

# The Pentaamminemethylcobalt(III) Cation: Synthesis and Spectroscopic Characterization

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The preparation and spectroscopic characterization of  $[\text{Co}(\text{NH}_3)_5(\text{CH}_3)]^{2+}$  is reported. This coordination cation was obtained as the analytically pure nitrate salt and was characterized in solution by  $^{13}\text{C}$  and  $^{59}\text{Co}$  NMR, UV–visible spectrophotometry, and cation exchange HPLC. The position of the first absorption band of the visible absorption spectrum of  $[\text{Co}(\text{NH}_3)_5(\text{CH}_3)]^{2+}$  ( $\lambda_{\text{max}}$  ( $\epsilon_{\text{max}}$ ,  $\text{M}^{-1} \text{cm}^{-1}$ ): 481 nm (50)) is very similar to that of the isoelectronic coordination cation  $[\text{Co}(\text{NH}_3)_6]^{3+}$ , thereby demonstrating that the coordinated methyl carbanion has ligand field properties similar to those of the isoelectronic ammonia molecule. Similarly the  $^{59}\text{Co}$  chemical shift value ( $\delta = 7370$  ppm) is close to that of the hexaamminecobalt(III) cation. The  $^{13}\text{C}$  NMR spectrum consists of a single peak at  $\delta = 3.2$  ppm, which is broad ( $\Delta\nu_{1/2} = 18.4$  Hz) due to scalar coupling to the  $^{59}\text{Co}$  nucleus. An estimate of the scalar one-bond cobalt–carbon coupling constant is  $^1J_{\text{Co-C}} = 105(5)$  Hz confirming the existence of a Co–C  $\sigma$ -bond. With respect to the nature of the ligands the title compound is the simplest model compound for the vitamin B<sub>12</sub> coenzyme.

## Introduction

Alkylcobalt(III) compounds containing solely saturated ligands have been reported only in a relatively few cases. The first example was a methylcobalt(III) compound containing the saturated macrocyclic ligand  $\text{Me}_6[14]\text{aneN}_4$  (*C-meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane), namely  $[\text{Co}(\text{Me}_6[14]\text{aneN}_4)(\text{OH}_2)(\text{CH}_3)]^{2+}$ .<sup>1a</sup> Since then a number of related alkylcobalt(III) compounds with saturated macrocyclic ligands have been prepared by employing various synthetic methods.<sup>1</sup> Some of these have been structurally characterized.<sup>1c–e</sup> Another series of classical (*i.e.* Werner-type) cobalt(III) compounds with a Co–C  $\sigma$ -bond have been prepared by coordination of the carbanion formed by the reaction of the corresponding (thioether)cobalt(III) compound in basic solution, and the kinetics and thermodynamics of this reaction have been studied in detail.<sup>2</sup> The latter method has also been employed for preparation of intramolecular alkylcobalt(III) compounds with Schiff-base ligands.<sup>3</sup> An unusual intramolecular alkylcobalt(III) compound has been obtained by deprotonation of a methylene group and subsequent coordination of the carbanion in a cobalt(III) compound with dacoda (the 1,5-diazacyclooctane-*N,N'*-diacetate dianion).<sup>4</sup> Alkylcobalt(III) compounds with unsaturated ligands are much more common. The vast majority of these compounds have been prepared with five nitrogen donor

atoms in addition to the coordinating alkyl group and can thus be regarded as model compounds for the vitamin B<sub>12</sub> coenzyme.<sup>5</sup>

The classical alkylcobalt(III) compounds mentioned above are generally relatively stable although some are light sensitive. It is thus clear that an unsaturated equatorial ligand system is by no means a necessary prerequisite to the formation of stable alkylcobalt(III) compounds. Hence it has been argued that it should be possible to make organocobalt(III) compounds with *e.g.* ammonia as equatorial ligands, although attempts to prepare *e.g.*  $[\text{Co}(\text{NH}_3)_4(\text{OH}_2)(\text{CH}_3)]^{2+}$  or  $[\text{Co}(\text{en})_2(\text{OH}_2)(\text{CH}_3)]^{2+}$  were unsuccessful (*en* = 1,2-ethanediamine).<sup>1b</sup> It may be noted that *cis*- $[\text{Co}(\text{NH}_3)_4(\text{NH}_2)(\text{CH}_3)]^+$  has been used as a model system of the vitamin B<sub>12</sub> coenzyme for molecular orbital calculations investigating the overlap population of the Co–C bond by applying a variety of electronic perturbations.<sup>6</sup>

