Cobalt Complexation with Unsymmetrical Tripodal Ligands

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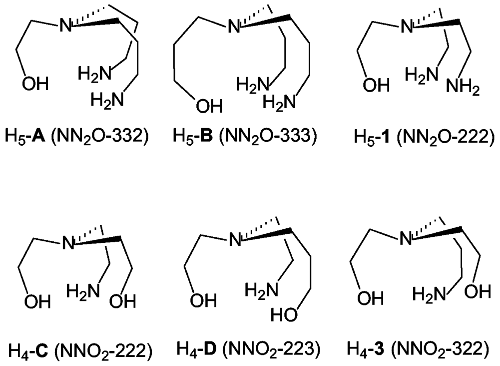
The reaction of the aliphatic unsymmetrical tripod [$N(CH_2CH_2NH_2)_2(CH_2CH_2OH)$], H_5-**1**, with cobalt(II) chloride in THF yields after aerial oxidation the dinuclear complex [(H_4-**1**)Co^{III}(μ-OH)Co^{III}(H_4-**1**)]($Co^{II}Cl_4$)Cl, [**5**]($CoCl_4$)Cl. The trianion **5**$^{3-}$ contains two cobalt atoms triply bridged by two alkoxo groups of the singly deprotonated ligand (H_4-**1**)$^-$ and a hydroxo group. The new ligand [$N(CH_2CH_2CH_2NH_2)(CH_2CH_2OH)_2$], H_4-**3**, providing an N_2O_2 donor set reacts with cobalt(II) chloride to give after aerial oxidation the hexanuclear complex [Co^{III}_4(H_2-**3**)$_4$$Co^{II}_2$$(HOMe)_2Cl_2$($\mu$-OH)$_4$], [**6**]$Cl_2$, containing an unprecedented mixed-valent $Co^{III}_4Co^{II}_2$ core.

Key words: Cobalt, Tripodal Ligands, Aminoalcohols, Crystal Structure

Introduction

Until recently, unsymmetrically built or substituted aliphatic tripodal ligands have received little attention. The main reason for this situation is the cumbersome, often time consuming synthesis of such derivatives [1]. We have initiated a program to synthesize and evaluate the coordination chemistry of N-centered unsymmetrical aliphatic tripodal ligands. Initially, aliphatic tetramine tripods with an unsymmetrical topology [2] were studied. Later alcohol functions were incorporated into the tripodal ligands [3]. We reported on aliphatic tripods providing an NOS_2 donor set [4] and described the preparation and coordination chemistry of a totally unsymmetric N-centered ligand with NH_2, OH and SH donor groups [5].

Cobalt complexes of aliphatic amine ligands have been studied for their potential in hydrolyzing phosphate esters [6]. We intended to prepare cobalt complexes of tripods providing an NN_2O or NNO_2 donor set and to investigate their catalytic activity in the hydrolysis of phosphate esters. However, substitution of an alkylamine donor in tris(2-aminoethyl)amine (tren) or tris(3-aminopropyl)amine (trpn) for an alkoxy donor generates a ligand with a much higher tendency to bridge metal centers with the *O*-donor function thereby enhancing the tendency to form polynuclear complexes. For example, the reaction of iron salts with the NNO_2 ligand H_4-**D** (Scheme 1) leads to cubane clusters [7], while the NNO_2 ligand H_4-**C** [3b] and the NN_2O ligands H_5-**A** [8], H_5-**B** [8] and H_5-**1** [3b, 9] react with zinc salts with formation of mono- or dinuclear zinc complexes.



H_5-**A** (NN_2O-332) H_5-**B** (NN_2O-333) H_5-**1** (NN_2O-222)

H_4-**C** (NNO_2-222) H_4-**D** (NNO_2-223) H_4-**3** (NNO_2-322)

Scheme 1. Unsymmetrical tripodal ligands.

In this contribution, we describe the synthesis of the unsymmetrical NN_2O ligand H_4-**3**. In addition, the products of the reaction of H_5-**1** [3b] with cobalt(II) chloride and of H_4-**3** with cobalt(II) chloride hexahydrate, both followed by aerial oxidation, are presented.

