sponding distances and angles for the two compounds are collected in Table IX.

The dimers observed for the tribromide and triiodide reported here represent a structural type which seems uncommon, although vibrational spectroscopic studies[17] have led to the prediction of this type of association. The only X-ray determination of a structure which is similar is that of the 1,2-cyclohexylene-bridged $Te_2Br_6C_6H_{10}$, obtained from $TeBr_4$ and cyclohexene.[14] A survey of the nonionic dibromides, R_2TeBr_2,[8,9] and tribromides[11,14] shows these compounds to be essentially monomeric with weak but significant Te---Br interactions down to 3.591 Å[8] (cf. the van der Waals contact of 4.15 Å). The diiodides[1-7,23] and triiodides[12,13] show similar, but perhaps stronger Te---I interactions (between otherwise monomeric species) as short as 3.692 Å[3] and I---I distances as low as 3.239 Å[12] (cf. van der Waals contacts of 4.35 and 4.30 Å, respectively). By comparison, the analogous contacts between dimeric units in (4-EtOPh)$TeBr_3$ are very long: i.e., Te1---Br5′, 4.174 (2); Te1---Br6′, 4.054 (2); Te2---Br3′, 4.226; Te2---Br4′, 4.119 Å (representing only the slightest of interactions). Nevertheless, the Te1---Te2′ distance of 4.173 (2) Å is significantly less than the normal Te---Te van der Waals contact of 4.40 Å. In (4-MeOPh)TeI_3 the interdimer interactions appear stronger: the Te1---I6′ and Te2---I4′ distances are 3.874 and 3.779 Å, respectively, although Te1 and Te2 of the other dimer unit are not in contact. The interaction between the dimeric units is further manifested in the larger fold (see above) between the pyramid bases in the triiodide than in the tribromide, as a result of the weak bonding of the bridging iodines to a third tellurium atom. The molecule $Te_2Br_6C_6H_{10}$[14] which also possesses bridging halogen atoms reveals certain differences which might be ascribed to the constraint of the cyclohexylene group; thus, the dihedral angle between pyramid bases is approximately 53°, the Te–Br(bridging) distances are shorter (2.870 and 2.890 (8) Å) than those in (4-EtOPh)$TeBr_3$ (from 2.884 to 2.992 (2) Å), and, interestingly, there are quite short Br-Br intermolecular interactions of a type absent in (4-EtOPh)$TeBr_3$ [Br(terminal)---Br(terminal) down to 3.55 Å; Br(terminal)---Br(bridge) down to 3.59 Å (a normal Br---Br van der Waals contact is 3.90 Å)].

Terminal halogen to tellurium distances vary over a quite large range: from a low of 2.490 Å to a high of 2.675 Å for Te–Br and from 2.769 to 3.099 Å for Te–I in the trihalides alone. Such bonds are evidently easily deformed by inter- and intramolecular influences, but the literature contains too few examples for a detailed analysis. The bond distance observed in (4-EtOPh)$TeBr_3$, which ranges from 2.509 to 2.548 (2) Å, and those in (4-MeOPh)TeI_3, from 2.776 (1) to 2.797 (1) Å, are all within the previously observed limits.

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Registry No. (4-EtOPh)$TeCl_3$, 36310-31-3; (4-EtOPh)$TeBr_3$, 36310-32-4; (4-EtOPh)TeI_3, 36310-33-5; [(4-EtOPh)TeI_3]$_2$, 73597-13-4; [(4-EtOPh)$TeBr_3$]$_2$, 73611-44-6.

Supplementary Material Available: Tables of observed and calculated structure amplitudes (27 pages). Ordering information is given on any current masthead page.

Contribution from the Institute of Inorganic Chemistry, University of Fribourg,
CH-1700 Fribourg, Switzerland, and the Crystallography Laboratory, Oxford, Great Britain

Preparation of [Co(η^2-Htame)(η^3-tame)X]^n, a New Type of Cobalt(III)–Acidopentaamine Complex with a Dangling Amine, and the Crystal Structure of [Co(η^2-Htame)(η^3-tame)Cl]$Cl_3 \cdot 2H_2O$

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The preparation of new acidopentaamine complexes, with the general formula [Co(η^2-Htame)(η^3-tame)X]^n (X = Cl^-, Br^-, OH^-, H_2O, SO_4^{2-}, SCN^-; tame = 1,1,1-tris(aminomethyl)ethane), and their chemical and spectroscopic properties are reported. The complexes contain one terdentate and one bidentate tame, leaving one dangling amine. The crystal structure of [Co(η^2-Htame)(η^3-tame)Cl]$Cl_3 \cdot 2H_2O$ has been determined to elucidate the configuration. This complex salt crystallizes in the space group $P2_1/c$, with $Z = 4$ ($a = 13.306$ (5) Å, $b = 9.777$ (2) Å, $c = 16.040$ (3) Å, $\beta = 101.73$ (2)°, $V = 2043.1$ Å^3). The structure has been refined to a final R_w of 0.092 from 2638 independent reflections. The hydrolysis of [Co(η^2-Htame)(η^3-tame)Cl]$^{3+}$ at pH 7.6–8.8 has been studied, and an acceleration due to the deprotonation of the dangling amine was observed.

Cobalt(III) complexes of partially coordinated polyamines are commonly postulated as reactive intermediates in isomerization and racemization reactions.[1,2] Only two complexes of this type have been reported in the literature, so far, to our knowledge. In a detailed study of Co^{III}penten complexes (*N*,*N*,*N′*,*N′*-tetrakis(β-aminoethyl)ethylenediamine) Schwarzenbach and Emmenegger[3] showed that, due to conformational strain in acid and base solutions, one chelate ring is opened and one primary amine group is replaced by a monodentate ligand. Alexander and Spillert[4] reported the preparation of [Co(η^1-Hen)(η^2-en)$_2$X]$^{3+}$, in which one en acts as a monodentate ligand. Preparing [Co(η^3-tame)$_2$]$^{3+}$ from $Na_3Co(CO_3)_3 \cdot 3H_2O$ and tame·3HCl (1,1,1-tris(aminomethyl)ethane) we always isolated in addition to the yellow hexaamine complex a red-violet byproduct. A slight modification of the reaction conditions allowed us to obtain the red-violet complex in yields higher than 60%. It was identified by chemical and spectroscopic methods as the acidopentaamine complex [Co(η^2-Htame)(η^3-tame)Cl]$^{3+}$ containing two tame, one acting as terdentate ligand and the other as a bidentate ligand, leaving a dangling amino group. Under these conditions the complex ion may have one of the two configurations shown in Chart I. Based on chemical and spectroscopic properties, it was not

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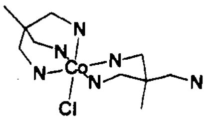
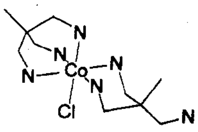
Chart I



A



B

possible to assign one of them. Hence for determination of the configuration of the complex ion [Co(η^2-Htame)(η^3-tame)Cl]$^{3+}$, the crystal structure of [Co(η^2-Htame)(η^3-tame)Cl]Cl$_3$·2H$_2$O was determined. Because a reorganization of the coordination sphere of the Co(III) would be necessary to convert configuration A to B, it is reasonable that the configuration of the complex ion is not changed upon dissolution of [Co(η^2-Htame)(η^3-tame)Cl]Cl$_3$·2H$_2$O.

Experimental Section

tame·3HCl was prepared from 1,1,1-tris(hydroxymethyl)ethane,[5] purum, purchased from Fluka AG: formula $C_5H_{18}N_3Cl_3$; M_r 226.53. Anal. Calcd: C, 26.49; H, 8.01; N, 18.54. Found: C, 26.45; H, 8.06; N, 18.40.

[Co(η^3-tame)$_2$]Cl$_2$ClO$_4$ (IV). A 2.266-g (0.01-mol) sample of tame·3HCl was dissolved in 5 mL of H$_2$O, and 2 g (0.0052 mol) of freshly prepared Na$_3$Co(CO$_3$)$_3$·3H$_2$O[6] was added. The suspension was stirred at room temperature until the evolution of CO$_2$ ceased. The solution was then heated on a water bath until the evolution of CO$_2$ stopped. A 1.7-g sample of 60% HClO$_4$ was slowly added, and the solution was put in the refrigerator. After 1 day the yellow precipitate, containing some red-violet impurities, was filtered off and recrystallized from a 7:3 mixture of H$_2$O–32% HCl. The product was vacuum dried: yield 1.52 g (70%); formula $C_{10}H_{30}N_6O_4Cl_3Co$; M_r 463.47. Anal. Calcd: C, 25.90; H, 6.52; N, 18.12; Cl, 22.93; Co, 12.70. Found: C, 26.00; H, 6.52; N, 18.23; Cl, 22.90; Co, 12.73.