One of the methods to prepare  $[\text{Co}([14]\text{aneN}_4)(\text{OH}_2)(\text{CH}_3)]^{2+}$  ( $[14]\text{aneN}_4$  = 1,4,8,11-tetraazacyclotetradecane) has employed alkylation of  $[\text{Co}([14]\text{aneN}_4)]^{2+}$  by methylhydrazine with dioxygen as the oxidizing agent<sup>1c</sup> by a route that had originally been developed for the preparation of organocobalt(III) compounds with unsaturated ligands.<sup>7</sup> We have successfully used this method to prepare  $[\text{Co}(\text{NH}_3)_5(\text{CH}_3)]^{2+}$  (Figure 1). In this paper the synthesis and the spectroscopic characterization of this coordination cation is reported. The interest in the pentaamminemethylcobalt(III) cation is that it is the simplest cobalt(III) compound with one coordinated carbon atom and five coordinated nitrogen atoms. In the context of coordination sphere this compound may thus be regarded as the archetype of model compounds for vitamin B<sub>12</sub> coenzyme.

## Experimental Section

**Materials and Instrumentation.** Methylhydrazine was purchased from Aldrich Chemical Co. and used as received. Hexaamminecobalt(III) chloride was prepared according to a literature method.<sup>8</sup> Other

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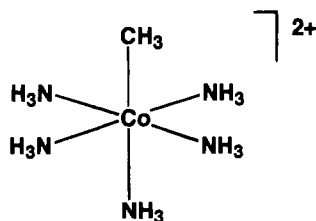


Figure 1. The pentaamminemethylcobalt(III) cation.

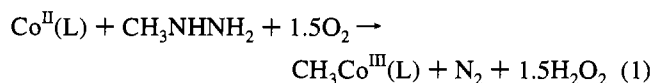
chemicals were of the highest purities available. NMR spectra were measured at 5.87 T on a Bruker AC 250 NMR spectrometer equipped with a 5 mm probe for  $^{13}\text{C}$  NMR measurements or a 10 mm broadband tunable probe for  $^{59}\text{Co}$  NMR measurements.  $\text{D}_2\text{O}$  (Sigma, 99.8 atom % D) was used to provide a deuterium lock. An additional line broadening of 1 Hz was employed for  $^{13}\text{C}$  NMR spectra before Fourier transformation to improve the signal-to-noise ratio.  $^{13}\text{C}$  chemical shift values ( $\delta$ ) are reported in ppm relative to internal sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS;  $\delta = 0, 17.66, 21.74, \text{ and } 57.02$  ppm).  $^{59}\text{Co}$  NMR spectra were measured using the RIDE (ring-down elimination) pulse sequence to suppress probe ringing.<sup>9</sup> With this pulse sequence the dead-time could be reduced to 15  $\mu\text{s}$ .  $^{59}\text{Co}$  chemical shift values ( $\delta$ ) are reported in ppm relative to an external  $\text{D}_2\text{O}$  solution of  $\text{K}_3\text{Co}(\text{CN})_6$  ( $\delta = 0$  ppm), using replacement of the sample. Ion exchange high-performance liquid chromatography was performed using a Waters HPLC system connected to a diode array detector. A Waters Protein Pak SP-5PW cation exchanger was used with 0.20 M  $(\text{NH}_4)_2\text{SO}_4$  adjusted to pH 10.0 with NaOH as eluent. The flow was 1.0 mL  $\text{min}^{-1}$  and the temperature was 25  $^\circ\text{C}$ . UV-visible absorption spectra were obtained on a Cary 3 spectrophotometer.

**Pentaamminemethylcobalt(III) Nitrate.** A 5.82 g (20 mmol) amount of cobalt(II) nitrate hexahydrate was dissolved in 3 mL of water. At 0  $^\circ\text{C}$ , 35 mL of 25% ammonia water was added, followed by 1.0 mL (19.1 mmol) of methylhydrazine. The temperature of the reaction mixture was slowly increased to 20  $^\circ\text{C}$ , and the mixture was stirred at this temperature for 4 h while exposed to atmospheric dioxygen. After the mixture was cooled to 0  $^\circ\text{C}$ , 60 mL of ice-cold acetone was added. The orange crystals were filtered off and washed with a 2:3 mixture of 25% ammonia water and acetone followed by washing with acetone. The crude product (2.9 g) was recrystallized by dissolving it in a minimum volume of ca. 6 M ammonia water followed by precipitation with ice cold methanol. The compound was stored at 4  $^\circ\text{C}$  over dry silica gel. Yield: 1.64 g (30%). Anal. Calcd for  $\text{CoCH}_3\text{N}_7\text{O}_6$ : C, 4.24; H, 6.41; N, 34.63. Found: C, 4.39; H, 6.37; N, 33.98.