Experimental Section

Chemicals and most solvents are purchased from Aldrich, Acros and Merck. THF and diethyl ether are distilled prior to use from sodium/benzophenone under argon. NMR spectra are recorded on a Bruker AC 200 NMR spectrometer. IR spectra are measured on a Bruker Vector 22 FT spectrome-

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ter as KBr pellets. MALDI mass spectra are obtained on a Bruker Reflex IV spectrometer. Elemental analyses are performed with a Vario EL III CHNS-O Elemental Analyzer at the Institut für Anorganische und Analytische Chemie, Westfälische Wilhelms-Universität Münster. Ligand H_5-**1** is prepared as described previously [3b].

N,N-Bis(2-hydroxyethyl)-3-aminopropionitrile H_2-**2**

Freshly distilled diethanolamine (57.11 g, 0.543 mol) is placed in a Schlenk flask under argon and cooled to −5 °C. To this is added dropwise acrylonitrile (28.83 g, 0.543 mmol). The reaction mixture is stirred over night at room temperature. Subsequently volatiles are removed under reduced pressure leaving analytically pure H_2-**2** as a colorless liquid in essentially quantitative yield. Yield 85.9 g (0.54 mol, 99%). – ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 3.80 (s, 2 H, OH), 3.53 (t, 4 H, CH_2OH), 2.82 (t, 2 H, NCH_2CH_2CN), 2.61 (t, 4 H, NCH_2CH_2OH), 2.49 (t, 2 H, NCH_2CH_2CN). – ^{13}C {^{1}H} NMR ($CDCl_3$, 50.3 MHz): δ = 119.2 (CN), 60.1 (CH_2OH), 55.8 (NCH_2CH_2OH), 50.6 (NCH_2CH_2CN), 16.3 (CH_2CN).

N,N-bis(2-hydroxyethyl)-propylenediamine H_4-**3**

Lithium aluminium hydride (4.00 g, 0.105 mol) is suspended in THF (120 ml) and placed in a 250 ml Schlenk flask. After stirring for 30 minutes while cooling to −5 °C, concentrated sulfuric acid (3.85 g, 0.038 mol) is added carefully dropwise (*Caution*: this is a strongly exothermic reaction with hydrogen evolution). The suspension is stirred for 60 minutes and *N,N*-bis(2-hydroxyethyl)-3-aminopropionitrile H_2-**2** (3.09 g, 0.02 mol) dissolved in THF (30 ml) is slowly added. The reaction mixture should not be allowed to boil during addition of the nitrile. The reaction mixture is stirred at room temperature for 8 h and then quenched by slow addition of degassed water (6.2 g, 0.34 mol) at 0 °C. The resulting suspension is filtered under argon. The filtrate contains H_4-**3** and side products, but most of the ligand is found in the solid residue. It is isolated by continuous extraction with methanol for one to three days. The methanol extract and the original filtrate are combined and dried over sodium sulfate. Removal of the solvent yields a colorless to yellow residue, which is suspended in dichloromethane and dried over sodium sulfate. The drying agent and precipitated lithium salts are separated by filtration through Celite®. Distillation under reduced pressure (180 °C, 0.05 mbar) gives H_4-**3** as a colorless viscous oil. Yield 1.03 g (6.35 mmol, 32%). – ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 3.51 (t, 4 H, NCH_2CH_2OH), 3.25 (s br, 4 H, $OH + NH_2$), 2.76 (t, 2 H, $NCH_2CH_2CH_2NH_2$), 2.54 (t, 4 H, NCH_2CH_2OH), 2.52 (t, 2 H, $NCH_2CH_2CH_2NH_2$), 1.56 (qi, 2 H, $NCH_2CH_2CH_2NH_2$). – ^{13}C {^{1}H} NMR (50.3 MHz, $CDCl_3$): δ = 59.4 (CH_2OH), 56.1 (NCH_2CH_2OH), 52.3 ($NCH_2CH_2CH_2NH_2$), 40.1 ($NCH_2CH_2CH_2NH_2$), 29.4 ($NCH_2CH_2CH_2NH_2$). – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3430 (s, OH), 3354 (s, NH), 3281 (s, NH), 2942 (s), 2868 (s), 1600 (m), 1462 (m), 1366 (m), 1151 (m), 1044 (s). – MALDI MS (337.0 nm, 3 ns): *m/z* (%) = 163.0 (100) $[MH]^+$, 106.1 (12) $[H_2N(CH_2CH_2OH)_2]^+$. – $C_7H_{18}N_2O_2$ (162.23): calcd. C 51.88, H 11.18, N 17.27; found C 51.50, H 11.55, N 16.95.

