The Chemistry of 1,3,5-Triazacyclohexane Complexes. 6.[1] Synthesis and Characterization of the Cobalt(II) Methoxide Core $\{Co_3(OMe)_4\}^{2+}$

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Received April 24, 1997[⊗]

We report the synthesis and characterization of the first η^3-1,3,5-trimethyl-1,3,5-triazacyclohexane (Me_3TAC) alkoxo complexes. Dehydration of $[Co(H_2O)_6](X)_2$ with 2,2-dimethoxypropane or $HC(OMe)_3$ and subsequent treatment with Me_3TAC results in the formation of the methoxo cube fragment clusters $[\{(Me_3TAC)Co\}_3(OMe)_4](X)_2$ ($X = B(C_6F_5)_4$ (**2a**) and $B(m\text{-}C_6H_3(CF_3)_2)_4$ (**2b**)). **2a** crystallizes in the triclinic space group $P\bar{1}$ ($a = 13.857(2)$ Å, $b = 16.843(3)$ Å, $c = 19.318(2)$ Å, $\alpha = 79.23(2)°$, $\beta = 76.855(13)°$, $\gamma = 70.10(2)°$, $Z = 2$) and **2b** in the monoclinic space group $P2_1$ ($a = 12.710(3)$ Å, $b = 23.251(3)$ Å, $c = 18.702(4)$ Å, $\beta = 101.16(2)°$, $Z = 2$). The cations contain a $\{Co_3(OMe)_4\}$ cube fragment core with an η^3-Me_3TAC bonded to each cobalt atom. Me_3TAC is bonded unsymmetrically due to hydrogen-bonding interactions with the anions. This broken symmetry can also be observed as solvent-, anion-, and H/D isotope-dependent splitting of the signals in ^1H and ^2H NMR. A byproduct of the reaction is the protonated Me_3TAC. The analogous monoacid adduct $Me_3TAC\cdot HCl$ has been characterized by X-ray crystallography (orthorhombic space group *Pbca*, $a = 11.0366(9)$ Å, $b = 12.2986(6)$ Å, $c = 13.9949(7)$ Å, $Z = 8$).

Introduction

Transition metal cubane clusters $\{M_4X_4\}^{n+}$ are well-precedented units in inorganic chemistry as models for active sites in various proteins, e.g. $\{Fe_4S_4\}^{n+}$ and $\{Mn_4(OR)_4\}^{n+}$.[3] Cubane fragments $\{M_3X_4\}^{n+}$ are found in some proteins and important precursors for the synthesis of mixed metal clusters $\{M_3M'X_4\}^{n+}$.[4] In the present article, we describe a new synthetic route to such cubane fragment methoxo clusters of cobalt(II).

We are investigating the coordination chemistry of 1,3,5-trialkyl-1,3,5-triazacyclohexanes (R_3TAC) as the smaller homologues of the triazacyclononanes. In previous publications,[5] we have shown that neutral and cationic complexes of Cr(III), Fe(III), Cu(I/II), and Zn(II) with η^3-coordinated N-alkylated 1,3,5-triazacyclohexanes as ligands can be prepared with very small N−metal−N angles (60−65°) and severely bent M−N bonds. UV/visible spectra showed that the ligand field strength was much smaller than those in other amine complexes.[5b,c] The rigid triazacyclohexane gives rise to clearly separated signals for the endo and exo methylene protons in the NMR.[5c,d] Thus, these ligands are facially coordinating ligands with low steric demand that can be used as NMR probes in coordination chemistry.

Results and Discussion

In our search for cationic triazacyclohexane complexes, we investigated the reaction of R_3TAC with transition metal salts that are ligated only by weakly coordinating solvent molecules. While the reaction of $[Cu(MeCN)_4]^+$ and $[Ni(MeCN)_6]^{2+}$ gave the expected products $[(R_3TAC)Cu(MeCN)]^+$ [3d] and $[(R_3TAC)Ni(MeCN)_3]^{2+}$,[6] we observed a different reaction with $[Co(MeOH)_x]^{2+}$. Dehydration of the hexaaquo salts $[Co(H_2O)_6]X_2$ ($X = B(C_6F_5)_4$ (**1a**) or $B(m\text{-}C_6H_3(CF_3)_2)_4$ (**1b**)) with 2,2-dimethoxypropane[7] or $HC(OMe)_3$[8] presumably yields the corresponding $[Co(MeOH)_6]^{2+}$ salts. The organic side products, especially when dimethoxypropane was used, prevented the isolation of the pure methanol complexes from the brown solutions. However, addition of an excess of Me_3TAC to a freshly prepared THF solution of these salts resulted in an immediate color change to purple. The isolated compounds were the methoxo clusters **2a,b** (Figure 1) and the protonated ligand $[(Me_3TAC)_2H]X$, according to Scheme 1. Solid **2a,b** can be handled in the air for short times, while solutions are very sensitive. Treatment of solid **2a,b** with water slowly liberates free Me_3TAC.

