Cobalt Complexation with Unsymmetrical Tripodal Ligands

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The reaction of the aliphatic unsymmetrical tripod \([\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)\text{2}(\text{CH}_2\text{CH}_2\text{OH})]\), \(\text{H}_5\text{-1}\), with cobalt(II) chloride in THF yields after aerial oxidation the dinuclear complex \([(\text{H}_4\text{-1})\text{Co}^{\text{III}}(\mu\text{-OH})\text{Co}^{\text{III}}(\text{H}_4\text{-1})](\text{Co}^{\text{II}}\text{Cl}_4)\text{Cl}\), \([\text{5}]\text{(CoCl}_4)\text{Cl}\). The trianion \([\text{5}]\text{−}\) contains two cobalt atoms triply bridged by two alkoxo groups of the singly deprotonated ligand \((\text{H}_4\text{-1})\text{−}\) and a hydroxo group. The new ligand \([\text{N}(\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2)\text{2}(\text{CH}_2\text{CH}_2\text{OH})\text{2}]\), \(\text{H}_4\text{-3}\), providing an N 2O2 donor set reacts with cobalt(II) chloride to give after aerial oxidation the hexanuclear complex \([(\text{Co}^{\text{III}}2(\text{H}_2\text{-3})\text{3}\text{Co}^{\text{III}}2(\text{HOMe})\text{2Cl}_2(\mu\text{-OH})\text{2}](6\text{Cl}_2\), containing an unprecedented mixed-valent \(\text{Co}^{\text{III}}4\text{Co}^{\text{II}}2\) core.

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

Introduction

Until recently, unsymmetrically built or substituted aliphatic tripod 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 tripod ligands. Initially, aliphatic tetramine tripods with an unsymmetrical topology [2] were studied. Later alcohol functions were incorporated into the tripod ligands [3]. We reported on aliphatic tripods providing an NOS2 donor set [4] and described the preparation and coordination chemistry of a totally unsymmetric N-centered ligand with NH2, 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 NNO2 or NNO2 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 NNO2 ligand \(\text{H}_4\text{-D}\) (Scheme 1) leads to cubane clusters [7], while the NNO2 ligand \(\text{H}_4\text{-C}\) [3b] and the NNO2 ligands \(\text{H}_5\text{-A}\) [8], \(\text{H}_5\text{-B}\) [8] and \(\text{H}_5\text{-I}\) [3b, 9] react with zinc salts with formation of mono- or dinuclear zinc complexes.

In this contribution, we describe the synthesis of the unsymmetrical NNO2 ligand \(\text{H}_5\text{-3}\). In addition, the products of the reaction of \(\text{H}_5\text{-I}\) [3b] with cobalt(II) chloride and of \(\text{H}_5\text{-3}\) 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 spectrometre.
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 H₅-1 is prepared as described previously [3b].

$\text{N,N-Bis(2-hydroxyethyl)-3-aminopropionitrile H}_2$-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 for 60 minutes and then allowed to boil during addition of the nitrile. The reaction mixture is slowly added. The reaction mixture should not be allowed to boil during addition of the nitrile. The resulting suspension is filtered overnight at room temperature. Subsequently volatiles are removed under reduced pressure leaving analytically pure H₂-2 as a colorless liquid in essentially quantitative yield. Yield 85.9 g (0.54 mol, 99%). − 1H NMR (200.1 MHz, CDCl₃): δ = 3.80 (s, 2 H, OH), 3.53 (t, 4 H, CH₂(OH)), 2.82 (t, 2 H, NCH₂CH₂CN), 2.61 (t, 4 H, NCH₂CH₂OH), 2.49 (t, 2 H, NCH₂CH₂CN), 119.5 (C₂), 56.1 (NCH₂CH₂OH), 52.3 (NCH₂CH₂CH₂NH₂), 40.1 (NCH₂CH₂CH₂NH₂), 29.4 (NCH₂CH₂CH₂NH₂). − IR (KBr, cm⁻¹): ν = 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/e (%) = 163.0 (100) [MH⁺], 106.1 (12) [H₂N(CH₂CH₂OH)₂⁺]. − C₇H₁₈N₂O₂ (162.23): calcd. C 51.88, H 11.18, N 17.27; found C 51.50, H 11.55, N 16.95.