$[(H_4\text{-}\mathbf{1})Co^{III}(\mu\text{-}OH)Co^{III}(H_4\text{-}\mathbf{1})](Co^{II}Cl_4)Cl$, $[\mathbf{5}]\,(Co^{II}Cl_4)Cl$

Anhydrous cobalt(II) chloride (195 mg, 1.5 mmol) is suspended in THF (20 ml). Ligand H_5-**1** (220 mg, 1.5 mmol) is added and the reaction mixture is stirred for 5 days. The amount of cobalt(II) chloride decreases and a small residue of blue powder is removed by filtration. Diffusion of diethyl ether into the resulting blue solution gives blue air sensitive crystals, presumably of complex **4**. These crystals are isolated by filtration, dissolved in methanol and exposed to air. The color changes from blue to red. Slow diffusion of diethyl ether into the red solution gives dark red single crystals of $[\mathbf{5}](Co^{II}Cl_4)Cl$ which are suitable for an X-ray diffraction study. Yield 90 mg (0.13 mmol, 18%). – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3363 (m), 3238 (m), 3192 (m), 3102 (m), 2963 (m, CH), 2880 (m, CH), 1605 (m), 1472 (m), 1309 (m), 1242 (s), 1153 (s), 1065 (w), 1038 (s), 984 (s). – MALDI MS (330 nm, 3 ns, DHB): *m/z* (%) = 366 (100) $[Co(H_4\text{-}\mathbf{1})_2O]^+$.

$[Co^{III}{}_4(H_2\text{-}\mathbf{3})_4Co^{II}{}_2(HOMe)_2Cl_2(\mu\text{-}OH)_4]Cl_2$, $[\mathbf{6}]Cl_2$

A solution of H_4-**3** (330 mg, 2.0 mmol) in methanol (10 ml) is added to a solution of $CoCl_2 \cdot 6H_2O$ (470 mg; 2.0 mmol) in methanol (15 ml). To this is added triethylamine (400 mg, 4.0 mmol) and the resulting red brown solution is stirred for 5 days. Diffusion of diethyl ether into the reaction mixture gives a precipitate of colorless needles ($HNEt_3Cl$) which are covered by a dark red amorphous material. Several recrystallization steps allow to remove the triethylammonium chloride and the isolation of dark red crystals of $[\mathbf{6}]Cl_2 \cdot 4CH_3OH \cdot H_2O$. Single crystals suitable for X-ray diffraction are obtained by this method at 4 °C. Yield 150 mg (0.11 mmol). – MALDI MS (330 nm, 3 ns, DHB) *m/z* (%) = 102 (100) $[HNEt_3]^+$, 163 (30) $[H_5\text{-}\mathbf{3}]^+$.