Thus, Me_3TAC deprotonated some of the coordinated MeOH to form an open methoxo cubane cluster with η^3-coordinated Me_3TAC on each cobalt atom. There is no indication that an additional $(Me_3TAC)Co^{2+}$ fragment can be added to complete the cubane cluster although many complete $M_4(OMe)_4$ cubanes are known (e.g., refs 3 and 9), and construction of a $\{(Me_3TAC)Co(OMe)\}_4^{4+}$ with the bond lengths and angles found in

⊗ Abstract published in *Advance ACS Abstracts,* November 1, 1997.

(1) Part 5: ref 5e.

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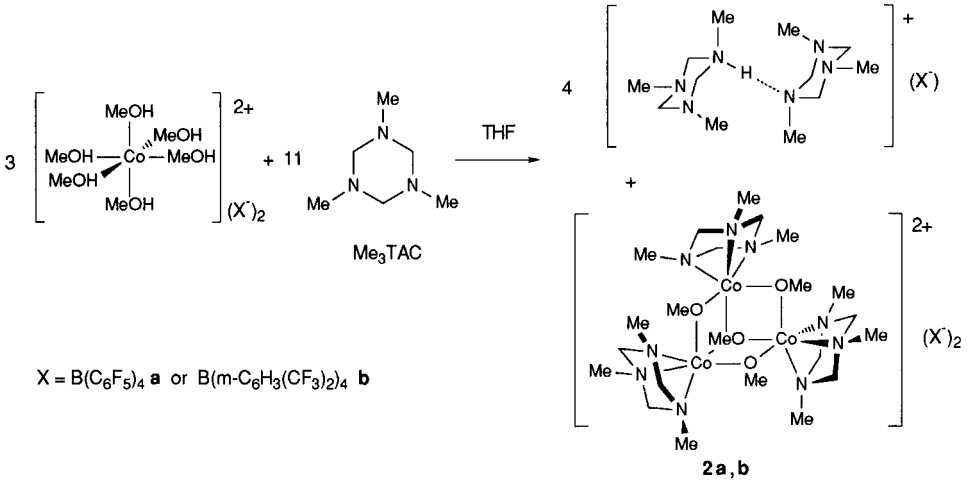
Scheme 1. Preparation of the Clusters **2a,b**



2 (see below) does not show any close nonbonded contacts significantly different from those found in **2**. Thus, the complete cubane cluster may not be formed due to the high 4+ charge rather than due to the steric interactions.

In the case of the reaction with **1a**, the protonation product of Me_3TAC was isolated and characterized by elemental analysis and NMR. This suggests a monoprotonated Me_3TAC which is hydrogen-bonded to a second Me_3TAC. Such monoacid adducts are known.[5e,10] In our modified[11] preparation of Me_3TAC from $MeNH_2$ and formaldehyde without added KOH, we extracted the product with CH_2Cl_2. This resulted in a side product that gave large colorless crystals that were identified as the adduct $Me_3TAC{\cdot}HCl$. The first X-ray crystal structure of such an adduct showed (Figure 2) that the proton is bonded to only one nitrogen atom (N3)[12] and hydrogen-bonded to Cl^-. Thus, it seems reasonable that, due to the large, weakly coordinating anion and the excess of Me_3TAC, another Me_3TAC is hydrogen-bonded instead of the anion.

The Co_3 cluster cation was formed reproducibly in good isolated yields with two different anions. They were characterized by ^1H NMR and X-ray crystallography. FAB mass spectra of solutions in CH_2Cl_2 show the Co_3 cluster and no evidence for any other cluster size.

Especially striking is the high resolution of the paramagnetic ^1H NMR spectra of **2a** and **2b** over a 550 ppm range, which are very similar except for the additional anion signals in **2b**. These paramagnetically shifted signals are due to both Fermi contact shifts mediating unpaired electron density from the cobalt(II) to the observed nuclei via chemical bonds and through-space dipolar shifts caused by the magnetic anisotropy of the cobalt(II).[13] The former depends on the strengths and relative orientations of the mediating bonds, while the latter depends on the distance from the metal and the angle to the magnetic main axis in axially symmetric complexes ($(3 \cos^2 \theta - 1)/r^3$). All hydrogen positions in **2** are three bonds away from the next cobalt atom. Thus, the Fermi contact shift should have a

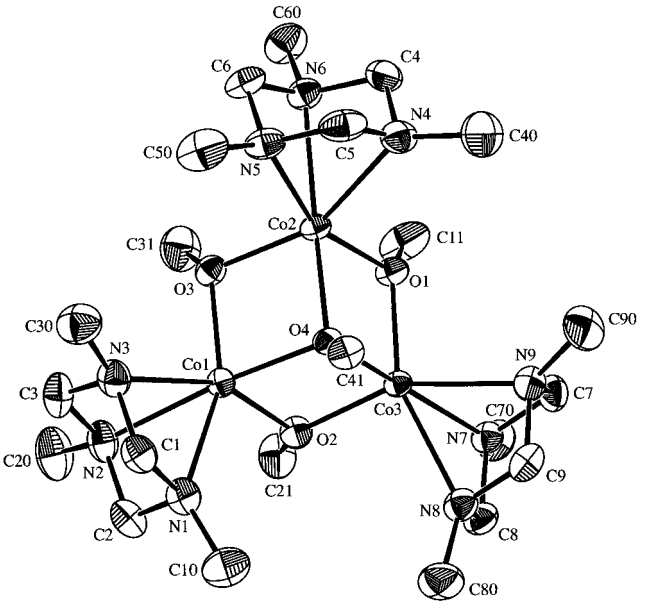


Figure 1. Molecular structure of the cation in **2a**. Thermal ellipsoids are shown at the 50% probability level.

