.10	4.04 ± 0.20	28.6 ± 0.3	−403.5	23.67 ± 0.13	51.6 ± 1.4
NO$_2^-$	129.81	4.15 ± 0.22	10.7 ± 0.2	−397.8	20.78 ± 0.40	22.2 ± 0.8
N$_3^-$	133.00	nm[c]	nm	−401.0	nm	nm
OH$_2$	134.11	3.95 ± 0.33	4.33 ± 0.07[a]	−400.6	24.13 ± 0.29	14.7 ± 0.3[b]
OH$^-$	129.04	2.84 ± 0.18	38.0 ± 2.8	−399.9	19.40 ± 0.83	82.6 ± 2.0

[a] $T_1(^{59}Co) = 107 \pm 1\ \mu s$. [b] $T_1(^{59}Co) = 110 \pm 1\ \mu s$. [c] nm = not measured.

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originate from differences in magnetic anisotropy of the cobalt(III) ion, the data indicate an inversion of sign for the anisotropy on going from CN^- to H_2O. In cobalamins the sign of the anisotropy was in fact inverted on going from cyanocobalamin to aquocobalamin.[19b] The present data do not, however, demonstrate whether the observed cis influence is a direct result of the cis ligand. The reduced span in the complexes with cyclam might also reflect a reduction of the trans influence as imposed, for example, by steric restrictions.

Alterations of the magnetic anisotropy by the various amine ligands as well as by the trans ligands thus seem to be in qualitative agreement with the methyl ^{13}C chemical shift data. However, this view would require the amine nitrogen chemical shift to display the reverse series when ordered by L. From the data in Table 4 (cf. parts A and B of Figure 7) it is seen that the order of $\delta(^{15}N)$ is $L = CN^- < NH_3 < N_3^- < H_2O < OH^- < NO_2^-$; i.e., the nitro ligand violates the common order of the methyl ^{13}C and en ^{15}N NMR data. The nitro ligand thus appears to result in a relative deshielding of the cis amine nitrogen nucleus. This seems to be a quite general phenomenon as it was also found in nitrogen NMR of amminecobalt(III),[20a] −rhodium(III),[20b] −platinum(II),[20c] and −platinum(IV)[20c] compounds. In fact, in amminecobalt(III) compounds the nitro ligand results in a progressive deshielding of an ammine ^{14}N nucleus by the increasing number of cis nitro ligands on going from $[Co(NH_3)_5(NO_2)]^{2+}$ to *trans*-$[Co(NH_3)_2(NO_2)_4]^-$.[20d] It may be noted that the NO_2^- ligand is the only trans ligand used which has the possibility of acting as a hydrogen bond acceptor toward the amine hydrogen atoms. To what extent this may influence the amine nitrogen nuclear shielding is not known to our knowledge. The N═O double bond of the nitro ligand has a magnetic anisotropy resulting in a shielding and a deshielding zone in its vicinity,[19c] and this through-space interaction may also contribute to deshielding of the cis amine ligand.

For isoelectronic pairs of compounds it is expected that ^{13}C and ^{15}N (or ^{14}N) chemical shifts follow a common pattern,[14] and it is therefore instructive to compare $\delta(^{13}CH_3)$ with ammine nitrogen chemical shifts. In the absence of ammine nitrogen NMR data for an analogous series, e.g., *trans*-$[Co(en)_2(NH_3)(L)]^{(n+1)+}$, the pentaammine series can be used instead. The order of the trans ammine nitrogen chemical shifts of the latter series ($L = CN^- > NO_2^- > NH_3 > N_3^- > H_2O$)[20a,d] is similar to that for *trans*-$[Co(en)_2(CH_3)(L)]^{n+}$, but the correlation between the two sets of chemical shifts is poorer than one might expect. This may be because the trans influence of a specific ligand L is not constant. The trans influence is likely to vary with, e.g., the Co−L bond length. The elongation of the bond trans to the methyl group is well documented, and this might be sufficient to violate the description of trans influences in terms of, e.g., a simple substituent parameter for each ligand.