X-ray structure determinations

Suitable crystals of $[\mathbf{5}](CoCl_4)Cl$ and $[\mathbf{6}]Cl_2 \cdot 4\,CH_3OH \cdot H_2O$ were mounted on a Bruker AXS 2000 CCD diffractometer equipped with a rotating molybdenum anode (λ = 0.71073 Å) and a CCD area detector. Diffraction data were measured at 153(2) K in the range $3.4 \le 2\theta \le 55.0°$ for $[\mathbf{5}](CoCl_4)Cl$ and $2.8 \le 2\theta \le 50.0°$ for $[\mathbf{6}]Cl_2 \cdot 4CH_3OH \cdot H_2O$. Structure solution [10] and refinement [11] were achieved with standard Patterson and Fourier techniques. All non-hydrogen atoms with the exception of three of the four non-coordinated methanol molecules and the water molecule in [**6**]$Cl_2 \cdot 4CH_3OHH_2O$ were refined with anisotropic displacement parameters. The positional parameters of the atoms of these solvent molecules, which are partially disordered, were refined with isotropic displacement parameters. Hydrogen atoms were added to the structure models in calculated positions with two exceptions: (i) no hydrogen positions were determined for disordered solvent molecules and (ii) the positional parameters for the proton at the bridging hydroxyl group in $[\mathbf{5}]^{3-}$ were identified and refined. The asymmetric unit of [**6**]$Cl_2 \cdot 4CH_3OHH_2O$ contains two independent halves of the cation $[\mathbf{6}]^{2+}$, each of which is related to the second half by an inversion center.

*Selected crystallographic details for [**5**](CoCl₄)Cl*

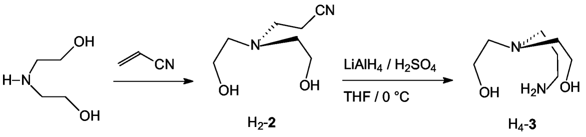
Formula $C_{12}H_{33}N_6Cl_5Co_3O_3$, $M = 663.48$, red crystal $0.11 \times 0.05 \times 0.04$ mm, $a = 22.2845(9)$, $b = 14.3459(6)$, $c = 14.9396(6)$ Å, $\beta = 92.603(1)^\circ$, $V = 4771.1(3)$ Å^3, $\rho_{\mathrm{calcd}} = 1.847$ g cm^{-3}, $\mu = 2.648$ mm^{-1}, empirical absorption correction ($0.7594 \le T \le 0.9015$), $Z = 8$, monoclinic, space group $C2/c$, 23049 intensities collected ($\pm h$, $\pm k$, $\pm l$), 5477 independent ($R_{\mathrm{int}} = 0.034$) and 4878 observed intensities [$I \ge 2\sigma(I)$], 266 refined parameters, $R = 0.0315$, $wR2 = 0.0697$, max. residual electron density 0.771 (-0.486) e Å^{-3}.

*Selected crystallographic details for [**6**]$Cl_2 \cdot 4CH_3OH \cdot H_2O$*

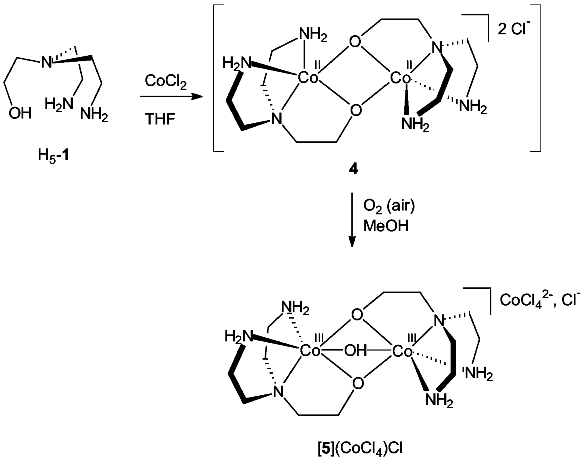
Formula $C_{34}H_{94}N_8Cl_4Co_6O_{19}$, $M = 1414.55$, red crystal $0.10 \times 0.09 \times 0.06$ mm, $a = 11.3675(5)$, $b = 14.6965(7)$, $c = 16.6642(8)$ Å, $\alpha = 89.2920(10)$, $\beta = 89.1960(10)$, $\gamma = 81.1320(10)^\circ$, $V = 2750.3(2)$ Å^3, $\rho_{\mathrm{calcd}} = 1.711$ g cm^{-3}, $\mu = 2.036$ cm^{-1}, empirical correction ($0.8228 \le T \le 0.8879$), $Z = 2$, triclinic, space group $P\bar{1}$, 22354 intensities collected ($\pm h$, $\pm k$, $\pm l$), 9703 independent ($R_{\mathrm{int}} = 0.036$) and 7906 observed intensities [$I \ge 2\sigma(I)$], 615 refined parameters, $R = 0.0481$, $wR2 = 0.1292$, max. residual electron density 3.107 (-1.387) e Å^{-3} (near disordered solvent molecules). Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-257323 for [**5**]($CoCl_4$)Cl and CCDC-257324 for [**6**]$Cl_2 \cdot 4CH_3OH \cdot H_2O$. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union road, CambridgeCB2 1EZ, UK [fax: int. code +44(1223)3 36-033, e-mail: deposit@ccdc.cam.ac.uk].