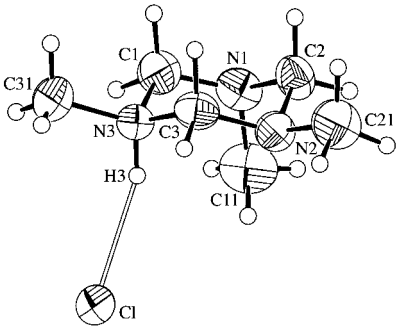


Figure 2. Molecular structure of $Me_3TAC{\cdot}HCl$. Thermal ellipsoids are shown at the 50% probability level.

Karplus-like dependence on the torsion angles. For the freely rotating methyl groups, a sizable contact shift should always be possible, while the rigid methylene hydrogens are held in fixed positions: the endo position has and the exo position does not have nearly orthogonal bonds. Thus, the endo position is expected to have small Fermi contact shifts. Dipolar shifts are small when the angle θ is close to 54°, as is the case for the endo protons. The two signal groups for the Me_3TAC methylene endo and exo protons are found at +10 and −17 ppm,

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Table 1. Selected Interatomic Distances (Å) and Angles (deg) in **2a** and **2b**

distances	**2a**	**2b**	angles	**2a**	**2b**
Co(1)−O(2)	1.958(2)	1.968(4)	O(2)−Co(1)−O(3)	106.57(7)	105.5(2)
Co(1)−O(3)	1.958(2)	1.956(5)	O(2)−Co(1)−O(4)	82.09(6)	82.5(2)
Co(1)−O(4)	2.108(2)	2.103(4)	O(3)−Co(1)−O(4)	83.16(6)	82.0(2)
Co(1)−N(1)	2.270(2)	2.297(7)	N(1)−Co(1)−N(2)	61.35(8)	60.5(3)
Co(1)−N(2)	2.286(2)	2.283(6)	N(1)−Co(1)−N(3)	59.77(8)	59.6(2)
Co(1)−N(3)	2.369(2)	2.425(6)	N(2)−Co(1)−N(3)	60.42(7)	58.8(3)
Co(2)−O(1)	1.958(2)	1.969(4)	O(1)−Co(2)−O(3)	105.71(7)	106.2(2)
Co(2)−O(3)	1.976(2)	1.959(4)	O(1)−Co(2)−O(4)	82.45(6)	82.2(2)
Co(2)−O(4)	2.110(2)	2.092(4)	O(3)−Co(2)−O(4)	82.67(7)	82.2(2)
Co(2)−N(5)	2.257(2)	2.249(6)	N(5)−Co(2)−N(6)	61.93(8)	61.4(3)
Co(2)−N(6)	2.266(2)	2.272(6)	N(5)−Co(2)−N(4)	60.93(8)	61.0(3)
Co(2)−N(4)	2.305(2)	2.332(6)	N(6)−Co(2)−N(4)	61.34(7)	61.5(2)
Co(3)−O(1)	1.959(2)	1.959(4)	O(1)−Co(3)−O(2)	105.79(7)	107.3(2)
Co(3)−O(2)	1.969(2)	1.973(4)	O(1)−Co(3)−O(4)	82.23(6)	82.3(2)
Co(3)−O(4)	2.118(2)	2.097(4)	O(2)−Co(3)−O(4)	81.57(6)	82.5(2)
Co(3)−N(7)	2.249(2)	2.261(5)	N(7)−Co(3)−N(9)	61.58(7)	60.8(2)
Co(3)−N(9)	2.296(2)	2.362(6)	N(7)−Co(3)−N(8)	61.05(7)	61.7(2)
Co(3)−N(8)	2.337(2)	2.298(6)	N(9)−Co(3)−N(8)	59.88(8)	59.9(2)
Co(1)−Co(2)	3.0367(8)	3.0425(12)			
Co(1)−Co(3)	3.0585(7)	3.0428(11)			
Co(2)−Co(3)	3.0478(5)	3.0377(11)			

clearly indicating η^3-coordination. Due to the small shift, the former is assigned as the endo proton signal. However, the splitting of these groups into at least six different signals shows that the compounds contain at least two different unsymmetrically bonded Me_3TAC forms, even in solution. This feature is most prominent in the signal groups for the ring methylene protons, which are most sensitive to differences in the M−N bonding. The other Me_3TAC signals show similar splitting but to a smaller extent. Different intensities of the individual signals in these groups when the anion (**2a** vs **2b**) or the solvent (CH_2Cl_2 vs THF) is changed indicate that the asymmetry may also be caused by distinct anion and/or solvent interaction with the cation in solution that is not fluctional at room temperature on the NMR time scale.

To verify the assignment and for better resolution, especially for the signals around +10 ppm, we prepared **2a** deuterium labeled on Me_3TAC (**2a**-*d*) and on the methoxide group (OCD_3-**2a**). The ^1H and ^2H NMR spectra of these partially deuterated compounds also showed clearly different intensities for the individual signals in each group. Thus, the occupation of the positions giving rise to these signals has a large $^1H/^2H$ isotope effect ranging from 4:1 to 1:4. This supports the involvement of some static hydrogen-bonding interaction between the cluster cation and the anions and/or the solvent, even in solution, as is found in the crystal structures. The remaining NMR signals at +500, +25, and +15 ppm are due to the methoxy groups and show similar anion, solvent, and isotope dependence.

