A Square Pyramidal Coordination Cap: The Co(III) Complex of a Novel Tetrapodal Pentadentate Ligand with an NN$_4$ Donor Set

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Introduction

Tris(2-aminoethyl)amine (tren) has a coordination chemistry so versatile as to make it the prototype of a tripodal tetradentate ligand.[1] Its structure is characterized by a "central" tertiary nitrogen atom carrying three equivalent amino-substituted side chains. In most cases, the ligand backbone is sufficiently flexible for all four lone pairs of the NN$_3$ donor set to point toward a single metal atom.[2,3] The ligand thus provides a trigonal pyramidal coordination cap and shows a marked propensity to stabilize complexes with an overall trigonal bipyramidal geometry.[4]

With a view to creating a concave ligand environment for octahedrally coordinating transition metal ions, we required as a fundamental building block a ligand of higher denticity than tren but with a similar overall arrangement of donor atoms: one central nitrogen atom was to be surrounded by *four* equivalent amino-substituted side chains, the former being set up to occupy the apical position of a coordination octahedron, while the latter would take the equatorial positions. To this end, we designed **5**, a pyridine derivative with four pendant primary amino groups. We expected this ligand to act as a geometrically specific square pyramidal NN$_4$ "donor cap" in mononuclear complexes, since the analysis of molecular models suggested that coordination of **5** would be accompanied by the formation of stereochemically favorable six-membered chelate rings in a boat conformation.[5] We now report the synthesis of this novel tetrapodal pentadentate ligand as well as the structure of its cobalt(III) complex.[6] A related ligand, 2-(2-pyridyl)-1,3-diaminopropane, has been used in the synthesis of a number of transition metal complexes,[7] but structural studies have only been reported for its doubly deprotonated bis(amide) congener.[8]

Experimental Section

CAUTION! Although no problems were encountered in this work, both transition metal perchlorate complexes with organic ligands and organic polyazides are potentially explosive and should be handled with proper precautions.

Materials and Spectroscopy. All manipulations were performed under dinitrogen using standard Schlenk techniques unless indicated otherwise. Solvents were dried and distilled before use. Reagents were AR grade or better and were purchased from Merck and Aldrich. 2,6-Diethylpyridine (**1**) is commercially available from ICN Biomedicals. The reactions for the transformation of polyalcohol **2** into polyamine **5** were based on a procedure by Busch *et al.*,[9] employing the products **2**−**4** without prior purification. $Na_3[Co(CO_3)_3]\cdot 3H_2O$ was prepared as described.[10] NMR and IR spectra were recorded on a JEOL JNM-EX 270 and Perkin Elmer 16PC FT-IR instrument, respectively. Mass spectra were obtained on a JEOL MSTATION 700 spectrometer. Elemental analysis was carried out using a Carlo Erba elemental analyzer 1106.

2,6-$C_5H_3N\{CMe(CH_2OH)_2\}_2$ (2). The preparation was carried out under a normal atmosphere. An autoclave was charged with 2,6-diethylpyridine (44 g, 0.33 mol) and aqueous formaldehyde solution (37%, 264 g, 3.3 mol), and the mixture was heated to 140 °C for 50 h. After the mixture cooled to room temperature, the viscous yellow solution was diluted with water, filtered, and stripped of volatiles in an oil pump vacuum. The remaining yellow syrup was taken up in chloroform, the solution filtered to remove polymeric impurities, and the solvent removed *in vacuo*. The resulting yellow, highly viscous material was sufficiently pure to be used in the subsequent derivatization (yield 39 g, 47% relative to **1**). ^{1}H-NMR (ppm, DMSO-d_6): δ 7.62 (AB$_2$ spin system, 3 lines, 1 H), 7.18 (AB$_2$, 2 lines, 2 H), 4.68 (m (br), $\mathrm{CH_2O}\mathit{H}$, 4 H), 3.60 (m, $\mathrm{C}\mathit{H}_2\mathrm{OH}$, 8 H), 1.16 (s, CH_3, 6 H).