## Results and Discussion

**Synthesis.** Alkylation of the pentaamminecobalt(II) cation by methylhydrazine with dioxygen as the oxidizing agent affords the pentaamminemethylcobalt(III) cation in fair yield (30%). The solid nitrate salt is stable for several months when stored at 4  $^\circ\text{C}$  over dry silica gel. It is soluble in dilute ammonia water to give a stable solution and may be spectroscopically characterized in this solution. It is interesting to note that the closely related compound  $[\text{Co}(\text{[14]aneN}_4)(\text{OH}_2)(\text{CH}_3)]^{2+}$  was reported to be sufficiently robust to allow for precipitation with concentrated perchloric acid.<sup>1b,c</sup>

We have so far made no attempts to determine the stoichiometry of the alkylation of the pentaamminecobalt(II) cation by methylhydrazine. Presumably the reaction proceeds similarly to the alkylation of cobalt(II) compounds with unsaturated ligands. In such a case the stoichiometry has been deduced<sup>10</sup> to be in accordance with eq 1. Equation 1 was deduced with L



= salen (the *N,N'*-ethylenebis(salicylideneiminato) dianion). The gas evolved in the reaction was predominantly dinitrogen,

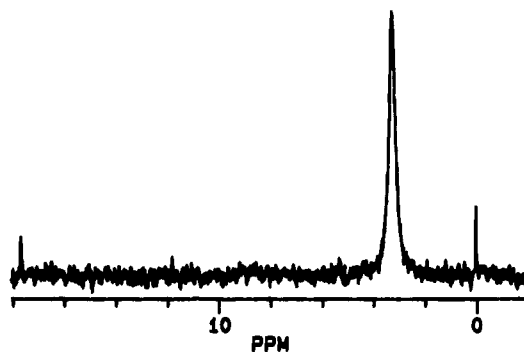


Figure 2.  $^{13}\text{C}$  NMR spectrum (142 000 acquisitions) of  $[\text{Co}(\text{NH}_3)_5(\text{CH}_3)](\text{NO}_3)_2$  in ca. 6 M ammonia water (50%  $\text{D}_2\text{O}$ ) at 300 K. The sharp signals at 0 and 17.66 ppm are from DSS.

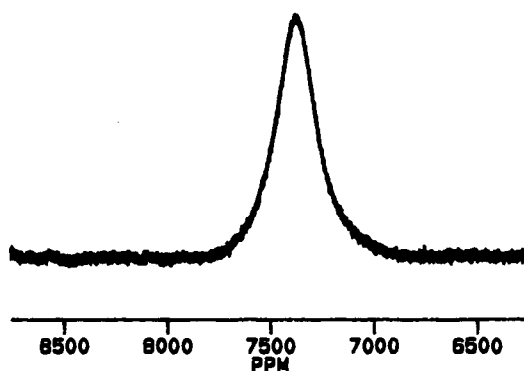


Figure 3.  $^{59}\text{Co}$  NMR spectrum (6000 acquisitions) of  $[\text{Co}(\text{NH}_3)_5(\text{CH}_3)](\text{NO}_3)_2$  in ca. 6 M ammonia water (50%  $\text{D}_2\text{O}$ ) at 300 K.

although in some cases methane was also detected. Alkylation of  $\text{Co}(\text{salen})$  with (5-hexenyl)hydrazine gave not only the corresponding (5-hexenyl)cobalt(III) compound but also a cobalt(III) compound with a coordinated cyclopentylmethyl group, which was taken as evidence for an organic radical intermediate.<sup>10</sup> These studies were carried out in dichloromethane, and it is not yet clear whether the same mechanism is operative in aqueous solution.