[Co(η^2-Htame)(η^3-tame)Cl]Cl$_2$ClO$_4$ (I) was prepared by the same method as [Co(η^3-tame)$_2$]Cl$_2$ClO$_4$, but a slurry of 10 g of SrCl$_2$·6H$_2$O in 10 mL of H$_2$O was used as solvent instead of 5 mL of H$_2$O: yield 1.62 g (65%); formula $C_{10}H_{31}N_6O_4Cl_4Co$; M_r 500.14. Anal. Calcd: C, 24.01; H, 6.24; N, 16.80; Cl, 28.35; Co, 11.78. Found: C, 24.39; H, 6.26; N, 16.93; Cl, 28.24; Co, 11.70.

[Co(η^2-Htame)(η^3-tame)Cl]Cl$_3$·2H$_2$O was obtained from I by recrystallizing the crude product from 4 N HCl: yield 60%; formula $C_{10}H_{35}N_6O_2Cl_4Co$; M_r 472.17. Anal. Calcd: C, 25.43; H, 7.47; N, 17.79; Cl, 30.03; Co, 12.48. Found: C, 25.37; H, 7.66; N, 18.10; Cl, 29.97; Co, 12.52.

[Co(η^2-Htame)(η^3-tame)Br]Br$_3$·H$_2$O was obtained by reacting tame·3HCl with Na$_3$[Co(CO$_3$)$_3$]·3H$_2$O in a saturated solution of SrBr$_2$ and recrystallizing it from 1 N HBr: yield 50%, formula $C_{10}H_{33}N_6OBr_4Co$; M_r 631.98. Anal. Calcd: C, 19.00; H, 5.26; N, 13.29; Br, 50.57; Co, 9.32. Found: C, 18.95; H, 5.46; N, 13.22; Br, 50.74; Co, 9.45.

[Co(η^2-Htame)(η^3-tame)NCS](NCS)$_2$ClO$_4$. A 500-mg (0.001-mol) sample of I and 486 mg (0.006 mol) of KNCS were recrystallized from H$_2$O: yield 483 mg (85%); formula $C_{13}H_{31}N_9O_4S_3ClCo$; M_r 568.00. Anal. Calcd: C, 27.48; H, 5.50; N, 22.19; Co, 10.37. Found: C, 27.08; H, 5.40; N, 22.07; Co, 10.21.

[Co(η^2-tame)(η^3-tame)OH](ClO$_4$)$_2$ (III). A 500-mg (0.001-mol) sample of I was dissolved in 15 mL of H$_2$O, and 0.003 mol of AgClO$_4$ (Ag$_2$CO$_3$ dissolved in 60% HClO$_4$) was added. The pH was adjusted to 7 with 1 N NaOH and the AgCl removed. The clear solution was made alkaline with 1 N NaOH, evaporated without heating until crystallization started, and put in the refrigerator. After 1 day the brick red crystals were filtered off: yield 484 mg (95%); formula $C_{10}H_{31}N_6O_9Cl_2Co$; M_r 509.21. Anal. Calcd: C, 23.58; H, 6.13; N, 16.50; Cl, 13.92; Co, 11.57. Found: C, 23.42; H, 6.30; N, 16.37; Cl, 14.07; Co, 11.67.

[Co(η^2-Htame)(η^3-tame)OH](ClO$_4$)$_3$. A 509-mg (0.001-mol) sample of [Co(η^2-tame)(η^3-tame)OH](ClO$_4$)$_2$ was dissolved in 10 mL of 0.1 N HClO$_4$. The solution was concentrated to 2 mL without heating, 2 mL of ethanol was added, and the mixture was then put in the refrigerator. After 1 day the brick-red crystals were filtered off: yield 547 mg (90%); formula $C_{10}H_{32}N_6O_{13}Cl_3Co$; M_r 609.69. Anal. Calcd: C, 19.68; H, 5.29; N, 13.78; Cl, 17.45; Co, 9.67. Found: C, 19.79; H, 5.16; N, 13.75; Cl, 17.59; Co, 9.69.

[Co(η^2-Htame)(η^3-tame)H$_2$O](ClO$_4$)$_4$. A 509.2-mg (0.001-mol) sample of [Co(η^2-tame)(η^3-tame)OH](ClO$_4$)$_2$ was dissolved in 25 mL of 0.1 M HClO$_4$. The solution was concentrated without heating until the first crystals were observed and then put in the refrigerator. After 1 day the red product was filtered off and vacuum dried. [Co(η^2-Htame)(η^3-tame)H$_2$O](ClO$_4$)$_4$ is hygroscopic: yield 638 mg (90%); formula $C_{10}H_{33}N_6O_{17}Cl_4Co$; M_r 710.15. Anal. Calcd: C, 16.90; H, 4.68; N, 11.83; Cl, 19.97; Co, 8.30. Found: C, 16.47; H, 4.98; N, 12.08; Cl, 20.23; Co, 7.98.

[Co(η^2-Htame)(η^3-tame)SO$_4$]SO$_4$·3H$_2$O. A 500-mg (0.001-mol) sample of I was dissolved in 25 mL of H$_2$O, 935.4 mg (0.003 mol) of Ag$_2$SO$_4$ was added, and the pH of the solution was adjusted to 7 by NaOH. The AgCl was removed and the clear solution acidified by H$_2$SO$_4$. The solution was concentrated without heating until crystallization started and then put in the refrigerator. After 1 day the red crystals of [Co(η^2-Htame)(η^3-tame)SO$_4$]SO$_4$·3H$_2$O were filtered off and vacuum dried: yield 438 mg (85%); formula $C_{10}H_{37}N_6O_{11}S_2Co$; M_r 540.49. Anal. Calcd: C, 22.22; H, 6.90; N, 15.54; Co, 10.90. Found: C, 21.99; H, 6.91; N, 15.31; Co, 11.08.

[Co(η^2-diamol)(η^3-tame)NO$_2$]ClClO$_4$ (II) (diamol = 2,2-Bis(aminomethyl)propanol). A 500-mg (0.001-mol) sample of I was dissolved in 40 mL of H$_2$O, and 207 mg (0.003 mol) of NaNO$_2$ was added. The solution was heated on a water bath. After 10 min 4 mL of 1 N HClO$_4$ was slowly added. After 1 h of heating, the solvent was evaporated until crystallization started and the solution was then put in the refrigerator. After 1 day the precipitate was filtered off and recrystallized from H$_2$O: yield 309 mg (65%); formula $C_{10}H_{29}N_6O_7Cl_2Co$; M_r 457.21. Anal. Calcd: C, 25.27; H, 6.15; N, 17.68; Cl, 14.92; Co, 12.40. Found: C, 25.37; H, 6.07; N, 17.99; Cl, 15.24; Co, 12.11.

[Co(η^2-bstame)(η^3-tame)Cl]Cl$_2$ (bstame = *N*-(2,2-Bis(aminomethyl)propyl)benzenesulfonamide). A 500-mg (0.001-mol) sample of I was dissolved in 20 mL of 2 N NaOH. A 0.88-g (0.005-mol) sample of benzenesulfonyl chloride was added, the mixture was agitated at room temperature until the solution was homogeneous and evaporated to dryness, and the product was recrystallized from H$_2$O–ethanol: yield 243 mg (45%); formula $C_{16}H_{34}N_6O_2SCl_3Co$; M_r 539.84. Anal. Calcd: C, 35.59; H, 6.34; N, 15.56; Cl, 19.70; Co, 10.91. Found: C, 35.69; H, 6.67; N, 15.71; Cl, 19.54; Co, 10.71.

[Co(η^2-actame)(η^3-tame)CH$_3$COO]CH$_3$COOClO$_4$·7H$_2$O (V) (actame = *N*-(2,2-Bis(aminoethyl)propyl)acetamide). A 500-mg (0.001-mol) sample of I was dissolved in 20 mL of 1 N HCl and 80 mL of H$_2$O. A 3-g sample of NaCH$_3$COO·3H$_2$O was added, and the solution was cooled to 0 °C. A 25-mL solution of acetic anhydride was added. The solution was stirred for 4 h at 0 °C and then evaporated to dryness. The product was recrystallized from 1 N CH$_3$COOH: yield 500 mg (74%); formula $C_{16}H_{49}N_6O_{16}ClCo$; M_r 675.98. Anal. Calcd: C, 28.42; H, 7.30; N, 12.43; Cl, 5.24; Co, 8.71. Found: C, 28.59; H, 6.92; N, 12.93; Cl, 5.04; Co, 8.98.

Analyses. C, H, and N were determined in the microanalytical laboratory of the University of Fribourg (F. Nydegger). Co was determined as Co(SCN)$_4^{2-}$ by colorimetry.[7] The complexes were heated in 1 N NaOH, acidified with diluted HNO$_3$, and titrated with AgNO$_3$ to determine total Cl$^-$ content. An acid solution of the complex was passed over a cation exchanger (Dowex 50W-X8 50/100 mesh) and the Cl$^-$ titrated in the eluate to determine the ionogenic Cl$^-$. ClO$_4^-$ was determined as Cl$^-$ after reduction with Na$_2$CO$_3$ in a platinum crucible at 900–1000 °C.