Results and Discussion

A procedure similar to the one published for the preparation of H_5-**1** [3b] can be used to synthesize ligands H_2-**2** and H_4-**3** (Scheme 2). Michael addition of acrlonitrile to diethanolamine [12] gave H_2-**2** in nearly quantitative yield. The nitrile group of H_2-**2** was reduced with aluminium hydride, which was prepared from $LiAlH_4$ and concentrated sulfuric acid [13].



Scheme 2. Synthesis of the tripodal ligand H_4-**3**.



Scheme 3. Preparation of complex $[(H_4\text{-}\mathbf{1})Co^{III}(\mu\text{-}OH)Co^{III}(H_4\text{-}\mathbf{1})](Co^{II}Cl_4)Cl$, [**5**]($CoCl_4$)Cl.

Complex [**5**]($CoCl_4$)Cl was isolated from the reaction of ligand H_5-**1** with cobalt(II) chloride followed by aerial oxidation (Scheme 3). The reaction mixture of H_5-**1** and anhydrous cobalt(II) chloride in THF remained a suspension with a decreasing amount of cobalt(II) chloride upon stirring for several days. Filtration of this suspension afforded a dark blue solution. Diffusion of diethyl ether into this filtrate under anaerobic conditions precipitated dark blue single crystals of a cobalt(II) species (presumably **4**). These crystals dissolved in methanol. Upon aerial oxidation the blue methanol solution turned to red immediately. From this red solution dark red crystals of [**5**]($CoCl_4$)Cl precipitated upon addition of diethyl ether.

The presence of ligand $\mathbf{1}^{n-}$ in the red crystals can be concluded from an IR spectrum. The MALDI mass spectrum suggests a chemical composition of one cobalt atom and two molecules of ligand $(H_4\text{-}\mathbf{1})^-$. The X-ray diffraction analysis of the red crystals shows the composition to be [**5**]($CoCl_4$)Cl. Both Co^{III} and Co^{II}