2,6-$C_5H_3N\{CMe(CH_2OTs)_2\}_2$ (3). To a cooled (0 °C) solution of **2** (17 g, 67 mmol) in pyridine (200 mL) was added toluene-4-sulfonyl chloride (63.5 g, 333 mmol) in small portions during 150 min. The resulting mixture was allowed to warm to room temperature and stirred for 36 h. It was then poured into ice-water (800 mL) to give a brown precipitate which was collected, washed with water, and dried *in vacuo* (yield 25 g, 43%). ^{1}H-NMR (ppm, $CDCl_3$): δ 7.65 (d, $\mathrm{C_6H_2}\mathit{H}_2\mathrm{SO_3}$, 8 H), 7.50 (AB$_2$, 3 lines, 1 H), 7.32 (d, $\mathrm{C_6H_2}\mathit{H}_2\mathrm{CH_3}$, 8 H), 7.00 (AB$_2$, 2 lines, 2 H), 4.17 (d, ^2J(HH) = 9.54 Hz, -CH$_2$-, 4 H), 4.10 (d, ^2J(HH) = 9.54 Hz, -CH$_2$-, 4 H), 1.17 (s, CH_3, 6 H).

2,6-$C_5H_3N\{CMe(CH_2N_3)_2\}_2$ (4). To a solution of **3** (23 g, 26 mmol) in dimethyl sulfoxide (250 mL) was added sodium azide (10.3 g, 158 mmol) in one portion. The resulting suspension was stirred at 70 °C for 48 h, after which time the mixture was allowed to cool to room temperature and poured into water (400 mL). Extraction with ether (750 mL) gave an orange-brown organic phase which was separated, washed with water (40 mL), dried over Na_2SO_4, and stripped to leave a dark red oil which, according to its ^{1}H-NMR spectrum, is virtually pure tetraazide **4** (yield 8.2 g, 88%). ^{1}H-NMR (ppm, $CDCl_3$): δ 7.75 (AB$_2$, 3 lines, 1 H), 7.25 (AB$_2$, 2 lines, 2 H), 3.81 (d, ^2J(HH) = 11.91 Hz, -CH$_2$-, 4 H), 3.70 (d, ^2J(HH) = 11.91 Hz, -CH$_2$-, 4 H), 1.47 (s, CH_3, 6 H).

2,6-$C_5H_3N\{CMe(CH_2NH_2)_2\}_2$ (5). A solution of **4** (8.15 g, 22.9 mmol) in pyridine (10 mL) was added dropwise to a cooled (0 °C) solution of triphenylphosphine (28.9 g, 110 mmol) in pyridine (60 mL) during 1 h. After an induction period of ca. 10 min, the mixture began to evolve gas. With the addition of triphenylphosphine complete, the mixture was kept stirring at room temperature for 18 h. The solvent was then removed *in vacuo*, and the remaining oil was added with vigorous stirring to 150 mL of a 10% aqueous ammonia solution. The suspension was stirred for 12 h, after which time the precipitated triphenylphosphine oxide was separated by filtration and the yellow filtrate stripped to leave **5** as a yellow foam. ^{1}H-NMR (ppm, D_2O): δ 7.65 (AB$_2$, m, 1 H), 7.18 (AB$_2$, m, 2 H), 3.00 (d, ^2J(HH) = 13.2 Hz, -CH$_2$-, 4 H), 2.67 (d, ^2J(HH) = 13.2 Hz, -CH$_2$-, 4 H), 1.20 (s, CH_3, 6 H). This was taken up in ethanol (50 mL), and the solution was cooled to −68 °C and treated with HCl gas for 1 min to precipitate the hydrochloride salt as a light brown material. Elemental analysis is as yet unsatisfactory but best agrees with a formulation as **5**·5HCl (yield 8.9 g, ∼89%).