Determination of the p*K* Values. A 100-mL 10^{-3} M solution (0.1 N) of the complex was acidified with 0.1 N HCl and then titrated with 0.1 M NaOH under N$_2$. The pH values were measured by a glass electrode (Metrohm EA 109) and a separated calomel electrode (Metrohm EA 404) using a potentiograph (Metrohm E 536) equipped with a buret (Metrohm E 535). The glass electrode was calibrated by titration of 0.1 M HClO$_4$.

Base Hydrolysis. In a typical kinetic experiment, ca. 30 mg of I was dissolved in 3 mL of H$_2$O and 5 mL of 0.2 M morpholine hydrochloride. The calculated amount of 1 N NaOH was added with a syringe to obtain a given pH value and diluted up to 10 mL with H$_2$O. The change in absorption was followed at 2.02 μm^{-1} for at least 5 half-times on a Varian Techtron spectrometer. After each run the

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Table I. Crystal Data for [Co(η^2-Htame)(η^3-tame)Cl]$Cl_3 \cdot 2H_2O$

mol formula $C_{10}H_{35}Cl_4CoN_6O_2$
$M_r = 472.18$
$a = 13.306$ (5) Å
$b = 9.777$ (2) Å
$c = 16.040$ (3) Å
$\beta = 101.73$ (2)°
space group $P2_1/c$
$V = 2.043.1$ Å^3
$Z = 4$
$D_m = 1.54$ (1) g cm^{-3}
$D_c = 1.535$ g cm^{-3}
μ(Mo Kα) = 13.5 cm^{-1}

pH of the solution was checked with the glass electrode.

Spectra. The UV/vis spectra were measured with a Zeiss FMD 3 spectrograph. The IR spectra of all the complexes in KBr pellets were recorded on a Perkin-Elmer 457 IR spectrometer. The ^{1}H NMR spectra in D_2O solutions were measured on a Varian EM 390 NMR spectrometer, using sodium 4,4-dimethyl-4-silapentanesulfonate (DSS) as an internal standard.

Structure Determination of [Co(η^2-Htame)(η^3-tame)Cl]$Cl_3 \cdot 2H_2O$. A bright red needle crystal (size 0.7 × 0.1 × 0.1 mm) suitable for X-ray diffraction studies was selected. The crystal is monoclinic, belonging to space group $P2_1/c$ as uniquely determined by the systematic extinctions: $0k0$, $k = 2n + 1$, and $h0l$, $l = 2n + 1$. Approximate unit-cell dimensions were refined by least-squares analysis using observed diffractometer data for 25 reflections, automatically centered under computer control. The crystal data are summarized in Table I.

Data Collection and Reduction. Intensity data were collected under computer control by using a Nonius CAD-4F κ geometry diffractometer. The intensity of each independent reflection with $(\sin\theta)/\lambda < 0.66$ was measured by an $\omega/2\theta$ scan, a variable scan rate, and an ω scan angle of $(1.00 + 0.35 \tan\theta)°$. Mo K$\alpha$ radiation was used with a graphite monochromator. Reflections with $I < 3\sigma(I)$, where $\sigma(I)$ is the standard deviation on the basis of simple counting statistics, were not included in subsequent calculations. The intensities of three standard reflections, monitored at regular intervals, showed no systematic change. Lorentz and polarization corrections were applied, but no absorption corrections were made. A set of 2638 independent structure amplitudes was obtained.

Structure Determination and Refinement. All calculations were performed on the Oxford University ICL 1906A computer with the Oxford CRYSTALS package.[8]

The cobalt atom position was found from a Patterson synthesis, and, subsequently, all other atoms in the molecule were revealed by Fourier and difference Fourier syntheses. Refinement was by least squares with a large block approximation to the normal matrix. (Block 1: scale, dummy overall isotropic temperature factor.[9] Block 2: x, y, and z for the cation. Block 3: temperature factors for the cation. Block 4: x, y, and z and temperature factors for the chloride ions and water molecules.) All nonhydrogen atoms had anisotropic temperature factors. Difference syntheses permitted the location of the hydrogen atoms (except those of the water molecules) in their expected positions. They were included in the refinement with isotropic temperature factors and were constrained. The C–H and N–H lengths were constrained[10,11] to be 1.00 Å with an estimated standard deviation of 0.02 Å; bond angles around nitrogen (except N(6)) involving H were constrained to be 108° with an esd of 1°, and other bond angles involving H were constrained to be 109° with an esd of 1°. In addition, the difference in mean-square displacement along the bond direction of the two atoms (C or N and H) forming each bond was constrained to be zero with an esd of 0.005 Å^2. In the final stages of refinement, each reflection was assigned a weight $w^{1/2} = 1$ if $|F_o| \le 15$; otherwise $w^{1/2} = 15/|F_o|$ and the final weighted R_w was 0.092 (R_c = 0.063) for 2638 reflections. The "goodness of fit" for the determination of 333 parameters was 0.20. A final difference map, with a root-mean-square deviation of electron density of 0.11 e Å^{-3}, had no significant features.

Table II. Positional and Isotropic Thermal Parameters for [Co(η^2-Htame)(η^3-tame)Cl]$Cl_3 \cdot 2H_2O$

atom	x/a	y/b	z/c
Co(1)	0.2146 (1)	0.4420 (1)	0.42531 (8)
Cl(1)	0.1975 (2)	0.6228 (3)	0.5105 (2)
N(1)	0.3501 (6)	0.5162 (8)	0.4148 (5)
N(2)	0.1418 (6)	0.5473 (8)	0.3253 (5)
N(3)	0.2850 (6)	0.3362 (8)	0.5249 (5)
N(4)	0.0825 (5)	0.3753 (8)	0.4466 (5)
N(5)	0.2246 (5)	0.2834 (8)	0.3534 (4)
N(6)	0.4231 (7)	0.780 (1)	0.2088 (6)
C(1)	0.3728 (6)	0.558 (1)	0.3319 (6)
C(2)	0.1935 (7)	0.581 (1)	0.2527 (6)
C(3)	0.2970 (8)	0.655 (1)	0.2803 (6)
C(4)	0.3272 (8)	0.690 (1)	0.1972 (6)
C(5)	0.2805 (8)	0.787 (1)	0.3298 (7)
C(6)	0.2345 (7)	0.209 (1)	0.5457 (6)
C(7)	0.0641 (7)	0.225 (1)	0.4445 (6)
C(8)	0.2201 (8)	0.1428 (9)	0.3925 (6)
C(9)	0.1662 (7)	0.1457 (9)	0.4670 (6)
C(10)	0.1438 (9)	−0.004 (1)	0.4887 (7)
Cl(2)	0.5015 (2)	0.2555 (3)	0.4648 (2)
Cl(3)	0.3622 (2)	0.3906 (3)	0.7272 (2)
Cl(4)	0.0118 (2)	0.3173 (3)	0.2104 (2)
O(1)	0.0903 (6)	0.4426 (9)	0.6380 (5)
O(2)	0.4739 (8)	0.437 (1)	0.1240 (8)

atom	x/a	y/b	z/c	U, Å^2
H(1O1)	0.363 (2)	0.598 (2)	0.453 (1)	0.034 (7)
H(1O2)	0.402 (1)	0.446 (2)	0.439 (1)	0.030 (6)
H(2O1)	0.120 (2)	0.636 (2)	0.347 (1)	0.031 (7)
H(2O2)	0.078 (2)	0.496 (2)	0.301 (1)	0.023 (6)
H(3O1)	0.294 (2)	0.397 (2)	0.576 (1)	0.027 (6)
H(3O2)	0.354 (2)	0.311 (2)	0.516 (1)	0.045 (7)
H(4O1)	0.075 (2)	0.409 (2)	0.504 (1)	0.033 (7)
H(4O2)	0.027 (1)	0.418 (2)	0.403 (2)	0.031 (7)
H(5O1)	0.290 (2)	0.290 (2)	0.334 (1)	0.011 (6)
H(5O2)	0.168 (2)	0.289 (2)	0.303 (1)	0.026 (6)
H(6O1)	0.444 (4)	0.791 (7)	0.153 (2)	0.031 (7)
H(6O2)	0.408 (2)	0.871 (4)	0.231 (5)	0.057 (8)
H(6O3)	0.480 (2)	0.735 (5)	0.250 (4)	0.058 (8)
H(11)	0.442 (2)	0.602 (3)	0.343 (1)	0.021 (7)
H(12)	0.376 (2)	0.474 (2)	0.297 (1)	0.044 (8)
H(21)	0.147 (1)	0.641 (3)	0.212 (1)	0.024 (7)
H(22)	0.205 (2)	0.494 (2)	0.223 (1)	0.030 (7)
H(41)	0.269 (2)	0.740 (3)	0.160 (1)	0.035 (8)
H(42)	0.340 (2)	0.604 (2)	0.168 (1)	0.046 (8)
H(51)	0.344 (3)	0.845 (4)	0.337 (4)	0.036 (8)
H(52)	0.267 (6)	0.761 (2)	0.387 (2)	0.038 (8)
H(53)	0.220 (4)	0.839 (4)	0.297 (3)	0.038 (8)
H(61)	0.192 (2)	0.230 (2)	0.589 (1)	0.033 (7)
H(62)	0.289 (2)	0.141 (2)	0.570 (2)	0.030 (7)
H(71)	0.022 (2)	0.201 (2)	0.487 (2)	0.032 (7)
H(72)	0.027 (2)	0.197 (2)	0.386 (2)	0.038 (8)
H(81)	0.291 (2)	0.109 (2)	0.413 (1)	0.035 (7)
H(82)	0.183 (2)	0.079 (2)	0.348 (1)	0.01 (3)
H(111)	0.208 (2)	−0.058 (3)	0.497 (5)	0.051 (9)
H(112)	0.116 (5)	−0.006 (2)	0.542 (3)	0.056 (9)
H(113)	0.092 (5)	−0.044 (3)	0.441 (3)	0.037 (8)