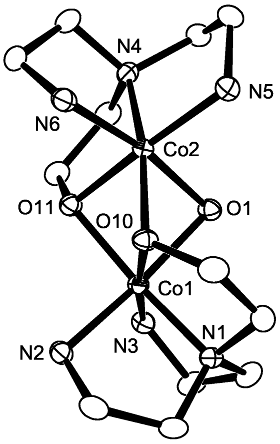


Fig. 1. Molecular structure of the dinuclear cation $[\mathbf{5}]^{3+}$. Hydrogen atoms are omitted. Selected bond lengths [Å] and angles [°]: Co1-Co2 2.5242(4), Co1-O1 1.915(2), Co1-O10 1.909(2), Co1-O11 1.919(2), Co1-N1 1.919(2), Co1-N2 1.925(2), Co1-N3 1.943(2), Co2-O1 1.923(2), Co2-O10 1.922(2), Co2-O11 1.909(2), Co2-N4 1.917(2), Co2-N5 1.932(2), Co2-N6 1.918(2); O1-Co1-O10 79.34(7), O1-Co1-O11 83.34(7), O1-Co1-N1 93.60(8), O1-Co1-N2 169.41(8), O1-Co1-N3 95.04(8), O10-Co1-O11 81.47(7), O10-Co1-N1 88.28(7), O10-Co1-N2 90.28(8), O10-Co1-N3 173.39(8), O11-Co1-N1 169.68(8), O11-Co1-N2 93.10(8), O11-Co1-N3 101.49(8), N1-Co1-N2 88.15(8), N1-Co1-N3 88.58(8), N2-Co1-N3 93.44(8), O1-Co2-O10 78.83(7), O1-Co2-O11 83.38(7), O1-Co2-N4 99.81(8), O1-Co2-N5 90.70(8), O1-Co2-N6 169.92(8), O10-Co2-O11 81.40(7), O10-Co2-N4 169.33(8), O10-Co2-N5 102.07(8), O10-Co2-N6 92.32(8), O11-Co2-N4 87.93(8), O11-Co2-N5 172.47(8), O11-Co2-N6 90.59(8), N4-Co2-N5 88.50(9), N4-Co2-N6 87.99(9), N5-Co2-N6 95.91(9), Co1-O1-Co2 82.24(7), Co1-O10-Co2 82.44(6), Co1-O11-Co2 82.51(6).

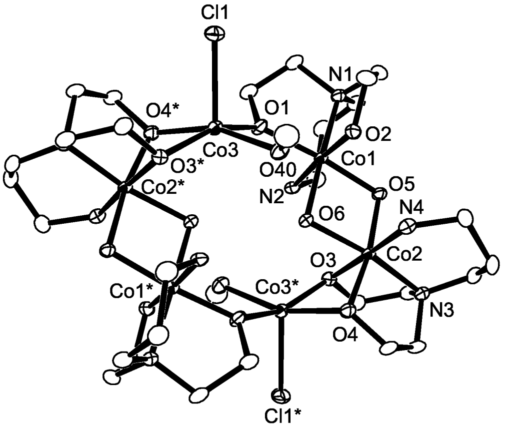


Fig. 2. Molecular structure of one of the two hexanuclear cations $[\mathbf{6}]^{2+}$ in the unit cell. Hydrogen atoms are omitted. Starred atoms represent coordinates related by an inversion center. Selected bond lengths [Å] and angles [°]: Co1-O1 1.891(3), Co1-O2 1.911(3), Co1-O5 1.924(3), Co1-O6 1.943(3), Co1-N1 1.960(4), Co1-N2 1.941(4), Co2-O3 1.922(3), Co2-O4 1.867(3), Co2-O5 1.920(3), Co2-O6 1.927(3), Co2-N3 1.944(4), Co2-N4 1.939(4), Co3-Cl1 2.4108(12), Co3-O1 1.989(3), Co3-O3* 2.047(3), Co3-O4* 2.070(3), Co3-O40 2.071(3), Co1-Co2 2.8941(8), Co1-Co3 3.5293(8), Co2-Co3* 2.7832(8); Co1-O1-Co3 130.9(2), Co2-O3-Co3* 88.98(12), Co2-O4-Co3* 89.81(12), Co1-O5-Co2 97.67(13), Co1-O6-Co2 98.82(13).

are present in the crystals. Co$^{\mathrm{II}}$ is found in the tetrahedral $[\mathrm{CoCl_4}]^{2-}$ dianions which together with Cl^- constitute the anions in the crystal structure. The cation $[\mathbf{5}]^{3+}$ is a triply bridged dinuclear Co$^{\mathrm{III}}$ complex with $(\mathrm{H_4}$-$\mathbf{1})^-$ as a tetradentate ligand (Fig. 1). Only the alcohol functions of the ligands are deprotonated. They act as bridges between two Co$^{\mathrm{III}}$ centers. The third bridge is formed by a hydroxo group.