The IR spectrum of **2a**-*d* shows only two C−D stretching vibrations at 2218 and 2086 cm^{-1}, similar to other Me_3TAC-*d* complexes.[5d] Similarly, the IR spectrum of OCD_3-**2a** shows only the two C−D stretching vibrations at 2174 and 2045 cm^{-1} expected for a CD_3 group. Thus, evidence for hydrogen bonding to the anions cannot be found in the IR spectra.

The magnetic moments of **2a,b** (4.9 and 4.0 μ_B/Co, respectively) in solution at 293 K slightly exceed the spin-only value for Co^{2+} (3.87 μ_B) and are similar to that of an $\{N_4Co(\mu^2\text{-OMe})_2\}$[14] complex (4.23 μ_B). More accurate cryomagnetic measurements on crystalline **2b** in the range of 86−306 K shows nearly Curie ($\Theta = -0.7(6)$ K) behavior with a magnetic moment of 4.63(1) μ_B/Co. Thus, there is no evidence for magnetic coupling between the cobalt atoms at these temperatures.

The UV/vis spectra (16 800, 18 700, 21 400 cm^{-1}) show a ligand field strength that is a little higher than that in $Co(OMe)_2$[15] (12 000, 17 900, 21 000 cm^{-1}) and is typical for Co(II) in an O_6 environment.[16] We have shown before[5b,c] that the ligand field strength of R_3TAC is more comparable to those of O donor ligands than to those of other amines. Thus, the UV/vis spectra are in agreement with the $(Me_3TAC)Co(OMe)_3$ ligand sphere in these clusters.

Structures of 2a and 2b. **2a** and **2b** can be recrystallized from CH_2Cl_2 and were investigated by X-ray crystallography. Both contain the cluster cations $[\{(Me_3TAC)Co\}_3(OMe)_4]^{2+}$, which is shown with the numbering scheme in Figure 1 for that in **2a** and looks identical to that in **2b**. Selected interatomic distances and angles are given in Table 1. The crystals contain one (**2a**) or two (**2b**) molecules of CH_2Cl_2 per cluster which are hydrogen-bonded primarily to the anions and in **2b** also to the cation. These solvent molecules cannot be removed in vacuo according to the elemental analyses. Additional weak to strong hydrogen bonds are found between the anions and the cluster cation, with several H···F contacts closer than the sum of the van der Waals radii[17] (260 pm) (closest contact, 196 pm).

The accuracy of the structure of **2b** suffers from extensive disorder in the CF_3 groups of the anions. The structure for **2a**, however, is much more precise and shows a very similar cluster cation. The cluster cation consists of a cubane fragment, $\{(\mu^3\text{-OMe})Co_3(\mu^2\text{-OMe})_3\}^{2+}$. The longer Co−($\mu^3$-OMe) (**2a**, 210.8−211.8 pm; **2b**, 209.2−210.3 pm) and the Co−(μ^2-OMe) (**2a**, 195.8−197.6 pm; **2b**, 195.6−197.3 pm) distances are within a narrow range and typical for μ^2- and μ^3-OMe groups (e.g., refs 3 and 18). This suggests nearly C_{3v} symmetry in the cluster core. However, this symmetry is not adapted by the three facially coordinating Me_3TAC groups. As expected, the Co−N bonds trans to the long Co−(μ^3-OMe) bonds are shorter than most of the other Co−N bonds (**2a**, 224.7−228.6 pm; **2b**, 226.1−228.3 pm). The two other Co−N bonds on each Me_3TAC are surprisingly dissimilar (**2a**, 224.9−236.9 pm; **2b**, 224.9−242.5 pm). In fact, only one of the two Co−N bonds trans to the short Co−(μ^2-OMe) bonds is significantly longer

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than the former. It is difficult to explain this unexpected bond length distribution within the cation alone, although the pyramidalized μ^2-OMe group introduces some asymmetry into the cluster. More important are probably the various hydrogen-bonding contacts mentioned above. Thus, anion and/or solvent interaction can influence the Co−N bonding in a magnitude similar to the different influence of the $\mu^{2/3}$-OMe groups.

Conclusion

The 1,3,5-triazacyclohexane Me_3TAC can serve as a facially coordinating ligand in cobalt(II) alkoxide clusters. The splitting of the Me_3TAC signals shows that the NMR spectra are very sensitive to slight differences in the anion and/or solvent interactions with the cluster cation. Thus, triazacyclohexanes may serve as sensitive NMR probes as well as facially protecting groups in transition metal alkoxo clusters. We will investigate the general synthetic potential of these complexes for the synthesis of alkoxo clusters.