Throughout the refinement calculations, the atomic scattering curves for Co, Cl, O, N, and C of Doyle and Turner[12] were used. For hydrogen the values of Cromer and Mann[13] were taken. Values of the anomalous components of $\Delta f'$ and $\Delta f''$ in the scattering factors of Co and Cl were acquired from Cromer and Liberman.[14] The final atomic parameters are given in Tables II and III. Tables of observed structure amplitudes and structure factors calculated from the atomic parameters in Tables II and III are available.[15] Table IV contains the bond lengths and angles for the nonhydrogen atoms, with estimated standard deviations calculated from the full variance–covariance matrix.

Chemical Properties

The reactivity of [Co(η^2-Htame)(η^3-tame)Cl]$^{3+}$ (I) clearly indicates a noncoordinated amine group. Some typical reactions of the complex cation are shown in Scheme I. Re-

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Table III. Anisotropic Thermal Parameters[a] for $[Co(\eta^2\text{-Htame})(\eta^3\text{-tame})Cl]Cl_3 \cdot 2H_2O$

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Co(1)	0.0229 (5)	0.0200 (5)	0.0207 (5)	−0.0005 (5)	0.0042 (4)	−0.0023 (5)
Cl(1)	0.054 (2)	0.028 (1)	0.033 (1)	−0.008 (1)	0.017 (1)	−0.005 (1)
N(1)	0.023 (4)	0.030 (4)	0.025 (4)	0.007 (3)	0.002 (3)	−0.008 (3)
N(2)	0.030 (4)	0.023 (4)	0.027 (4)	0.004 (3)	−0.004 (3)	−0.002 (4)
N(3)	0.037 (5)	0.027 (4)	0.021 (4)	0.003 (3)	−0.002 (3)	−0.005 (4)
N(4)	0.020 (4)	0.024 (4)	0.037 (4)	0.004 (4)	0.012 (3)	−0.002 (3)
N(5)	0.016 (3)	0.030 (4)	0.024 (4)	−0.001 (3)	0.011 (3)	−0.002 (3)
N(6)	0.046 (6)	0.054 (6)	0.050 (6)	0.009 (5)	0.027 (5)	−0.004 (5)
C(1)	0.017 (4)	0.040 (5)	0.033 (5)	0.009 (5)	0.012 (4)	−0.000 (4)
C(2)	0.033 (5)	0.032 (6)	0.023 (5)	0.000 (4)	0.002 (4)	0.005 (4)
C(3)	0.033 (5)	0.028 (5)	0.028 (5)	0.006 (4)	0.003 (4)	−0.002 (4)
C(4)	0.044 (6)	0.040 (6)	0.033 (6)	0.010 (5)	0.011 (5)	0.002 (5)
C(5)	0.045 (6)	0.025 (5)	0.041 (6)	0.004 (5)	0.008 (5)	−0.002 (5)
C(6)	0.032 (5)	0.029 (5)	0.031 (5)	0.005 (4)	0.006 (4)	−0.001 (4)
C(7)	0.031 (5)	0.026 (5)	0.040 (6)	0.002 (4)	0.008 (4)	−0.004 (4)
C(8)	0.037 (6)	0.023 (5)	0.035 (5)	−0.002 (4)	0.010 (4)	0.002 (4)
C(9)	0.035 (5)	0.020 (5)	0.030 (5)	−0.001 (4)	0.008 (4)	−0.002 (4)
C(10)	0.046 (7)	0.025 (5)	0.047 (7)	0.010 (5)	0.000 (5)	−0.012 (5)
Cl(2)	0.034 (1)	0.049 (2)	0.042 (1)	−0.003 (1)	0.009 (1)	−0.001 (1)
Cl(3)	0.057 (2)	0.059 (2)	0.033 (1)	−0.005 (1)	0.009 (1)	−0.004 (1)
Cl(4)	0.045 (2)	0.042 (2)	0.055 (2)	−0.005 (1)	−0.014 (1)	−0.012 (1)
O(1)	0.050 (5)	0.062 (5)	0.061 (5)	0.012 (5)	0.023 (4)	0.015 (5)
O(2)	0.063 (7)	0.070 (7)	0.117 (9)	−0.017 (7)	0.012 (6)	−0.007 (6)

[a] The form of the anisotropic temperature factor is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)]$.

Scheme I

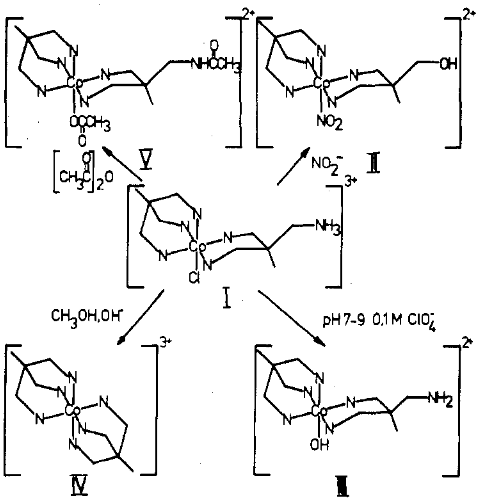

Table IV. Bond Lengths (Å) and Bond Angles (Deg) in $[Co(\eta^2\text{-Htame})(\eta^3\text{-tame})Cl]Cl_3 \cdot 2H_2O$

Co(1)–Cl(1)	2.274 (3)	N(1)–C(1)	1.48 (1)
Co(1)–N(1)	1.982 (7)	N(2)–C(2)	1.50 (1)
Co(1)–N(2)	1.984 (7)	N(3)–C(6)	1.49 (1)
Co(1)–N(3)	1.973 (7)	N(4)–C(7)	1.49 (1)
Co(1)–N(4)	1.968 (7)	N(5)–C(8)	1.52 (1)
Co(1)–N(5)	1.953 (7)	N(6)–C(4)	1.53 (1)
C(1)–C(3)	1.51 (1)	C(6)–C(9)	1.53 (1)
C(2)–C(3)	1.54 (1)	C(7)–C(9)	1.54 (1)
C(3)–C(4)	1.51 (1)	C(8)–C(9)	1.51 (1)
C(3)–C(5)	1.55 (1)	C(9)–C(10)	1.55 (1)
Cl(1)–Co(1)–N(1)	88.3 (2)	N(1)–C(1)–C(3)	115.6 (7)
Cl(1)–Co(1)–N(2)	89.4 (2)	N(2)–C(2)–C(3)	113.8 (7)
Cl(1)–Co(1)–N(3)	90.6 (2)	C(1)–C(3)–C(2)	108.7 (8)
Cl(1)–Co(1)–N(4)	87.2 (2)	C(1)–C(3)–C(4)	111.1 (8)
Cl(1)–Co(1)–N(5)	177.7 (2)	C(1)–C(3)–C(5)	113.0 (8)
N(1)–Co(1)–N(2)	92.6 (3)	C(2)–C(3)–C(4)	103.7 (7)
N(1)–Co(1)–N(3)	88.3 (3)	C(2)–C(3)–C(5)	109.0 (8)
N(1)–Co(1)–N(4)	174.7 (3)	C(4)–C(3)–C(5)	110.9 (8)
N(1)–Co(1)–N(5)	93.9 (3)	N(6)–C(4)–C(3)	112.9 (8)
N(2)–Co(1)–N(3)	179.1 (3)	N(3)–C(6)–C(9)	111.9 (7)
N(2)–Co(1)–N(4)	90.3 (3)	N(4)–C(7)–C(9)	110.8 (7)
N(2)–Co(1)–N(5)	90.9 (3)	N(5)–C(8)–C(9)	112.0 (7)
N(3)–Co(1)–N(4)	88.8 (3)	C(6)–C(9)–C(7)	109.8 (8)
N(3)–Co(1)–N(5)	89.1 (3)	C(6)–C(9)–C(8)	111.3 (8)
N(4)–Co(1)–N(5)	90.5 (3)	C(6)–C(9)–C(10)	107.7 (8)
Co(1)–N(1)–C(1)	122.2 (5)	C(7)–C(9)–C(8)	111.3 (8)
Co(1)–N(2)–C(2)	121.0 (5)	C(7)–C(9)–C(10)	108.9 (8)
Co(1)–N(3)–C(6)	117.4 (5)	C(8)–C(9)–C(10)	107.8 (8)
Co(1)–N(4)–C(7)	118.2 (6)		
Co(1)–N(5)–C(8)	117.5 (5)		