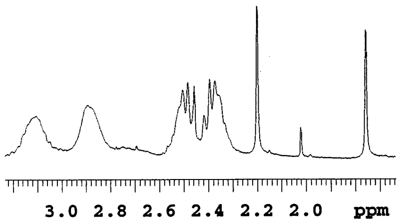

Figure 8. ^1H NMR spectrum of the methyl-^{13}C-enriched *trans*-$[Co(en)_2(^{13}CH_3)(N_3)]ClO_4$ in D_2O. The signals and 1.76 and 2.20 ppm assigned to the doublet from $Co-^{13}CH_3$ are separated by 133.0 Hz. The signal at 2.02 ppm is from $Co-^{12}CH_3$.

Methyl $^1J_{CH}$ Coupling Constants. The ^1H NMR spectra of methyl-^{13}C-enriched preparations of *trans*-$[Co(en)_2(CH_3)(L)]^{n+}$ show a well-resolved splitting of the methyl resonance signal into a doublet, allowing $^1J_{CH}$ to be determined (Figure 8). The results are presented in Table 4, and it is seen that $^1J_{CH}$ is subject to a significant variation depending on the trans ligand. The span of $^1J_{CH}$ is comparable to that of *trans*-$[Co(Hdmg)_2(CH_3)(L)]$ ($L = CH_3^-$, 3,5-Me_2PhS^-, Cl^-).[21a] Since there are only a small number of methyl $^1J_{CH}$ coupling constants for comparable coordination compounds, reference may also be made to organic compounds. The methylcobalt(III) compounds may be viewed as a $CH_{3-}L$ moiety which is intercepted by a CoN_4^{3+} fragment. For the anionic trans ligands the order of $^1J_{CH}$ is $L = CN^- < OH^- < NO_2^- < N_3^-$. This is also the order of $^1J_{CH}$ for acetonitrile (136.1 Hz), methanol (141.0 Hz), and nitromethane (146.0 Hz).[22] $^1J_{CH}$ for methyl azide has to our knowledge not been reported. For the neutral trans ligands, $^1J_{CH}$ is smaller for the ammine complex than for the aqua complex (Table 4). In line with the above discussion, it would be interesting to compare with $^1J_{CH}$ for $CH_3NH_3^+$ and $CH_3OH_2^+$. Methanol is a very weak base,[22b] and a $^1J_{CH}$ coupling constant of the conjugate acid can therefore not be obtained in aqueous solution. Although NMR studies of $CH_3OH_2^+$ have been carried out,[22c,d] $^1J_{CH}$ has to our knowledge not been reported. It is apparent that $^1J_{CH}$ values are decreased in *trans*-$[Co(en)_2(CH_3)(L)]^{n+}$ compared to $CH_{3-}L$, and in particular, the span is smaller. The latter may be ascribed to the longer distances. Marzilli and co-workers[21a] have suggested that the variation in the $^1J_{CH}$ coupling constant primarily reflects the σ-donor ability of the trans ligand. This was later corroborated by an analysis of $^1J_{CH}$ in extended series of *trans*-$[Co(Hdmg)_2(CH_3)(L)]$ (L = phosphine or phosphite ligands).[21b]

One-Bond Metal−Ligand Coupling Constants from Relaxation Measurements. All methyl ^{13}C nuclear spin−lattice relaxation times (T_1) are in the range of several seconds (Table 4) as is typical[22a] for small molecules. By contrast, the observed spin−spin relaxation times (T_2) are smaller by about 2 orders of magnitude. This is consistent

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with the broadening of the ^{13}C resonance signal of the carbon atom coordinated to cobalt(III) being caused by scalar relaxation (sc) of the ^{13}C nucleus. The contributions of scalar relaxation to the total relaxation rates T_1 and T_2 of a nucleus X, which is subject to scalar coupling to a nucleus A with spin I, are[23]

$$\frac{1}{T_{1X}^{\ sc}} = \frac{8\pi^2 J_{AX}^{\ 2}}{3} I(I+1)\left[\frac{T_{2A}}{1 + (\omega_X - \omega_A)^2 T_{2A}^{\ 2}}\right] \qquad (1)$$

and

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

with X = ^{13}C or ^{15}N and A = ^{59}Co. The actual differences in resonance frequencies (ω) between X and A means that scalar relaxation only contributes to T_{2X}. Provided that other relevant relaxation mechanisms contribute evenly to T_{1X} and T_{2X}, the contribution from scalar coupling may be calculated as[24]

$$\frac{1}{T_{2X}^{\ sc}} = \frac{1}{T_{2X}(\text{obsd})} - \frac{1}{T_{1X}(\text{obsd})} \qquad (3)$$

From the data in Table 4 it is apparent that the corrections for T_{1X} are of the same order as the uncertainty on T_{2X}.