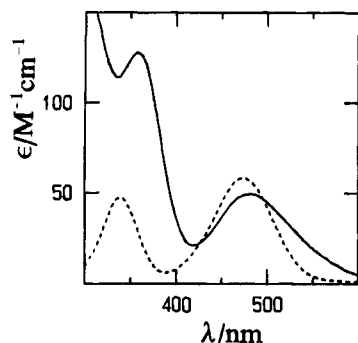
**Characterization.** A particular characteristic of organocobalt(III) compounds is the very broad  $^{13}\text{C}$  NMR signal of the coordinated carbanion caused by scalar coupling between the  $^{59}\text{Co}$  nucleus (spin  $I = 7/2$ , 100% natural abundance) and the  $^{13}\text{C}$  nucleus ( $I = 1/2$ ).<sup>2b</sup> The  $^1\text{H}$  decoupled  $^{13}\text{C}$  NMR spectrum of  $[\text{Co}(\text{NH}_3)_5(\text{CH}_3)]^{2+}$  in ca. 6 M ammonia water (50%  $\text{D}_2\text{O}$ ) at 300 K consists of a single broad signal at  $\delta = 3.2$  ppm (Figure 2). For comparison the  $^{13}\text{C}$  nucleus of the methyl group of methylcobalamin resonates at  $\delta = 6.5$  ppm, and it was found that the methyl  $^{13}\text{C}$  resonance frequency of  $\text{B}_{12}$  derivatives is quite sensitive to the *trans* ligand.<sup>11</sup> Fitting of a Lorentzian to the  $^{13}\text{C}$  NMR signal in Figure 2 yielded a line width of  $\Delta\nu_{1/2} = 18.4$  Hz.

Figure 3 shows the  $^{59}\text{Co}$  NMR spectrum of  $[\text{Co}(\text{NH}_3)_5(\text{CH}_3)]^{2+}$  in ca. 6 M ammonia water (50%  $\text{D}_2\text{O}$ ) at 300 K. It displays a very broad signal at  $\delta = 7370$  ppm with a line width of  $\Delta\nu_{1/2} = 13.2$  kHz. This signal was assigned to the pentaamminemethylcobalt(III) cation. The very large line width should be compared with the full spectral window of 166 kHz. For a Lorentzian line shape this line width corresponds to a spin-spin relaxation time  $T_2 = 24$   $\mu\text{s}$  which should be compared

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**Figure 4.** UV-visible absorption spectra of  $[\text{Co}(\text{NH}_3)_5(\text{CH}_3)](\text{NO}_3)_2$  (—) and  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  (---) in 5.0 M ammonia water at 20 °C.

with the dead-time of 15  $\mu\text{s}$  (see Experimental Section). The present case illustrates the problems of obtaining very broad NMR signals by pulse techniques. However, the chemical shift value and the line width correspond well to those observed for a related alkylcobalt(III) compound ( $[\text{Co}(\text{tacn})(\text{C-aeaps})](\text{ClO}_4)_2$ ,  $\delta = 6540$  ppm and  $\Delta\nu_{1/2} = 12.48$  kHz in acetonitrile- $d_3$  at 330 K (tacn is 1,4,7-triazacyclononane and C-aeaps is the 1,6-diamino-3-thia-4-hexanide anion)).<sup>2b</sup> The  $^{59}\text{Co}$  chemical shift value ( $\delta = 7370$  ppm) is only little lower than that of the isoelectronic coordination cation  $[\text{Co}(\text{NH}_3)_6]^{3+}$  ( $\delta = 8178$  ppm<sup>12</sup>) showing that the coordinated methyl carbanion has ligand field properties similar to those of the isoelectronic ammonia molecule.

The  $^{59}\text{Co}$  NMR signal of the hexaamminecobalt(III) cation is a narrow line due to the  $O_h$  symmetry of this compound. However, in the isoelectronic pentaamminemethylcobalt(III) cation there is a large electric field gradient due to the charge of the coordinated methyl carbanion. Hence quadrupolar relaxation becomes very efficient resulting in a very large line width of the  $^{59}\text{Co}$  NMR signal from this compound.

For  $\omega^2\tau_c^2 \ll 1$  the spin-spin relaxation time  $T_2$  for the  $^{59}\text{Co}$  nucleus is related to the electric field gradient tensor according to eq 2,<sup>13</sup> where  $\tau_c$  is the rotational correlation time and the

$$\frac{1}{T_2} = \frac{3\pi^2}{10} \frac{2I+3}{I^2(2I-1)} \left(1 + \frac{\eta^2}{3}\right) \left(\frac{e^2Qq}{h}\right)^2 \tau_c \quad (2)$$