action with acetic anhydride yields under mild conditions amide V of the dangling amino group. The Cl^- in the coordination sphere is replaced by the acid group, and no hexaamine complex formed by replacement of Cl^- by the dangling amine under the condition of this reaction. Analogous reactions are observed with sulfochlorides yielding sulfonamides. Reaction of I with NO_2^- in acid solution leads to deamination of the dangling amine and formation of $[Co(\eta^2\text{-diamol})(\eta^3\text{-tame})NO_2]^{2+}$ (II). Base hydrolyses of I under controlled conditions yield the hydroxo complex in a clean reaction without any formation of hexaamine species. The kinetics of the base hydrolysis has been studied in some detail (vide infra). In aqueous alcohol or unbuffered alkaline solution the only product of the hydrolysis is the hexaamine species $[Co(\eta^3\text{-tame})_2]^{3+}$ (IV). If the latter is formed once, there is no possibility of opening one single chelate ring. Hence it seems that $[Co(\eta^3\text{-tame})_2]^{3+}$ is the thermodynamically more stable species in the system. $[Co(\eta^2\text{-Htame})(\eta^3\text{-tame})X]^n$ is only kinetically stable. This situation is different in the penten complexes, studied in great detail by Schwarzenbach and Emmenegger,[3] where the hexaamine is strongly destabilized by conformational strain, and one of the five chelate rings can be opened and closed at will.

The titration of I shows a buffer region around pH 8, due to the deprotonation of the dangling ammonium group, as is shown by the fact that this acid–base equilibrium is absent in complexes with a chemically modified dangling amino group. Unfortunately, the p*K* of the latter cannot be obtained from the titration curve directly because base hydrolysis sets in at high pH values. In $[Co(\eta^2\text{-Htame})(\eta^3\text{-tame})H_2O]^{4+}$ this problem is absent. The aquo complex, however, is a diprotic acid in aqueous solution, with $pK_1 = 4.65 \pm 0.08$ and $pK_2 = 7.33 \pm 0.06$ (0.1 N $NaClO_4$). The first step is accompanied by a distinct color change, indicating the deprotonation of the coordinated water. In contrast the second deprotonation around pH 8 is not accompanied by a color change in the

Table V. pK Values of Dangling Amines and Coordinated H_2O in Co(III) Complexes

	ionic strength	pK_1 (H_2O)	pK_2 (NH_3^+)	ref
[Co(η^2-Htame)(η^3-tame)H_2O]$^{4+}$	0.1 ($NaClO_4$)	4.65 ± 0.08	7.33 ± 0.06	this work
[Co(η^2-Htame)(η^3-tame)Cl]$^{3+}$	0.1 (NaCl)		~8.0[a]	this work
[Co(η^5-penten)H_2O]$^{4+}$	0.1 (KNO_3)	4.78	7.84	3
[Co(η^1-Hen)(η^2-en)$_2$Cl]$^{3+}$			7.1	4
[Co(NH_3)$_5H_2O$]$^{3+}$	1.0	6.36 ± 0.05		16
cis-[Co(en)$_2NH_3H_2O$]$^{3+}$	2.0	6.30 ± 0.05		16
trans-[Co(en)$_2NH_3H_2O$]$^{3+}$	2.0	6.06 ± 0.05		16
[Cu(η^2-Htame)(η^3-tame)]$^{3+}$	0.5 (KNO_3)		8.22 ± 0.02	17

[a] From kinetic measurements.

Table VI. Rates of Base Hydrolysis of Some Cobalt–(III) Pentaamine Complexes

	k_{OH}, M^{-1} s^{-1}	T °C	medium	ref
[Co(η^2-Htame)(η^3-tame)Cl]$^{3+}$	(5.71 ± 0.69) × 10^2	13	0.1 N NaCl	this work
	(1.68 ± 0.23) × 10^3	20		
[Co(tmd)(tame)Cl]$^{2+}$	57.3	25	0.5 N $NaClO_4$	19
[Co(bamp)(tmd)Cl]$^{2+}$	7700	25	1.0 N $NaClO_4$	20
κ-[Co(dien)(en)Cl]$^{2+}$	50 200	25	0.1 N $NaClO_4$	21
π-[Co(dien)(en)Cl]$^{2+}$	138	25	0.1 N $NaClO_4$	21
ω-[Co(dien)(en)Cl]$^{2+}$	10.6	25	0.1 N $NaClO_4$	21

Scheme II

$$[\mathrm{Co}(\eta^2\text{-Htame})(\eta^3\text{-tame})\mathrm{Cl}]^{3+} \underset{}{\overset{K_\mathrm{B}}{\rightleftharpoons}} [\mathrm{Co}(\eta^2\text{-tame})(\eta^3\text{-tame})\mathrm{Cl}]^{2+} + \mathrm{H}^+ \quad (1)$$

$$[\mathrm{Co}(\eta^2\text{-tame})(\eta^3\text{-tame})\mathrm{Cl}^{2+} + \mathrm{H_2O} \xrightarrow{k'_\mathrm{OH}} [\mathrm{Co}(\eta^2\text{-tame})(\eta^3\text{-tame})\mathrm{H_2O}]^{3+} + \mathrm{Cl}^- \quad (2)$$

$$[\mathrm{Co}(\eta^2\text{-tame})(\eta^3\text{-tame})\mathrm{H_2O}]^{3+} \xrightarrow{\text{fast}} [\mathrm{Co}(\eta^2\text{-Htame})(\eta^3\text{-tame})\mathrm{OH}]^{3+} \quad (3)$$

visible region. The pK values of [Co(η^2-Htame)(η^3-tame)H_2O]$^{4+}$ are in good agreement with pK values of other similar compounds (Table V). What is striking is the high acidity of the coordinated H_2O in complexes with dangling ammonium groups as compared to other aquopentaamine complexes. It is most probably a consequence of the additional positive charge in the proximity of the deprotonation site.

The base hydrolysis of I has been studied between pH 7.6 and 8.8 in a morpholine buffer at 13 and 20 °C. In contrast to that of ordinary base hydrolysis the reaction rate is not linearly dependent on [OH^-].[18] The observed rate law might, however, be interpreted by postulating a S_N1cB mechanism (Scheme II) with the dangling amine as the conjugated base.

$$\text{rate} = k_\mathrm{exptl}[\mathrm{Co}(\eta^2\text{-Htame})(\eta^3\text{-tame})\mathrm{Cl}]^{3+} \quad (4)$$

$$k_\mathrm{exptl} = \frac{k'_\mathrm{OH}K_\mathrm{B}[\mathrm{OH}^-]}{1 + K_\mathrm{B}[\mathrm{OH}^-]} \qquad k_\mathrm{OH} = k'_\mathrm{OH}K_\mathrm{B} \qquad K_\mathrm{B} = K_2/K_\mathrm{W}$$

$$K_2 = \frac{[\mathrm{Co}(\eta^2\text{-tame})(\eta^3\text{-tame})\mathrm{Cl}^{2+}][\mathrm{H_3O}^+]}{[\mathrm{Co}(\eta^2\text{-Htame})(\eta^3\text{-tame})\mathrm{Cl}^{3+}]}$$

This mechanism yields rate law 4 under the following assumptions: (i) acid–base equilibrium 1 of the dangling amine is fast and (ii) the direct hydrolysis of [Co(η^2-Htame)(η^3-tame)Cl]$^{3+}$ is slow compared to reaction 2 and can be neglected. Rate law 4 predicts the linear relation between k_exptl^{-1} and [OH^-]$^{-1}$, which has been found (Figure 1). k'_{OH} is determined by the intercept, and K_B is calculated from the slope. K_B is related to the pK of the dangling amine. The good agreement between the pK of the dangling amine in [Co(η^2-Htame)(η^3-tame)OH]$^{3+}$ determined by titration and in [Co(η^2-Htame)(η^3-tame)Cl]$^{3+}$, obtained from the rate law of the base hydrolyses, strongly supports the proposed mechanism. The determined rate constant k_{OH} is given in Table VI. The data show that k_{OH}, which is the product of k'_{OH}, the first-order rate constant for the hydrolysis of the conjugate base, and K_B, is similar for [Co(η^2-Htame)(η^3-tame)Cl]$^{3+}$ and the other acidopentaamine complexes. Hence, as K_B is considerably smaller in the latter complexes (ca. 10^{-1} M^{-1}) compared to 10^{+6} M^{-1} in [Co(η^2-Htame)(η^3-tame)Cl]$^{3+}$, the net acceleration of the hydrolysis in the conjugated base has to be smaller. This is not surprising, as the acceleration in ordinary acidopentaamine complexes is considered to be due mainly to the relative stabilization of the pentacoordinated transition state by the π-donating amide.[18] This mechanism, however, is not possible in this special case. Hence the acceleration has to be due only to the reduced positive charge of the complex ion.