Experimental Section

General Considerations. All manipulations were carried out by standard Schlenk, vacuum, and glovebox techniques unless stated otherwise. THF, Et_2O (dried and stored over Na/benzophenone), CH_2Cl_2, and $CDCl_3$ (dried, degassed, and stored over CaH_2) were freshly condensed into the reaction flasks. Me_3TAC,[10] d_1-Me_3TAC-*d*,[5d] $LiB(C_6F_5)_4\cdot(H_2O)_3(Et_2O)$,[19] and $NaB(m\text{-}C_6H_3(CF_3)_2)_4\cdot(H_2O)_2$[20] (isolated from H_2O/Et_2O) were prepared according to modified literature procedures. ^2H NMR of Me_3TAC-*d* showed that it contains 0.8 D on ring methylene groups and 0.2 D on the methyl groups. The following instruments were used: for IR spectra, a Perkin Elmer 580 B; for UV/vis spectra, a Beckman DU 650; for ^1H NMR spectra, a Bruker ARX 200 (200 MHz); and for ^2H NMR, a Bruker ARX 400 (400 MHz). Elemental analyses were performed on a Perkin-Elmer Series II CHN/O analyzer 2400 or at the analytical facility of the Humboldt Universität zu Berlin. Melting points were determined on a HWS-SG 2000 apparatus and are uncorrected. Magnetic moments were determined in solutions (CH_2Cl_2) at 293 K according to the Evans method[21] or in crystalline form according to the Faraday method and were corrected for temperature-independent paramagnetism and the diamagnetic contribution using Pascal's constants.[22] FAB mass spectra were obtained at the analytical facility of the FU Berlin.

Me_3TAC. An aqueous solution of $MeNH_2$ (700 mL, 40%, 8.13 mol) was added dropwise to an ice-cold solution of formaldehyde (580 g, 37%, 7.15 mol). After the addition, the solution was stirred for 1 day at room temperature and then extracted six times with CH_2Cl_2 (300 mL). The solvent was destilled off the combined extracts. Cooling of the residue to room temperature overnight resulted in large colorless crystals of $Me_3TAC\cdot HCl$ which were separated, washed with THF and Et_2O, and dried in vacuo (15 g, 4%). ^1H NMR ($CDCl_3$, 200 MHz): δ 11.44 (s, 1H, N*H*$^+$), 3.80 (s, 6H, NC*H*$_2$), 2.60 (s, 3H, C*H*$_3$NH$^+$), 2.58 (s, 6H, C*H*$_3$N). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 39.53 (*C*H$_3$), 73.77 (*C*H$_2$). Anal. Calcd for $C_6H_{16}N_3Cl$: C, 43.50; H, 9.73; N, 25.36. Found: C, 43.51; H, 10.17; N, 26.45. The remaining liquid was destilled at 74 °C/20 mmHg, dried over Na, and recondensed at 10^{-2} mmHg to yield dry Me_3TAC (100 g, 33%).

$[Co(H_2O)_6][B(C_6F_5)_4]_2\cdot(Et_2O)_2$ (1a). $LiB(C_6F_5)_4\cdot(H_2O)_3(Et_2O)$ (6.1 g, 7.5 mmol) was dissolved in water (10 mL). Addition of an aqueous solution of $CoSO_4\cdot(H_2O)_7$ (2 g, 7.6 mmol in 20 mL) resulted in the separation of an orange oil, which was washed with water (20 mL). The aqueous phases were extracted three times with Et_2O (50 mL). The combined extracts were washed three times with water (20 mL). The solvent was removed in vacuo from the combined extracts and the orange oil. The residue was washed twice with toluene (20 mL) and twice with pentane (20 mL) and dried in vacuo after each washing, resulting in a pink solid of **1a** (4.1 g, 65%).[23] ^1H NMR (CH_2Cl_2, 400 MHz): δ +67.5 ($W_{1/2} \approx$ 1200 Hz, 12H, *H*$_2$O), +4.55 ($W_{1/2} \approx$ 40 Hz, 8H, O(C*H*$_2$CH$_3$)$_2$), +1.02 ($W_{1/2} \approx$ 25 Hz, 12H, O(CH$_2$C*H*$_3$)$_2$). μ_{eff} = 4.2 μ_B. Anal. Calcd for $C_{56}H_{32}B_2CoF_{40}O_8$: C, 40.20; H, 1.93; Co, 3.52. Found: C, 39.99; H, 1.94; Co, 3.35.

$[Co(H_2O)_6][B(m\text{-}C_6H_3(CF_3)_2)_4]_2\cdot(Et_2O)$ (1b). $NaB(m\text{-}C_6H_3(CF_3)_2)_4\cdot(H_2O)_2$ (2.11 g, 2.3 mmol) was dissolved in Et_2O (100 mL). This solution was extracted with an aqueous solution of $CoSO_4\cdot(H_2O)_7$ (2 g, 7.6 mmol in 150 mL) in three portions and then three times with water (20 mL). The solvent was removed in vacuo from the organic phase. The orange residue was washed twice with toluene (30 mL) and three times with pentane (20 mL) and dried in vacuo after each washing, resulting in an orange solid of **1b** (2.2 g, 97%). Found: C, 40.94; H, 2.32; Co, 2.88. ^1H NMR (CH_2Cl_2, 400 MHz): δ +76.1 ($W_{1/2} \approx$ 700 Hz, 12H, *H*$_2$O), 7.65 ($W_{1/2} \approx$ 10 Hz, 16H, *o*-C$_6$*H*$_3$(CF$_3$)$_2$), 7.49 ($W_{1/2} \approx$ 10 Hz, 8H, *p*-C$_6$*H*$_3$(CF$_3$)$_2$), +0.93 ($W_{1/2} \approx$ 25 Hz, 6H, O(CH$_2$C*H*$_3$)$_2$). μ_{eff} = 4.6 μ_B. Anal. Calcd for $C_{68}H_{45}B_2CoF_{48}O_7$: C, 41.51; H, 2.36; Co, 3.00.