$[CoCl(2,6\text{-}C_5H_3N\{CMe(CH_2NH_2)_2\}_2)](Cl)(ClO_4)\cdot H_2O$ (6). To a mixture of **5**·5 HCl (2.0 g, 4.6 mmol) and $Na_3[Co(CO_3)_3]\cdot 3H_2O$ (1.8

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Table 1. Crystallographic Data for $[CoCl(2,6\text{-}C_5H_3N\{CMe(CH_2NH_2)_2\}_2)](Cl)(ClO_4)\cdot H_2O$ (**6**)

chemical formula	$C_{13}H_{27}Cl_3CoN_5O_5$	formula weight	498.68
a	7.688(1) Å	space group	$P\bar{1}$ (No. 2)
b	10.720(2) Å	T	293(2) K
c	12.981(2) Å	λ	0.710 73 Å
α	68.86(1)°	D_{calc}	1.662 g cm^{-3}
β	88.77(1)°	μ	1.299 mm^{-1}
γ	86.90(1)°	$R1^a$ [(I > 2σ(I)]	0.0548
V	996.4(3) $Å^3$	$wR2^b$	0.1521
Z	2		

[a] $R1 = \sum(|F_o| - |F_c|)/\sum|F_o|$. [b] $wR2 = (\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2])^{0.5}$, where $w = 1/[\sigma^2(F_o^2) + (0.0009P)^2]$ and $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Selected Distances and Angles for **6**

atoms	distance (Å)	atoms	distance (Å)
Co1−N10	1.928(3)	Co1−N3	1.956(4)
Co1−N1	1.951(4)	Co1−N4	1.957(4)
Co1−N2	1.955(4)	Co1−Cl1	2.2645(12)

atoms	angle (deg)	atoms	angle (deg)
N10−Co1−Cl1	178.57(11)	C11−C5−C7	112.2(5)
N10−Co1−N1	90.3(2)	C11−C5−C1	110.7(4)
N10−Co1−N2	89.9(2)	C11−C5−C2	108.7(5)
N1−Co1−N2	90.2(2)	C5−C1−N1	113.7(4)
N1−Co1−N3	90.8(2)	C5−C2−N2	112.7(4)
Co1−N10−C11	120.3(3)	C1−N1−Co1	118.6(3)
N10−C11−C5	117.0(4)	C2−N2−Co1	119.1(3)
C12−C11−C5	122.9(5)		

g, 4.9 mmol) was added a mixture of water and methanol (1:1, 50 mL) in one portion, which resulted in immediate evolution of CO_2. The mixture was refluxed for 30 min and filtered, and the dark red filtrate was charged onto a Dowex 50WX2 cation exchange column (∅ 15 mm, length 250 mm). Gradient elution with HCl gave an orange fraction (3 M HCl, 600 mL). The volume of the solution was reduced to 30 mL, $NaClO_4\cdot H_2O$ (2 g) added, and the solution cooled to precipitate **6** as a microcrystalline red material (1.3 g, 54% relative to **5**). ^1H-NMR (ppm, DMSO-d_6): δ 8.19 (AB_2, 3 lines, 1 H, H^4), 7.69 (AB_2, 2 lines, 2 H, $H^{3,5}$), 5.85 (s (br), 4 H, -NH*H*), 5.29 (s(br), 4 H, -N*H*H), 2.74 (m, -C*H*HNH_2, 4 H), 2.25 (m, -CH*H*NH_2, 4 H), 1.46 (s, CH_3, 6 H). ^{13}C-NMR (ppm, DMSO-d_6): δ 165.11 (s, C2/6), 141.03 (s, C4), 121.08 (s, C3/5), 47.15 (s, ⟩*C*⟨), 44.23 (s, -*C*H_2-), 21.30 (s, -*C*H_3). MS (FAB^+): *m/z* (relative intensity) 345 (47), M^{2+}; 79 (100), C_5H_5N. MS (ESI^+): 344 (100), M^{2+}; 173 (84), M^+, correct isotope patterns in both cases. IR (cm^{-1} in KBr): 3441 (s), 3228 (m), 1598 (m), 1470 (w), 1121 (vs), 627 (m). Anal. Calcd for $C_{13}H_{27}Cl_3CoN_5O_5$: C, 31.31; H, 5.46; N, 14.04. Found: C, 31.61; H, 5.45; N, 13.81. Single crystals were grown by slowly cooling a boiling aqueous solution of **6**.