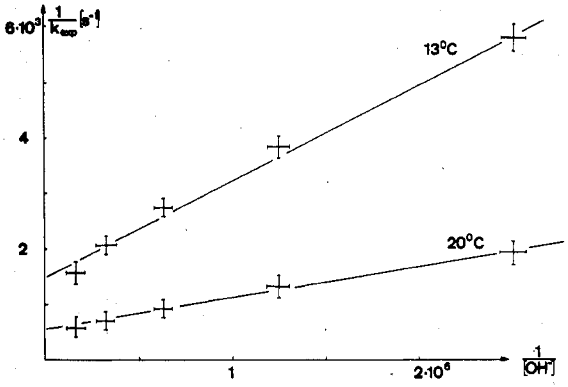

Figure 1. k_exptl^{-1} vs. [OH^-]$^{-1}$ for the hydrolyses of [Co(η^2-Htame)(η^3-tame)Cl]$^{3+}$.

Spectroscopic Properties

Figure 2 shows the d–d spectra of some [Co(η^2-Htame)(η^3-tame)X]$^{n+}$ complexes. The absorption maxima and the extinction coefficients are collected in Table VII. For comparison the data of the analogous [Co(NH_3)$_5$X]$^{n+}$ complexes are given too. The close agreement of the values indicate that the chromorphores in these two series are nearly identical. The spectra have been interpreted by using the

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Table VII. d–d Spectra of $[Co(\eta^2\text{-Htame})(\eta^3\text{-tame})X]^n$ and Related Complex Cations and the Analogous $[Co(NH_3)_5X]^{n-1}$ Complexes

	λ, μm⁻¹ (log ε)					
	$^1A_1$-^1E	$^1A_1$-$^1A_2$	$^1A_1$-$^1E/^1B_2$	Dt^c	$10Dq$ (X)^c	ref
$[Co(\eta^2\text{-Htame})(\eta^3\text{-tame})Br]^{3+}$	1.835 (1.81)	2.150 (sh)	*b*	0.0331	1.328 (Br)	
$[Co(NH_3)_5Br]^{2+}$	1.823 (1.71)	2.196 (sh)		0.0321	1.366 (Br)	22
$[Co(\eta^2\text{-Htame})(\eta^3\text{-tame})Cl]^{3+}$	1.895 (1.78)	2.150 (sh)	2.750 (1.83)	0.0262	1.570 (Cl)	
$[Co(NH_3)_5Cl]^{2+}$	1.872 (1.71)	2.135 (sh)	2.750 (1.72)	0.0266	1.559 (Cl)	22
$[Co(\eta^2\text{-Htame})(\eta^3\text{-tame})NCS]^{3+}$	2.015 (2.23)^a		*b*	0.0251	1.610 (NCS)	
$[Co(NH_3)_5NCS]^{2+}$	2.008 (2.25)			0.0224	1.70 (NCS)	24
$[Co(\eta^2\text{-tame})(\eta^3\text{-tame})OH]^{2+}$	2.010 (1.88)^a		2.765 (1.87)	0.0262	1.57 (OH)	
$[Co(NH_3)_5OH]^{2+}$	1.988 (1.80)		2.702 (1.85)	0.0272	1.54 (OH)	23
$[Co(\eta^2\text{-Htame})(\eta^3\text{-tame})OH_2]^{4+}$	2.060 (1.78)^a		2.875 (1.87)	0.0148	1.961 (OH_2)	
$[Co(NH_3)_5OH_2]^{3+}$	2.030 (1.68)		2.898 (1.65)	0.0171	1.887 (OH_2)	22
$[Co(\eta^3\text{-tame})_2]^{3+}$	2.125 (1.95)^a		2.040 (1.89)		2.487 (NH_3)	
$[Co(NH_3)_6]^{3+}$	2.105 (1.75)		2.950 (1.66)		2.487 (NH_3)	25
$[Co(\eta^2\text{-diamol})(\eta^3\text{-tame})NO_2]^{2+}$	2.195 (2.00)^a		*b*	0.0160	3.047 (NO_2)	
$[Co(NH_3)_5NO_2]^{2+}$	2.185 (1.98)			0.0181	3.110 (NO_2)	22

^{a} Assumed to be the average of the two bands. ^{b} Overlapped by CT transition. ^{c} In μm⁻¹.

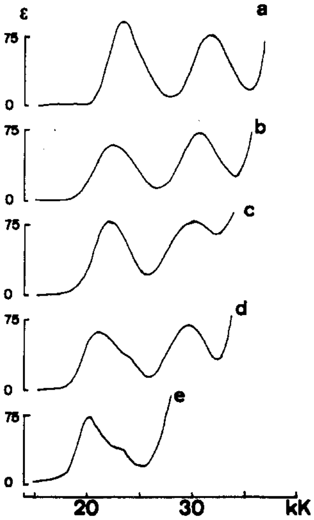

Figure 2. Visible spectra of $[Co(\eta^2\text{-Htame})(\eta^3\text{-tame})X]^n$ and related complexes: (a) $[Co(\eta^3\text{-tame})_2]^{3+}$; (b) $[Co(\eta^2\text{-Htame})(\eta^3\text{-tame})OH_2]^{4+}$; (c) $[Co(\eta^2\text{-Htame})(\eta^3\text{-tame})OH]^{3+}$; (d) $[Co(\eta^2\text{-Htame})(\eta^3\text{-tame})Cl]^{3+}$; (e) $[Co(\eta^2\text{-Htame})(\eta^3\text{-tame})Br]^{3+}$.

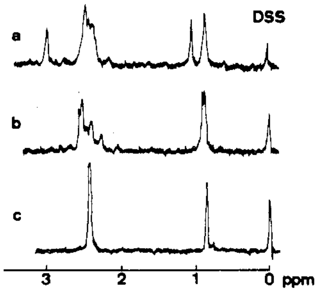

Figure 3. ^1H NMR spectra of (a) $[Co(\eta^2\text{-Htame})(\eta^3\text{-tame})OH_2]^{4+}$, (b) $[Co(\eta^2\text{-tame})(\eta^3\text{-tame})OH]^{2+}$, and (c) $[Co(\eta^3\text{-tame})_2]^{3+}$.

formulae developed by Wentworth and Piper.[22] The semiempirical parameters obtained are identical for the two series of compounds. This indicates clearly that, in the $[Co(\eta^2\text{-Htame})(\eta^3\text{-tame})X]^{n+}$ complexes, the coordination polyhedra are not distorted by any configurational strain.

Figure 3 shows the ^1H NMR spectra of $[Co(\eta^2\text{-Htame})(\eta^3\text{-tame})OH_2]^{4+}$, $[Co(\eta^2\text{-tame})(\eta^3\text{-tame})OH]^{2+}$, and

Table VIII. ^1H NMR Spectra of $[Co(\eta^2\text{-Htame})(\eta^3\text{-tame})X]^{n+}$ and Related Compounds

	shift,^{a} multiplicity,^{b} rel intens		
	CH_3	CH_2(coord)	CH_2(dang)
tame	0.78, s, 3		2.42, s, 6
$[Co(\eta^3\text{-tame})_2]Cl_2ClO_4$	0.86, s, 3	2.47, s, 6	
$[Co(\eta^2\ \text{Htame})(\eta^3\text{-tame})Cl]Cl_2ClO_4$	0.90, s, 3 1.08, s, 3	2.50, m, 10	3.15, s, 2
$[Co(\eta^2\text{-Htame})(\eta^3\text{-tame})Br]Br_3$	0.90, s, 3 1.08, s, 3	2.50, m, 10	3.15, s, 2
$[Co(\eta^2\text{-Htame})(\eta^3\text{-tame})NCS](NCS)_2ClO_4$	0.90, s, 3 1.13, s, 3	2.40, m, 10	3.06, s, 2
$[Co(\eta^2\text{-Htame})(\eta^3\text{-tame})SO_4]SO_4$	0.90, s, 3 1.12, s, 3	2.35, m, 10	3.10, s, 2
$[Co(\eta^2\text{-Htame})(\eta^3\text{-tame})OH_2](ClO_4)_4$	0.93, s, 3 1.15, s, 3	2.30, m, 10	3.02, s, 2
$[Co(\eta^2\text{-Htame})(\eta^3\text{-tame})OH](ClO_4)_3$	0.86, s, 3 1.05, s, 3	2.40, m, 10	3.05, s, 2
$[Co(\eta^2\text{-tame})(\eta^3\text{-tame})OH](ClO_4)_2$	0.86, s, 3 0.87, s, 3	2.30, m, 12^c	
$[Co(\eta^2\text{-diamol})(\eta^3\text{-tame})NO_2]ClClO_4$	0.95, s (br), 6	2.70, m, 12^c	
3:1 tame–HCl	1.32, s, 3		3.25, s, 6

^{a} Ppm vs. DSS. ^{b} s = singlet, m = multiplet, and br = broad. ^{c} CH_2(coord) and CH_2(dang) could not be distinguished.