$\text{N,N-bis(2-hydroxyethyl)-propylenediamine H}_3$-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 H₂-2 (3.09 g, 0.02 mol) dissolved in THF (20 ml). Ligand H₄-1 (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 [5][CoCl₃]Cl which are suitable for an X-ray diffraction study. Yield 90 mg (0.13 mmol, 18%). − IR (KBr, cm⁻¹): ν = 3363 (m), 3238 (m), 3192 (m), 3102 (m), 2963 (m), 2880 (m, CH), 2800 (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/e (%) = 366 (100) [Co(H₂-1)₂O]⁺.

$\text{CoCl}_x\cdot\text{H}_2\text{O}$

A solution of H₄-3 (330 mg, 2.0 mmol) in methanol (10 ml) is added to a solution of CoCl₂·6H₂O (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 (HNEt₃Cl) 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 [6][CoCl₃]Cl₂·4CH₃OH·H₂O. 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/e (%) = 102 (100) [HNEt₃]⁺, 163 (30) [H₂-3]⁺.

$\text{X-ray structure determinations}$

Suitable crystals of [5][CoCl₃]Cl and [6][CoCl₃]·4CH₃OH·H₂O 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 ≤ 2θ ≤ 55.0° for [5][CoCl₃]Cl and 2.8 ≤ 2θ ≤ 50.0° for [6][CoCl₃]·4CH₃OH·H₂O. Structure solution [10] and refinement [11] were achieved with standard Patterson and Fourier tech-
Selected crystallographic details for [5][CoCl₄]Cl

Formula C₁₂H₁₃N₆Cl₅Co₅O₁₃, M = 663.48, red crystal 0.11 x 0.05 x 0.04 mm, a = 22.2845(9), b = 14.3459(6), c = 14.9396(6) Å. A, α = 92.603(1), β = 89.1960(10), γ = 81.1320(10). V = 2750.3(2) Å³, μ = 2.036 cm⁻¹, empirical absorption correction (0.7594 ≤ T ≤ 0.8879), Z = 2, triclinic, space group P1, 22345 intensities collected (±h, ±k, ±l), 5477 independent (Rint = 0.034) and 4878 observed intensities [I ≥ 2σ(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]Cl₂·4CH₃OH·H₂O

Formula C₃₄H₉₄N₈Cl₄Co₆O₁₉, M = 1414.55, red crystal 0.10 x 0.09 x 0.06 mm, a = 11.3675(5), b = 14.6965(7), c = 16.6642(8) Å, α = 89.2920(10), β = 89.1960(10), γ = 81.1320(10). V = 2750.3(2) Å³, μ = 2.036 cm⁻¹, empirical absorption correction (0.8228 ≤ T ≤ 0.8879), Z = 2, triclinic, space group P1, 22345 intensities collected (±h, ±k, ±l), 9703 independent (Rint = 0.036) and 7906 observed intensities [I ≥ 2σ(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][CoCl₄]Cl and CCDC-257324 for [6]Cl₂·4CH₃OH·H₂O. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union road, Cambridge CB2 1EZ, UK [fax: int. code +44(1223)36-033, e-mail: deposit@ccdc.cam.ac.uk].

Results and Discussion

A procedure similar to the one published for the preparation of H₅⁻₁ [3b] can be used to synthesize ligand and H₅⁻₃ (Scheme 2). Michael addition of acrylonitrile to diethanolamine [12] gave H₂⁻₂ in nearly quantitative yield. The nitrile group of H₂⁻₂ was reduced with aluminium hydride, which was prepared from LiAlH₄ and concentrated sulfuric acid [13].