Crystallography. All measurements of **6** were made on a Siemens P4 four-circle diffractometer (Mo Kα radiation, λ = 0.710 73 Å, graphite monochromator). The structure was solved by direct methods (SHELXTL-PLUS) and refined using the program package SHELXL93. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms except for those in the water molecule were located in the difference Fourier map and refined with fixed isotropic displacement parameters. The residual electron density was +1.093/−0.694 e$Å^{-3}$ (located at the perchlorate anion). Crystal data and data collection parameters are listed in Table 1, and selected distances and angles are given in Table 2.

Results and Discussion

The pentaamine ligand **5** is synthesized as outlined in Figure 1. The first step involves the construction of the carbon backbone of the ligand from a suitable pyridine precursor and makes use of the known reactivity of 2-alkylpyridines toward formaldehyde.[11] In a series of orienting reactions, we found that 2,6-dimethylpyridine gives mixtures of products with varying degrees of hydroxymethylation in the side chains.[12] As these mixtures are difficult to separate, we chose to limit the number of reactive α-hydrogen atoms in each side chain to two by using 2,6-diethylpyridine (**1**).[13] This compound reacts with formaldehyde to furnish the desired tetraol **2**, which may then be transformed into **5** by use of a three-step sequence of reactions:[9] tosylation (**3**), tosylate−azide exchange (**4**), and reduction (**5**). The reduction of the tetraazide **4** is conveniently achieved with triphenylphosphine[14] and proceeds with liberation of dinitrogen to give the tetrakis(iminophosphorane), which is then hydrolyzed to yield the pentaamine **5**. Since the latter is strongly basic in aqueous solution, it is best isolated as the pentakis(hydrochloride) salt, which may be used in its crude form for the subsequent complexation reaction. We are currently seeking ways to obtain pure material by recrystallization of **3** and/or of **5**·5HCl. Whereas the yields of the first two steps to give **3** are so far moderate (ca. 45%), the subsequent reactions leading to **5** proceed with very good yields (ca. 90%).

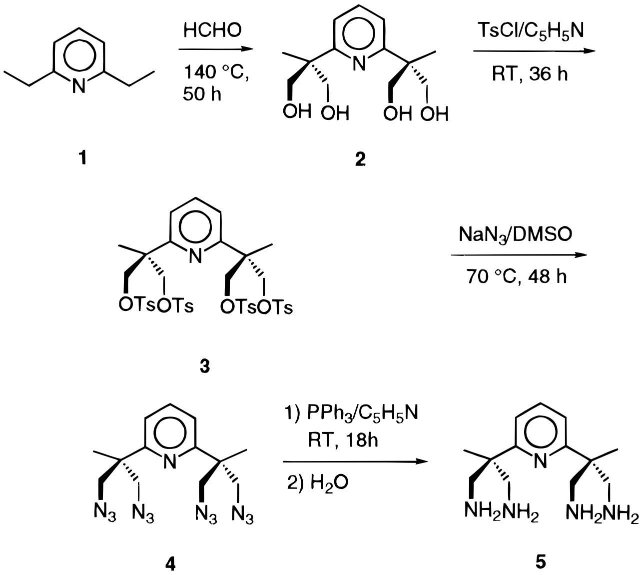

Figure 1. Synthesis of 2,6-bis(1′,3′-diamino-2′-methylprop-2′-yl)pyridine (**5**).

5·5HCl readily reacts with $Na_3[Co(CO_3)_3]\cdot 3H_2O$[10] in a 1:1 water/methanol mixture with concomitant evolution of carbon dioxide to give a red solution from which a red crystalline material can be isolated upon the addition of sodium perchlorate. Elemental analysis of this material indicates the presence of a mixed chloride perchlorate salt containing 1 equiv of water as lattice solvent, compatible with a formulation of the complex as [Co(**5**)Cl](Cl)(ClO_4)·H_2O (**6**). In the ^1H-NMR spectrum of **6**, the AB_2 spin system of the pyridine ring protons gives rise to one signal of triplet and one of doublet multiplicity in the intensity ratio 1:2. The assignment of the methyl group protons is likewise straightforward (cf. Experimental Section). Interestingly, both the methylene and the amine protons give rise to a set of two resonances, indicating that the geminal protons on *both* the N donor atoms and the methylene groups of the carbon backbone are diastereotopic. Consequently, the exchange of the amine protons must be slow on the NMR time scale under the given conditions.[15] Both sets of resonances are broadened, and shoulders can be observed; coupling between the amine