$[\{(Me_3TAC)Co\}_3(OMe)_4][B(C_6F_5)_4]_2$ (2a). **1a** (800 mg, 0.48 mmol) was stirred with 2,2-dimethoxypropane (4 mL). After 2 h, the volatiles were removed in vacuo, and the residue was treated with additional dimethoxypropane (2 mL). After removal of the volatiles in vacuo, the brown residue was dissolved in THF (20 mL), and Me_3TAC (0.2 mL, 1.4 mmol) was added. The brown solution turned purple immediately after the addition. After 2 h of stirring, the volatiles were removed in vacuo, and the residue was washed three times with Et_2O (10 mL).[24] Drying in vacuo yielded 205 mg (63%) of purple **2a**. Crystals can be obtained by recrystallization from CH_2Cl_2, mp 170−178 °C dec. ^1H NMR (CD_2Cl_2, 200 MHz): δ +510, +26, +18 ($W_{1/2} \approx$ 400 Hz, O*Me*), +97...101 (27H, *Me*$_3$TAC), +7...12 (9H, NC*H*$_{endo}$H$_{exo}$N), −15...−20 ($W_{1/2} \approx$ 100 Hz, 9H, NCH$_{endo}$*H*$_{exo}$N). ^{19}F NMR (CD_2Cl_2, 188 MHz): δ −55.6 (s, 16F), −85.6 (t, $J \approx$ 34 Hz, 8F), −88.6 (s, 16F). λ_{max}, nm (CH_2Cl_2)(ϵ, M^{-1} cm^{-1}): 467 (8), 530 (30), 596 (6). $\mu_{eff}(Co_3)$ = 8.5 μ_B (per Co_3) or 4.9 μ_B (per Co). Anal. Calcd for **2a**$\cdot CH_2Cl_2$ ($C_{71}H_{59}N_9B_2Cl_2Co_3F_{40}O_4$): C, 40.01; H, 2.79; N, 5.91. Found: C, 39.74; H, 2.67; N, 5.83.

$[\{(Me_3TAC\text{-}d)Co\}_3(OMe)_4][B(C_6F_5)_4]_2$ (2a-*d*). **2a**-*d* was prepared in a manner analogous to the preparation of **2a** from **1a** and Me_3TAC-*d*. ^2H NMR (CH_2Cl_2, 61 MHz): δ +94...96 ($W_{1/2} \approx$ 30 Hz, 0.6D, *Me*$_3$TAC), +6...9 ($W_{1/2} \approx$ 20 Hz, 1.1D, NC*D*$_{endo}$H$_{exo}$N), −14...−19 ($W_{1/2} \approx$ 20 Hz, 1.1D, NCH$_{endo}$*D*$_{exo}$N). IR (KBr) ν (cm^{-1}): 2218 w, 2086 w (br).

$[\{(Me_3TAC)Co\}_3(OMe)_{4-x}(OCD_3)_x][B(C_6F_5)_4]_2$ (OCD_3-2a) ($x \approx$ 2.7). OCD_3-**2a** was prepared in a manner analogous to the preparation **2a**. However, after drying of **1a** (0.16 mmol) with $CH(OMe)_3$ (6.4 mmol) and removal of all volatiles in vacuo, the residue was stirred with CD_3OD (0.25 mL, 1.75 mmol) for 30 min at 60 °C. The solvent was removed in vacuo, THF and then Me_3TAC were added, and workup was continued as above. ^2H NMR (CH_2Cl_2, 61 MHz): δ +493...497, +22, +15 ($W_{1/2} \approx$ 40 Hz, O*Me*). IR (KBr) ν (cm^{-1}): 2174 w, 2045 m.

$[\{(Me_3TAC)Co\}_3(OMe)_4][B(m\text{-}C_6H_3(CF_3)_2)_4]_2$ (2b). **1b** (1.19 g, 0.60 mmol) was stirred with 2,2-dimethoxypropane (5 mL). After 2 h, the volatiles were removed in vacuo, and the residue was treated with additional dimethoxypropane (2 mL). After removal of the volatiles in vacuo, the brown residue was dissolved in THF (10 mL), and Me_3TAC (0.2 mL, 1.4 mmol) added. The brown solution turned purple immediately after the addition. After 2 h of stirring, the volatiles were removed in vacuo, and the residue was washed twice with Et_2O (10 mL). Drying in vacuo yielded 400 mg (83%) of purple **2b**, mp 147−152 °C dec. ^1H NMR (CD_2Cl_2, 200 MHz): δ +504, +25, +18 ($W_{1/2} \approx$ 400 Hz, O*Me*), +95...99 (27 H, *Me*$_3$TAC), +8...12 (9H,

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(23) An Et_2O-free salt can be obtained after washing with $CHCl_3$ under substantial reduction of the yield.
(24) Removal of the volatiles in vacuo from the combined Et_2O solutions and washing of the residue with pentane gave a yellowish solid (494 mg, 78%). ^1H ($CDCl_3$): δ 9.71 (br, 1H, N*H*), 3.22 (br, 12H, NC*H*$_2$N), 2.33 (br, 18H, NC*H*$_3$). Anal. Calcd for $C_{30}H_{16}N_3BF_{20}$ ($(Me_3TAC)_2HB(C_6F_5)_4$): C, 46.08; H, 3.33; N, 8.96. Found: C, 46.15; H, 3.28; N 9.18.