quantity  $eq = V_{zz}$  is, by definition, that component of the electric field gradient tensor having the largest magnitude in the principal-axis system. The other symbols have their usual meaning. The asymmetry parameter  $\eta = (V_{xx} - V_{yy})/V_{zz}$  is zero for an axially symmetric field gradient.  $A = e^2Qq/h$  is called the quadrupole coupling constant. With  $\tau_c$  known it is thus possible to calculate the quadrupole coupling constant for the  $^{59}\text{Co}$  nucleus from the nuclear spin-spin relaxation time provided that quadrupolar relaxation is the only mechanism of relaxation. The rotational correlation time of  $[\text{Co}(\text{NH}_3)_6]^{3+}$  in

aqueous solution has been estimated to be 10.35 ps.<sup>14</sup> It is reasonable to assume that the same value of  $\tau_c$  is valid for  $[\text{Co}(\text{NH}_3)_5(\text{CH}_3)]^{2+}$  since the two coordination cations must have very similar radii. With  $\tau_c = 10.35$  ps and  $T_2 = 24.1$   $\mu\text{s}$  eq 2 yields  $A = 99.7$  MHz. This value is somewhat larger than those of some related coordination cations such as e.g.  $[\text{Co}(\text{NH}_3)_5(\text{OH})]^{2+}$  (38.8 MHz) and  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$  (35.2 MHz).<sup>14</sup> These values are based on the assumption that relaxation due to quadrupole interaction is the only significant mechanism of relaxation. However, for some cobalt(III) compounds magnetic field dependent relaxation rates have been observed, and in these cases the contribution from quadrupolar relaxation may be obtained by extrapolation to zero field.<sup>15</sup> If the magnetic field dependence of the  $^{59}\text{Co}$  nuclear relaxation time is small, as it is in the case of e.g.  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ ,<sup>15</sup> neglect of this contribution to  $T_2$  causes only a small error in the estimation of  $A$ .

Provided that the spin-spin relaxation time,  $T_{2,C}$ , of the  $^{13}\text{C}$  nucleus and the spin-lattice relaxation time,  $T_{1,Co}$ , of the  $^{59}\text{Co}$  nucleus is known, the scalar one-bond coupling constant,  $J_{C-Co}$ , may be calculated from eq 3.<sup>13</sup> Equation 3 is valid for  $1/T_{1A} \gg$

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

$J_{AX}$ . In the present case  $X = C$ ,  $A = \text{Co}$ , and  $I = 7/2$ . With  $T_{2,C}$  determined from the line shape of the  $^{13}\text{C}$  NMR signal and  $T_{1,Co}$  taken equal to  $T_{2,Co}$ , eq 3 yields  $J_{C-Co} = 105$  Hz. The uncertainty of the calculated coupling constant was estimated to be  $\pm 5$  Hz. For comparison, earlier determinations of cobalt-carbon coupling constants in alkylcobalt(III) compounds were found to be between 79 and 117 Hz,<sup>2b,16</sup> and the value found here of approximately 100 Hz is certainly within the expected range. This confirms the existence of a Co-C  $\sigma$ -bond in this coordination compound.

HPLC analysis confirmed that pentaamminemethylcobalt(III) cation is a dication. The analysis was performed in an ammonium/ammonia buffer at pH 10 because the compound is stable under this condition. With this eluent  $[\text{Co}(\text{NH}_3)_5(\text{CH}_3)]^{2+}$  eluted as the only peak. The retention time was 6 min which was typical for a dication. For comparison the retention time for  $[\text{Co}(\text{NH}_3)_6]^{3+}$  was 11 min under these conditions.

The UV-visible absorption spectrum of  $[\text{Co}(\text{NH}_3)_5(\text{CH}_3)](\text{NO}_3)_2$  in 5.0 M ammonia water is shown in Figure 4 ( $\lambda_{\text{max}}$  ( $\epsilon_{\text{max}}$ ,  $\text{M}^{-1} \text{cm}^{-1}$ ): 358 nm (128), 481 nm (50)). For comparison, that of  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  is also shown ( $\lambda_{\text{max}}$  ( $\epsilon_{\text{max}}$ ,  $\text{M}^{-1} \text{cm}^{-1}$ ): 338 nm (48), 474 nm (58)). The position of the first absorption band of the two isoelectronic coordination cations is seen to be very close. This confirms the  $^{59}\text{Co}$  NMR results that the coordinated methyl carbanion has ligand field properties similar to those of the ammonia molecule.

Crystal structure determinations and ligand exchange reactions of the pentaamminemethylcobalt(III) cation and related compounds are now being carried out.

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