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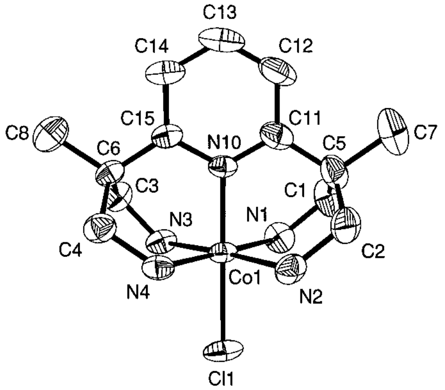

Figure 2. Molecular structure of the cation in **6** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

and methylene protons as well as geminal coupling and coupling to the N nucleus can be expected in each case. The overall equivalence of the four aminomethyl groups in the complex is indicated by the presence of a single signal in the ^{13}C NMR spectrum at δ 44.23 ppm. ^{15}N-NMR data show a correlation between the N−H proton resonances at δ 5.29 and 5.85 ppm with a ^{15}N singlet at δ−25 ppm (DMSO-d_6; referenced against NH$_4$ in NH$_4$NO$_3$ as zero).

The spectroscopic data of **6** suggest a complex in which the ligand forms the desired square pyramidal coordination cap. An X-ray structure analysis of **6** confirms the overall composition and reveals a complex three-dimensional network of hydrogen bonds between the cations, the perchlorate anions, and the water molecules.[16] The molecular structure of the cation, which has no crystallographically imposed symmetry, is shown in Figure 2. The cobalt atom is coordinated in an octahedral fashion, with angles $\mathrm{N_{ax}{-}Co{-}N_{eq}}$ and $\mathrm{N_{eq}{-}Co{-}N_{eq}}$ in a range between 88.7(2)° and 92.8(1)° [N10−Co−Cl1 178.57(11)°]. The pyridine ring is a virtually regular hexagon. Its nitrogen atom occupies the axial position of a square pyramidal NN$_4$ arrangement of donor atoms, which leads to the formation of six six-membered chelate rings, all of which adopt a boat conformation. As may be expected, metal coordination slightly forces the two bidentate ortho substituents of the pyridine ring out of their ideal positions, pulling them toward the equatorial plane. This is reflected by systematic deviations of the bond angles around the corresponding sp^2 and sp^3 carbon atoms of the ligand framework from their ideal values (120° and 109° 28′, respectively) [e.g., N10−C11−C5 117.0(4)°, C12−C11−C5 122.9(5)°; C5−C1−N1 113.7(4)°, C5−C2−N2 112.7(4)°]. Larger deviations are observed for the bond angles at the equatorial nitrogen atoms, which range from 117.1(3)° to 119.1(3)°. In keeping with these observations, the $\mathrm{Co{-}N_{ax}}$ bond is slightly shorter [Co1−N10 192.8(3) pm] than the four $\mathrm{Co{-}N_{eq}}$ bonds [195.1(4)−195.7(4) pm]. It should be noted, however, that a similar trend in bond distances [$\mathrm{Co^{III}}$−N(pyridine) < $\mathrm{Co^{III}}$−N(ammonia)] is also observed for mixed Co(III) pyridine ammine complexes in which the ligands are nonchelating and thus impose no steric constraints.[17,18] All Co−N bond distances in **2** lie within the range observed for these and related complexes.[19] The Co−Cl bond distance [Co1−Cl1 226.45(12) pm] is likewise unexceptional.[19]

Our results show clearly the chelating ability of the novel pentaamine ligand **5** toward a single metal center. The availability of molecules such as **2** and **5** opens up several lines of inquiry. In addition to extending the coordination chemistry of **5** to other metal ions, we are currently studying exchange reactions of the donor groups in **2** as well as template-assisted derivatization reactions of the amino functionalities in **5**.

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Supporting Information Available: Full crystal data and tables of atomic coordinates, thermal parameters, and bond distances and angles (5 pages). Ordering information is given on any current masthead page.

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