Table 2. Crystal Data for $Me_3TAC{\cdot}HCl$, **2a**·(CH_2Cl_2), and **2b**·$(CH_2Cl_2)_2$

	$Me_3TAC{\cdot}HCl$	**2a**·(CH_2Cl_2)	**2b**·$(CH_2Cl_2)_2$
formula	$C_6H_{16}ClN_3$	$C_{71}H_{59}B_2Cl_2Co_3F_{40}N_9O_4$	$C_{88}H_{85}B_2Cl_4Co_3F_{48}N_9O_4$
formula weight	165.67	2131.58	2584.86
space group	*Pbca* (No.61)	$P\bar{1}$ (No. 2)	$P2_1$ (No. 4)
a, Å	11.0366(9)	13.857(2)	12.710(3)
b, Å	12.2986(6)	16.843(3)	23.251(3)
c, Å	13.9949(7)	19.318(2)	18.702(4)
α, deg		79.23(2)	
β, deg		76.855(13)	101.16(2)
γ, deg		70.10(2)	
V, $Å^3$	1899.6(2)	4098.9(10)	5423(2)
Z	8	2	2
ρ_{calcd}, g cm^{-3}	1.159	1.727	1.583
μ (Mo Kα), cm^{-1}	3.44	7.94	6.73
T, °C	20	−123	−83
λ, Å	0.71073	0.71073	0.71073
R^a	0.0463	0.0348	0.0715
$R_w{}^b$	0.1179	0.0848	0.1840

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

NC$H_{endo}$$H_{exo}$N), 7.57 ($W_{1/2} \approx 10$ Hz, 16H, *o*-$C_6H_3(CF_3)_2$), 7.41 ($W_{1/2} \approx 10$ Hz, 8H, *p*-$C_6H_3(CF_3)_2$), −15...−19 ($W_{1/2} \approx 100$ Hz, 9H, $NCH_{endo}H_{exo}N$). λ_{max}, nm (CH_2Cl_2)(ϵ, M^{-1} cm^{-1}): 467 (5), 532 (26), 595 (5). $\mu_{eff}(Co_3) = 7.0\ \mu_B$ (per Co_3) or 4.0 μ_B (per Co) (Evans method). Anal. Calcd for $C_{86}H_{81}N_9B_2Co_3F_{48}O_4$: C, 42.77; H, 3.38; N, 5.22. Found: C, 43.86; H, 3.53; N, 5.00.

Crystals of **2b** can be obtained by cooling a solution to 0 °C. The CH_2Cl_2 in the crystal cannot be removed in vacuo. $\mu_{eff}(Co_3) = 8.02(1)\ \mu_B$ (per Co_3) or 4.63(1) μ_B (per Co) (Faraday method). FAB MS (CH_2Cl_2/*m*-NO_2-benzyl-OH (Mx) matrix/Xe): FAB(+), 657 [$(Me_3TAC)_3Co_3(OMe)_4$(=CL) − (OMe)]$^+$, 715 [(CL) + (CH_2Cl_2) − ($MeN(CH_2)_2$)]$^+$, 729 [(CL) + (CH_2Cl_2) − (MeN=CH_2)]$^+$, 951 [(CL) + 2(Mx) − (MeN=CH_2)]$^+$, 994 [(CL) + 2(Mx)]$^+$; FAB(-), 863 [B(*m*-$C_6H_3(CF_3)_2)_4$]$^-$.

X-ray Structure Determination of $Me_3TAC{\cdot}HCl$. A summary of the crystal data, data collection, and refinement is given in Table 2. A colorless crystal was mounted on a glass fiber and transferred to a Stoe STADI4 four-circle diffractometer.[25] Lattice parameters derived from the setting angles of 28 reflections in the range of $27° \leq 2\theta \leq 32.5°$ were obtained. Data were collected in the $\varpi - 2\theta$ scan mode. After every 2 h, three standard reflections were monitored, and the crystal was reoriented in case of deviation between 0.1° and 0.15°. Intensity data were corrected for Lorentz and polarization effects. Structure solution was performed with direct methods (SHELXS-86)[26] and subsequent difference Fourier synthesis (SHELXL-93).[27] Refinement on F^2 was carried out by full-matrix least-squares techniques (SHELXL-93). Non-hydrogen atoms were refined with anisotropic thermal parameters, whereas hydrogen atoms were refined isotropically. Neutral atom scattering factors were taken from Cromer and Mann.[28] Illustrations were performed with ZORTEP.[29]

X-ray Structure Determination of 2a and 2b. A summary of the crystal data, data collection, and refinement is given in Table 2. The air-sensitive purple crystals were selected using a modified device, similar to that of Veith and Bärnighausen,[30] mounted on a glass fiber and transfered to a Stoe IPDS area detector equipped with a low-temperature device. Refined lattice parameters derived from 2000 reflections after data collection were obtained. Data of **2a** were collected in the rotation ϕ movement method. The crystal was rotated in 1.7° steps to yield 124 exposures, and each of them was irradiated for 3 min. Data of **2b** were collected in the oscillation ϕ movement method. The crystal was oscillated in 1.2° steps to yield 150 exposures, and each of them was irradiated for 3 min.