All three Co-O-Co angles measure about 82°. The six Co-O distances fall in a narrow range from 1.909(2) to 1.923(2) Å. The Co-N distances are also very similar [1.917(2) to 1.943(2) Å]. The distance between cobalt centers measures 2.5242(4)˜Å. Triply bridged dinuclear Co$^{\mathrm{II}}$ and Co$^{\mathrm{III}}$ complexes are known with acac (acac = 2,4-pentadionate) [14], acetate [15], phosphine oxide [16] and alkoxide or hydroxide anions [16, 17] as bridging ligands. In most cases cobalt is coordinated by six oxygen atoms. Two of the described complexes are closely related to $[\mathbf{5}]^{3+}$. An $\mathrm{N_3O_3}$ donor set like in $[\mathbf{5}]^{3+}$ is found in the dinuclear Co$^{\mathrm{III}}$ complexes with triazacyclononane (tacn) [17c] and dipropylene triamine [17d]. In these cases the Co$^{\mathrm{III}}$ centers are bridged by three hydroxo ligands. This leads to slightly longer Co-Co distances [2.565(1) Å and 2.579(1) Å] compared to $[\mathbf{5}]^{3+}$.

We propose a dinuclear Co$^{\mathrm{II}}$ intermediate **4** (Scheme 3) for the formation of $[\mathbf{5}]^{3+}$. In contrast to Co$^{\mathrm{III}}$, Co$^{\mathrm{II}}$ is often found four- or five-coordinate. However, the intermediate was not further characterized and therefore a mononuclear Co$^{\mathrm{II}}$ intermediate cannot be ruled out.

Ligand $\mathrm{H_4}$-**3** was added to $\mathrm{CoCl_2\cdot 6H_2O}$ in methanol in the presence of two equivalents of triethylamine. The color of the solution turned brownish red upon stirring in air for 5 days. Colorless triethylammonium chloride and dark red prisms precipitated after slow addition of diethyl ether. A MALDI mass spectrum of a mixture of both crystals shows the protonated ligand $(\mathrm{H_5}$-$\mathbf{3})^+$ and the triethylammonium cation. Mechanical separation of triethylammonium chloride allowed the isolation of the red crystals. They were recrystallized from methanol and found by X-ray diffraction to have the composition $[Co^{III}_4(H_2\text{-}\mathbf{3})_4Co^{II}_2(HOMe)_2Cl_2(\mu\text{-}OH)_4]Cl_2 4CH_3OH{\cdot}H_2O$ $[\mathbf{6}]Cl_2 \cdot 4CH_3OH{\cdot}H_2O$.

Complex $[\mathbf{6}]^{2+}$ is a dicationic hexanuclear Co^{III}_4 Co^{II}_2 cluster (Fig. 2). Six cobalt atoms, four ligand molecules, four bridging hydroxo anions, two methanol molecules and two chloride ligands form a centrosymmetric wheel $[Co^{II}Cl(CH_3OH)(\mu\text{-}H_2\text{-}\mathbf{3})Co^{III}(\mu\text{-}OH)_2Co^{III}(\mu\text{-}H_2\text{-}\mathbf{3})]_2{}^{2+}$. One (Co1-Co3) or both (Co2-Co3*) of the alkoxo groups of each coordinated ligand act as bridges between Co^{III} and Co^{II} centers. The assignment of cobalt oxidation states is consistent with the observed Co-O bond lengths, which are longer for Co^{II} (average: 2.04 Å) than for Co^{III} (average 1.91 Å). Similar values are found in literature [14–17].

The hexanuclear arrangement of the cobalt atoms in $[\mathbf{6}]^{2+}$ is unique. A tetranuclear $Cu^{II}_2Co^{III}_2$ ring is known with diethanolamine as a ligand [18]. In this molecule diethanolamine coordinated to Co^{III} is doubly deprotonated with one alkoxo function bridging two metal centers and the other one coordinating to only one metal. EPR experiments established that the tetranuclear complex retains its structure in methanol or DMF solution.

In summary, coordination of both H_5-**1** or H_4-**3** promotes the oxidation of Co^{II} to Co^{III}. Further variations of aliphatic tripodal ligands may provide more interesting structural arrangements in cobalt coordination chemistry, because the ligand topology is one governing force in the cluster formation aside from the nature of the metal site or the solubility of the resulting coordination compounds.

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