Table IX. Possible Hydrogen-Bonding Contacts for $[Co(\eta^2\text{-Htame})(\eta^3\text{-tame})Cl]Cl_3\cdot 2H_2O$

X–H···Y^a	X–H, Å	H···Y, Å	X···Y, Å	X–H···Y, deg
N(1)–H(1O1)···Cl(2)^{ii}	1.00 (2)	2.47 (2)	3.324 (8)	144 (2)
N(1)–H(1O2)···Cl(2)^{i}	1.00 (2)	2.27 (2)	3.247 (8)	165 (2)
N(2)–H(2O1)···Cl(4)^{iii}	1.00 (2)	2.54 (2)	3.317 (8)	135 (1)
N(2)–H(2O2)···Cl(4)^{i}	1.00 (2)	2.33 (2)	3.186 (8)	144 (2)
N(2)–H(2O2)···O(1)^{iv}	1.00 (2)	2.69 (3)	3.26 (1)	117 (2)
N(3)–H(3O1)···Cl(3)^{i}	1.00 (2)	2.42 (2)	3.242 (8)	140 (1)
N(3)–H(3O2)···Cl(2)^{i}	0.99 (2)	2.33 (2)	3.313 (9)	169 (2)
N(4)–H(4O1)···O(1)^{i}	1.00 (2)	2.14 (2)	3.12 (1)	165 (2)
N(4)–H(4O2)···O(1)^{iv}	1.00 (2)	2.07 (2)	3.01 (1)	154 (2)
N(5)–H(5O1)···Cl(3)^{v}	0.99 (2)	2.76 (2)	3.442 (7)	126 (1)
N(5)–H(5O2)···Cl(4)^{i}	0.99 (2)	2.31 (2)	3.278 (8)	165 (2)
N(6)–H(6O1)···Cl(2)^{vi}	0.99 (2)	2.19 (3)	3.155 (9)	164 (6)
N(6)–H(6O2)···Cl(3)^{vii}	1.00 (2)	2.40 (4)	3.35 (1)	158 (7)
N(6)–H(6O2)···O(2)^{vi}	1.00 (2)	2.61 (7)	3.15 (2)	114 (5)
N(6)–H(6O3)···Cl(3)^{ii}	1.00 (2)	2.40 (5)	3.29 (1)	148 (7)
O(1)···Cl(1)^{i}			3.240 (9)	
O(1)···Cl(4)^{viii}			3.065 (9)	
O(2)···Cl(2)^{vi}			3.25 (1)	
O(2)···Cl(3)^{ii}			3.35 (1)	

^{a} The superscripts refer to the following equivalent positions: (i) x, y, z; (ii) $1-x, 1-y, 1-z$; (iii) $x, {}^1/_2+y, {}^1/_2-z$; (iv) $\bar{x}, 1-y, 1-z$; (v) $x, {}^1/_2-y, z-{}^1/_2$; (vi) $1-x, {}^1/_2+y, {}^1/_2-z$; (vii) $x, 1{}^1/_2-y, z-{}^1/_2$; (viii) $x, {}^1/_2-y, {}^1/_2+z$.

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Table X. Torsion Angles[a] (Deg) in [Co(η^2-Htame)(η^3-tame)Cl]$Cl_3\cdot 2H_2O$

Co(1)-N(3)-C(6)-C(9)	+27.08	N(3)-C(6)-C(9)-C(10)	+163.41
Co(1)-N(4)-C(7)-C(9)	+26.38	N(4)-C(7)-C(9)-C(10)	+164.36
Co(1)-N(5)-C(8)-C(9)	+23.59	N(5)-C(8)-C(9)-C(10)	+167.29
C(6)-C(9)-C(10)-H(111)	−66.87	C(6)-C(9)-C(10)-H(112)	+53.16
C(7)-C(9)-C(10)-H(112)	−65.91	C(7)-C(9)-C(10)-H(112)	+53.93
C(8)-C(9)-C(10)-H(113)	−66.88	C(8)-C(9)-C(10)-H(111)	+53.25
Co(1)-N(1)-C(1)-C(3)	+51.90	Co(1)-N(2)-C(2)-C(3)	−54.47
N(1)-C(1)-C(3)-C(2)	−66.30	N(2)-C(2)-C(3)-C(1)	+67.49

[a] The torsion angle about the bond J-K is the angle the bond K-L is rotated from the IJK plane. It is positive when the rotation is clockwise on looking from IJ to KL.

[Co(η^3-tame)$_2$]$^{3+}$. In Table VIII the spectral characteristics of several complexes are given. The splitting of the signal, due to the methyl groups of tame, is a clear indication that the two tame in these complexes are not equivalent. The latter splitting is strongly influenced by the protonation of the dangling amine. The splitting is large in the protonated form and small in the deprotonated form (Figure 3). A comparison with the shift of the methyl signal upon protonation of the free ligand demonstrates that this effect is mainly due to inductive effects. Structural changes in the conformation of the chelate ring as a consequence of the Coulombic repulsion between the two positive charges cannot be excluded completely.

Structure of [Co(η^2-Htame)(η^3-tame)Cl]$Cl_3\cdot 2H_2O$

The chemical and spectroscopic properties of the [Co(η^2-Htame)(η^3-tame)X]$^{n+}$ complexes clearly indicate a structure with two different tame, one acting as terdentate ligand and the other as bidentate ligand with one free amine group. Under these conditions, two different configurations are possible (Chart I). On the basis of absence of any [Co(η^3-tame)$_2$]$^{3+}$ formation during base hydrolysis, configuration A with the free amine group "trans" to the acido ligand seems more likely. A definite assignment is not possible, however, on the spectroscopic evidence. The problem had to be settled by crystal structure determination.

Description of the Structure. The crystal structure (Figure 4) consists of discrete [Co(η^2-Htame)(η^3-tame)Cl]$^{3+}$ cations, Cl$^-$ ions, and water molecules. The constituent ions and water molecules are held together by a three-dimensional network of hydrogen-bonding and electrostatic interactions. The [Co(η^2-Htame)(η^3-tame)Cl]$^{3+}$ ion forms numerous N-H···Cl and N-H···O hydrogen bonds with the chloride ions Cl(2), Cl(3) and Cl(4) and the water oxygens O(1) and O(2). In fact every N-H hydrogen is involved in some close interaction with a chlorine or oxygen atom. Only two bifurcated N-H hydrogen interactions are evident, and these are the N(2)-H(202) interaction with Cl(4)$^{\mathrm{i}}$ and O(1)$^{\mathrm{iv}}$ and the N(6)-H(602) interaction with Cl(3)$^{\mathrm{vii}}$ and O(2)$^{\mathrm{vi}}$. The N-H···Cl and N-H···O interactions listed in Table IX have N···Cl and N···O distances and N-H···Cl and N-H···O angles within the range of the literature values[9] of 3.15–3.51 Å, 2.87–3.07 Å, 122–171°, and 119–175°, respectively, for unbranched bonds. The N-H···Cl and N-H···O angles for the bifurcated interactions are 144 (2), 158 (7)° and 117 (2), 114 (5)°, respectively. Table IX shows that the O···Cl distances range from 3.065 (9) to 3.35 (1) Å, a larger range than that of the neutron diffraction distances listed by Hamilton and Ibers,[26] 3.09–3.18 Å.

The Cation Geometry. The cation is shown in Figure 4 and the bond lengths and angles are given in Table IV. The cobalt atom has a slightly distorted octahedral coordination of one chlorine and five nitrogen atoms. The Co(1)–Cl(1) length of 2.274 (3) Å is comparable to the values of 2.286 (2) Å in Co(NH$_3$)$_5$Cl^{2+} [27] and 2.26 Å in *trans*-CoCl$_2$(tn)$_2^+$ [28] (tn is 1,3-diaminopropane). The average Co(1)–N distance of 1.972 (12) Å is in excellent agreement with the values of 1.968 (10) Å found in Co(NH$_3$)$_5$Cl^{2+},[27] 1.968 (11) Å in [Co(NH$_3$)$_6$]$^{3+}$,[29] and 1.972 (9) Å in Co(η^3-tame)$_2^{3+}$.[30] The Co–N length trans to Cl(1) of 1.953 (7) Å is shorter than the cis distances, but it is not considered that there is a significant trans effect due to the chlorine substituent. The C–N and C–C distances are quite normal, as can be seen from Table IV.

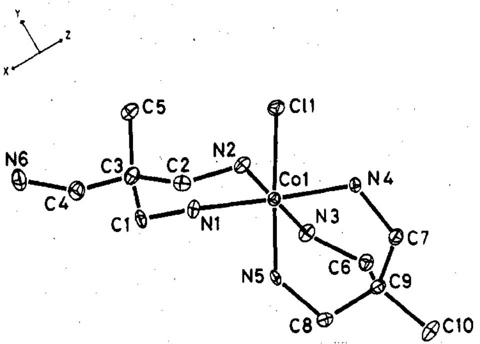

Figure 4. The [Co(η^2-Htame)(η^3-tame)Cl]$^{3+}$ ion with 50% probability ellipsoids for the nonhydrogen atoms.