Complex [5][CoCl₄]Cl was isolated from the reaction of ligand H₅⁻¹ with cobalt(II) chloride followed by aerial oxidation (Scheme 3). The reaction mixture of H₅⁻¹ 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][CoCl₄]Cl precipitated upon addition of diethyl ether.

The presence of ligand H₅⁻¹ 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 (H₄⁻·Co⁻)⁻. The X-ray diffraction analysis of the red crystals shows the composition to be [5][CoCl₄]Cl. Both Co⁴⁺ and Co⁴⁺
Fig. 1. Molecular structure of the dinuclear cation \([5]^3^+\). 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-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), O1-Co1-N1 88.28(7), O1-Co1-N2 90.28(8), O1-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 102.07(8), O10-Co2-N5 92.32(8), O10-Co2-N6 92.78(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), O1-Co1-Co2 82.44(6), Co1-O11-Co2 82.51(6).

are present in the crystals. CoII is found in the tetrahedral \([CoCl_4]^{2-}\) dianions which together with Cl\(^-\) constitute the anions in the crystal structure. The cation \([5]^3^+\) is a triply bridged dinuclear CoIII complex with (H\(_4\)-1\(^-\)) as a tetradentate ligand (Fig. 1). Only the alcohol functions of the ligands are deprotonated. They act as bridges between two CoIII 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]. Triply bridged dinuclear CoII and CoIII 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 \([5]^3^+\). An N\(_2\)O\(_4\) donor set like in \([5]^3^+\) is found in the dinuclear CoIII complexes with triazacyclononane (tacn) \([17c]\) and dipropylene triamine \([17d]\). In these cases the CoIII centers are bridged by three hydroxo ligands. This leads to slightly longer Co-Co distances \([2.565(1) \text{ Å} \text{ and } 2.579(1) \text{ Å}\] compared to \([5]^3^+\).

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

Ligand H\(_2\)-3 was added to CoCl\(_2\) · 6H\(_2\)O 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 (H\(_2\)-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 \([\text{Co}^{III}_4(\text{H}_2\cdot 3)_4\text{Co}^{II}_2(\text{HOMe})_2\text{Cl}_2(\mu-\text{OH})_2]_2\text{Cl}_4\cdot 4\text{CH}_3\text{OH}\cdot \text{H}_2\text{O}\) [6].

Complex [6] is a dicaticionic hexanuclear Co\text{III}_4 Co\text{II}_2 cluster (Fig. 2). Six cobalt atoms, four ligands, and four bridging hydroxo anions, two methanol molecules and two chloride ligands form a centrosymmetric wedge \([\text{Co}^{III}_4\text{Cl}(\text{CH}_3\text{OH})(\mu-\text{H}_2\cdot 3)\text{Co}^{II}_4(\mu-\text{OH})_2\text{Co}^{III}_4(\mu-\text{H}_2\cdot 3)]_2^{2+}\). One (Co1-Co3) or both (Co2-Co3) of the alkoxo groups of each coordinated ligand act as bridges between Co\text{III} and Co\text{II} centers. The assignment of cobalt oxidation states is consistent with the observed Co-O bond lengths, which are longer for Co\text{II} (average 1.91 Å) than for Co\text{III} (average 1.91 Å). Similar values are found in literature [14–17].

The hexanuclear arrangement of the cobalt atoms in [6] is unique. A tetranuclear Cu\text{II}_2Co\text{III}_2 ring is known with diethanolamine as a ligand [18]. In this molecule diethanolamine coordinated to Co\text{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\text{5}- or H\text{4}-promotes the oxidation of Co\text{II} to Co\text{III}. Further variations of aliphatic tripodals may provide more interesting structural arrangements in cobalt coordination chemistry, because the ligand topology is one governing factor in the cluster formation aside from the nature of the metal site or the solubility of the resulting coordination compounds.

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