Thus, in cases where the ^{59}Co spin−lattice time can be determined with sufficient accuracy, the one-bond scalar coupling constants to ^{13}C or ^{15}N can be estimated. However, for the present cobalt(III) compounds ^{59}Co relaxation times are typically in the microsecond range, and only in the case of *trans*-[Co(en)$_2$(CH$_3$)(H$_2$O)]$^{2+}$ could a ^{59}Co relaxation time be measured by the inversion−recovery technique. As the measured relaxation time may show some variation from sample to sample, T_1(^{59}Co), T_1(^{13}C), and T_2(^{13}C) were measured in three subsequent measurements on the same sample, only retuning the probe. In this way it was attempted to minimize errors that might otherwise arise from variations in the ^{59}Co relaxation rate. Application of eqs 2 and 3 to the relaxation data in Table 4 yields $^1J_{\text{Co}-\text{C}}$ = 102(5) Hz for *trans*-[Co(en)$_2$(CH$_3$)(H$_2$O)]$^{2+}$. This value is very close to that of *trans*-[Co(Hdmg)$_2$(CH$_3$)(H$_2$O)] ($^1J_{\text{Co}-\text{C}}$ = 100 Hz),[8] indicating that the unsaturation of the dimethylglyoximato ligand does not have any major influence on the cobalt−carbon one-bond coupling constant. For the remaining coordination compounds in Table 4, the ^{59}Co line widths[6c] exceed 15 kHz, and T_1(^{59}Co) determinations based on measurement of the line widths were considered too uncertain to allow for any reasonable estimate of $^1J_{\text{Co}-\text{C}}$.

In ^{15}N-enriched samples T_1(^{59}Co), T_1(^{15}N), and T_2(^{15}N) were measured in three subsequent measurements on the same sample. The ^{15}N spin−lattice relaxations are well above 1 s as is typically found in small molecules.[25] Application of eqs 2 and 3 to the relaxation data yields $^1J_{\text{Co}-\text{N}}$ = 55(5) Hz for *trans*-[Co(en)$_2$(H$_2$O)(CH$_3$)]$^{2+}$. By comparison, $^1J_{\text{Co}-\text{N}}$ = 63.8 Hz has been found for [Co(en)$_3$]$^{3+}$.[26]

Comparison of $^1J_{\text{Co}-\text{C}}$ and $^1J_{\text{Co}-\text{N}}$ can be carried out in terms of the reduced coupling constants[27] as defined by $K = 4\pi^2 J/(h\gamma_A\gamma_X)$. This gives the values $|^1K_{\text{Co}-\text{C}}| = 15 \times 10^{20}$ N A^{-2} m^{-3} and $|^1K_{\text{Co}-\text{N}}| = 19 \times 10^{20}$ N A^{-2} m^{-3} for *trans*-[Co(en)$_2$(H$_2$O)(CH$_3$)]$^{2+}$. For [Co(NH$_3$)$_6$]$^{3+}$ it was found[26] that $^1J_{\text{Co}-\text{N}}$ = 62.5 Hz, yielding $|^1K_{\text{Co}-\text{N}}| = 21.7 \times 10^{20}$ N A^{-2} m^{-3}. Thus, the methyl carbanion has a smaller reduced constant for one-bond coupling to ^{59}Co compared with the coordinated ammonia molecule.

Conclusion

X-ray crystallography shows that the Co(III)−C bond lengths in the investigated compounds display a rather narrow range from1.972(3) to 1.9804(18) Å. Despite this, the methyl ^{13}C chemical shifts show a significant variation with the nature of the cis amine ligand in addition to the influence of the trans ligand. In the *trans*-[Co(en)$_2$(CH$_3$)(L)]$^{n+}$ series, the orders of methyl ^{13}C and amine ^{15}N nuclear shieldings are reverse except for L = NO$_2^-$. The cobalt−carbon bond distances are close to those typically observed in methylcobalt(III) compounds with unsaturated equatorial ligands. Furthermore, the cis cobalt−nitrogen bond distances are typical for aminecobalt(III) compounds. From a structural viewpoint there is thus no evidence for any inherent instability of the new compounds despite the lack of an unsaturated ring system. The present class of compounds constitutes a link between the B$_{12}$ model compounds and the “classical” cobalt(III) amine compounds.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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