For the terdentate tame ligand, the mean angles N–Co–N, Co–N–C, N–C–C, and C–C–C of the chelate rings are 89.5 (9), 117.7 (4), 111.6 (7), 110.8 (9)°, respectively. The equivalent angles in the [Co(η^3-tame)$_2$]$^{3+}$ complex[30] have the mean values 88.92 (6), 117.37 (10), 111.66 (13), and 110.25 (14)°. The conformation of the terdentate tame ligand may be described as an asymmetric skew boat, very similar to that found in [Co(η^3-tame)$_2$]$^{3+}$. Torsion angles are given in Table X, and the skew-boat conformation is clearly indicated by the fact that all Co–N–C–C torsion angles have the same sign. The magnitudes of the C–C–C–H torsion are all approximately 60° and indicate almost complete staggering of the methyl groups with respect to the opposing C–C bonds. The complex (−)$_{546}$-[Co(*R*,*R*-ptn)$_3$]$^{3+}$ (ptn = 2,4-diaminopropane)[31] has a similar skew conformation of the six-membered chelate rings. Only the C–C–C angles differ significantly from those cited above. The close to tetrahedral values (110.8 (9) and 110.25 (14)°) found in [Co(η^2-Htame)(η^3-tame)Cl]$^{3+}$ and [Co(η^3-tame)$_2$]$^{3+}$, respectively, opposed to 117.2 (7)° in (−)$_{546}$-[Co(*R*,*R*-ptn)$_3$]$^{3+}$, are probably imposed by the quaternary central carbon atom. For the η^2-tame ligand, the angles N–Co–N, Co–N–C, N–C–C, and C–C–C of the chelate ring are 92.6 (3), 121.6 (6), 114.7 (9), and 108.7 (8)°, respectively. The equivalent angles in the (−)$_{589}$-Co(tn)$_3^{3+}$ complex[32] are 91 (1), 122.2 (7), 112 (1), and 113.6 (6)°,

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respectively. The low value for the C–C–C angle of the η^2-tame six-membered chelate ring is probably caused by the substituents on C(3). The six-membered ring has a chair conformation, as shown by the torsion angles in Table X. Comparison with $(-)_{589}$-$Co(tn)_3^{3+}$ [32] and an idealized chair conformation in $Co(tn)_3^{3+}$ [32] shows that the chelate ring is flattened out by interactions between nonbonded H atoms of adjacent chelate rings.

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Registry No. I, 73953-30-7; II, 73953-32-9; III, 73953-40-9; IV, 73953-33-0; [Co(η^2-Htame)(η^3-tame)Cl]$Cl_3 \cdot 2H_2O$, 73953-34-1; [Co(η^2-Htame)(η^3-tame)Br]Br_3, 73953-35-2; [Co(η^2-Htame)(η^3-tame)NCS]$(NCS)_2ClO_4$, 73953-38-5; [Co(η^2-Htame)(η^3-tame)-OH]$(ClO_4)_3$, 73953-41-0; [Co(η^2-Htame)(η^2-tame)H_2O]$(ClO_4)_4$, 73953-44-3; [Co(η^2-Htame)(η^3-tame)SO_4]SO_4, 73953-46-5; [Co-(η^2-bstame)(η^3-tame)Cl]Cl_2, 73953-47-6; [Co(η^2-actame)(η^3-tame)CH_3COO]$CH_3COOClO_4$, 73953-49-8; $Na_3Co(CO_3)_3$, 23311-39-9; tame·3HCl, 31044-82-3.

Supplementary Material Available: Observed and calculated structure factor amplitudes (Table XI) and k_{exptl} of the base hydrolyses (Table XII) (23 pages). Ordering information is given on any current masthead page.

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Unusual Structural and Chemical Trends within a Series of Binuclear Rhodium Carbonyl Halide Complexes and the Structure of One Member of This Series, *trans*-$[Rh_2Cl_2(CO)_2((C_6H_5)_2PCH_2P(C_6H_5)_2)_2]$

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The reaction of *trans*-$[Rh_2Cl_2(CO)_2(DPM)_2]$ (DPM = $(C_6H_5)_2PCH_2P(C_6H_5)_2$) with NaBr yields initially the unusual, asymmetric species $[Rh_2Br(\mu\text{-}CO)(CO)(DPM)_2][Br]$, which in solution loses CO yielding the "A-frame" species $[Rh_2Br_2(\mu\text{-}CO)(DPM)_2]$. When the above reaction is carried out with KI instead of NaBr, the complex $[Rh_2I(\mu\text{-}CO)(CO)(DPM)_2][I]$ is produced as the final product. These bromo- and iododicarbonyl complexes react with CO and SO_2 to yield the complexes $[Rh_2(CO)_2(\mu\text{-}L)(\mu\text{-}X)(DPM)_2][X]$ (L = CO, SO_2; X = Br, I). The dichloromonocarbonyl species $[Rh_2Cl_2(\mu\text{-}CO)(DPM)_2]$ was prepared by refluxing *trans*-$[Rh_2Cl_2(CO)_2(DPM)_2]$ in toluene. Reaction of the chloro- and bromomonocarbonyl complexes with an excess of CO yields $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}X)(DPM)_2][X]$ (X = Cl, Br). With the dichloromonocarbonyl species, slow stepwise addition of CO results instead in the formation of *trans*-$[Rh_2Cl_2(CO)_2(DPM)_2]$. Reaction of both monocarbonyl species with SO_2 produces an equimolar mixture of $[Rh_2X_2(\mu\text{-}SO_2)(DPM)_2]$ and $[Rh_2(CO)_2(\mu\text{-}SO_2)(\mu\text{-}X)(DPM)_2][X]$ (X = Cl, Br). The tricarbonylbromo species loses one terminal carbonyl ligand slowly in solution under an N_2 stream, yielding the above asymmetric bromo species, but does not lose CO in the solid state under vacuum. The analogous iodotricarbonyl complex does not lose CO even in solution. The bromo–SO_2 adduct loses both CO ligands in solution under an N_2 flush, yielding $[Rh_2Br_2(\mu\text{-}SO_2)(DPM)_2]$, whereas the iodo–$SO_2$ adduct loses neither CO nor SO_2. *trans*-$[Rh_2Cl_2(CO)_2(DAM)_2]$ (DAM = $(C_6H_5)_2AsCH_2As(C_6H_5)_2$) undergoes iodide exchange to give a mixture of *trans*-$[Rh_2I_2(CO)_2(DAM)_2]$ and $[Rh_2(I)(\mu\text{-}CO)(CO)(DAM)_2][I]$. These iodo–DAM species react with CO and SO_2, yielding $[Rh_2(CO)_2(\mu\text{-}L)(\mu\text{-}I)(DAM)_2][I]$ (L = CO, SO_2). The CO reaction is reversible in solution, but the SO_2 reaction is not. The structure of *trans*-$[Rh_2Cl_2(CO)_2(DPM)_2]$ has been determined by X-ray crystallography, verifying that it has a dimeric formulation essentially isostructural with its bis(diphenylarsino)methane analogue. The complex *trans*-$[Rh_2Cl_2(CO)_2(DPM)_2]$ crystallizes in the space group $P\bar{1}$ (No. C_i^1) with $a = 11.054$ (1) Å, $b = 12.564$ (1) Å, $c = 10.3191$ (9) Å, $\alpha = 99.899$ (6)°, $\beta = 115.708$ (7)°, and $\gamma = 65.082$ (7)° with $Z = 1$. On the basis of 3368 unique reflections the structure was refined by full-matrix, least-squares techniques to $R = 0.037$ and $R_w = 0.069$. The Rh–Rh separation is 3.2386 (5) Å, and the two parallel rhodium square planes are inclined to the Rh–Rh vector by ca. 75.9°.

Introduction

We have recently been interested in the reactions of binuclear rhodium complexes with small molecules[1–6] and as part of our studies in this area have been investigating the chemistries of *trans*-$[Rh_2Cl_2(CO)_2(DPM)_2]$,[7] **1**, and *trans*-$[Rh_2Cl_2(CO)_2(DAM)_2]$,[7] **2**. These dichlorodicarbonyl complexes have been shown to react with small molecules yielding species[6,8] which seem to contain ketonic[9] carbonyl ligands. Since the stabilities of ketonic carbonyl complexes have been found to differ with the DPM and DAM ligands,[6,10,11] we undertook an investigation into the possible effects of varying the halide ligands on the stabilities of these complexes. We therefore attempted the preparations of the *trans*-dibromo- and -diiodo–DPM complexes and the *trans*-diiodo–DAM complex, none of which had been reported.

During this study it also became apparent to us that it was of interest to obtain an accurate structural determination of complex **1**. Although, on the basis of powder diffraction studies,[12] it seemed that complex **1** was isomorphous with complex **2**, whose structure has been determined,[13] significant differences in their chemistries had led us to question the extent of their similarities. It had been noted, for example, that

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(7) Abbreviations used: DPM, bis(diphenylphosphino)methane; DAM, bis(diphenylarsino)methane; Me, methyl; Et, ethyl.

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