Table 3. Atomic Coordinates (Å × 10^4) for the Cation in **2a**

atom	*x*/*a*	*y*/*b*	*z*/*c*
Co(1)	233(1)	4142(1)	2368(1)
Co(2)	1516(1)	2542(1)	1674(1)
Co(3)	2392(1)	3132(1)	2726(1)
O(1)	2813(1)	2669(1)	1807(1)
C(11)	3600(2)	2804(2)	1250(2)
O(2)	1488(1)	4309(1)	2536(1)
C(21)	1858(2)	4993(2)	2211(2)
O(3)	603(1)	3709(1)	1439(1)
C(31)	895(5)	4173(3)	815(3)
C(31A)	193(14)	4087(8)	779(7)
O(4)	1001(1)	2869(1)	2729(1)
C(41)	571(2)	2406(2)	3268(2)
N(1)	−895(2)	4743(1)	3318(1)
N(2)	−851(2)	5501(1)	2181(1)
N(3)	−1580(2)	4387(1)	2477(1)
N(4)	2076(2)	1084(1)	1702(1)
N(5)	436(2)	1898(1)	1473(1)
N(6)	1906(2)	1979(1)	629(1)
N(7)	3866(2)	3275(1)	2911(1)
N(8)	2532(2)	3232(1)	3887(1)
N(9)	3473(2)	2016(1)	3347(1)
C(1)	−1756(2)	4473(2)	3236(1)
C(2)	−1005(2)	5599(2)	2938(2)
C(3)	−1683(2)	5222(2)	2057(2)
C(4)	2523(2)	1151(2)	939(1)
C(5)	1007(3)	1068(2)	1791(2)
C(6)	829(2)	1992(2)	699(1)
C(7)	4346(2)	2349(2)	3041(2)
C(8)	3366(2)	3616(2)	3593(1)
C(9)	2984(2)	2309(2)	4044(1)
C(10)	−837(3)	4698(2)	4073(2)
C(20)	−814(3)	6295(2)	1718(2)
C(30)	−2289(3)	3992(2)	2327(2)
C(40)	2721(3)	339(2)	2104(2)
C(50)	−696(3)	2054(2)	1633(2)
C(60)	2357(2)	2179(2)	−121(1)
C(70)	4632(2)	3691(2)	2494(2)
C(90)	3824(3)	1083(2)	3384(2)
C(80)	1870(3)	3614(2)	4518(2)

Intensity data were integrated and converted into an *hkl* file with the Stoe IPDS software (version 2.65). Structure solution was performed using the Patterson method (SHELXS-86)[26] and subsequent difference Fourier synthesis (SHELXL-93).[27] Refinement on F^2 was carried out by full-matrix least-squares techniques (SHELXL-93). Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included using a riding model with $d_{CH} = 0.96$ Å and $U_{iso} = 0.08$ $Å^2$. Neutral atom scattering factors were taken from Cromer and Mann.[28] Illustrations were performed with ZORTEP.[29] Final positional and equivalent isotropic thermal parameters for the cation in **2a** are given in Table 3.

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Structural Details for Complex 2a·(CH_2Cl_2). The methoxymethyl group C31 in the cation was found to be disordered in the ratio 60/40 (C31/C31A). Due to different hydrogen bond interaction of this methyl group with F114, a split atom model was introduced for half of the C_6F_5 ring to allow for a tilted phenyl ring in nearly the same ratio. Though disordered, all positions could be anisotropically refined.

Structural Details for Complex 2b·(CH_2Cl_2)$_2$. The complex crystallizes in the noncentrosymmetric space group $P2_1$. The Flack parameter was $\chi = 0.03(2)$ and confirmed the most probable structure.[31]

The F atoms attached to the C atoms C116, C127, C137, C147, and C226 had to be split into two CF_3 groups. Additionally, C226 also had to be split into C226/C26 in the corresponding ratio due to hydrogen bond interaction with one of the solvent molecules (H13A), which was refined disordered as two molecules with one common chlorine atom (Cl3). The disordered fluorine atoms attached to C127 and C226/C26 as well as the atoms of the two solvent molecules were refined isotropically. All disordered and isotropically refined atoms were restrained to ideal geometries.

Acknowledgment. We thank Prof. H. Schumann for the support of this work.

Supporting Information Available: Table listing all H··· F and H···Cl contacts that are smaller than the sum of the van der Waals radii, complete lists of all NMR and IR data, and a magnetic susceptibility plot and table (4 pages). X-ray crystallographic files, in CIF format, for Me_3TAC·HCl, **2a**, and **2b** are available, on the Internet only. Ordering and access information is given on any current masthead page.

IC9704593

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