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The Reactivity of Hexa(*N*-methylideneimine)Co^{III} Complexes towards Nucleophiles: Structure and Mechanism[‡]

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The reactivity of the ***h***exa(*N*-***m***ethylidene***i***mine)Co^{III} complex $[Co\text{-hmi-(taci)}_2]^{3+}$ (taci = 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol) towards the nucleophiles ammonia, aniline and cyanide was investigated and the main products were identified by spectroscopic methods and by a crystal structure analysis. The relative energies of the complexes formed and those of possible stereo isomers were analysed by means of molecular mechanics calculations. In the reaction with NH_3, two condensation products, $[Co(L^a)]^{3+}$ and $[Co(L^b)]^{3+}$, were identified with the two taci moieties linked by one or two N=CH–N(H)-CH_2–NH bridges, respectively. The reaction with aniline yielded the complex $[Co(L^c)(L^d)]^{3+}$ (where L^c is a mono-*N*-methylated and L^d a phenylformamidine-substituted taci), whereas the reaction with cyanide resulted in the formation of $[Co(L^e)]^{3+}$ having an NH–CH_2–C(NH_2)=N bridge between the two taci subunits. A mechanism that accounts for the different types of products can be suggested as follows: In $[Co(L^a)]^{3+}$, $[Co(L^b)]^{3+}$ and $[Co(L^c)(L^d)]^{3+}$, *N*-methylation was observed and this can be interpreted in terms of an intramolecular Cannizzaro type hydride shift. For $[Co(L^a)]^{3+}$ and $[Co(L^b)]^{3+}$ two subsequent addition steps of the nucleophile to adjacent imino groups must take place prior to the hydride shift, whereas for $[Co(L^c)(L^d)]^{3+}$ the hydride shift appears to have already occurred after the first addition step of aniline to an imino group. Formation of $[Co(L^e)]^{3+}$ can be explained in terms of a nucleophilic attack of CN^- to an imino group and a subsequent attack of a deprotonated amino group (which must have previously been formed by hydrolysis of a methylideneimino group) to the nitrile C-atom.

Introduction

Polyaza macrocycles and polyaza macrobicycles are interesting classes of chelators for transition metal cations, since the complexes formed thereof are often of exceptionally high stability and inertness.[1] A variety of synthetic procedures have been established for the preparation of such ligands and among them the template method, in which a set of subunits is precoordinated to a metal centre, is particularly effective.[2] Sargeson discovered that the condensation of an (amine)Co^{III} complex with formaldehyde under basic conditions, followed by a capping step, resulted in the formation of the corresponding cage complexes.[3] The capping reagent is usually a weakly acidic, tribasic component H_3X such as ammonia or nitromethane[4] and the entire reaction may be performed either in an aqueous or a nonaqueous medium. The procedure was found to be particularly effective for the capping of $[Co^{III}(en)_3]^{3+}$ (en = ethane-1,2-diamine) where the two cages sepulchrate (sep, X = N) and sarcophagine (sar, X = C-NO_2) could be isolated in high yields. It is generally believed that the reaction proceeds via intermediate methylideneimine formation with the capping agent being finally added with subsequent deprotonation to the coordinated imines (Scheme 1).[5] Although the entire procedure is usually performed as a one-pot reaction without isolation of intermediates, some of the imines are of sufficient stability to allow their characterisation[6] and some of them could even be crystallised.[7,8] We reported the crystal structure of the ***h***exa(*N*-***m***ethylidene***i***mine) (hmi) complex $[Co\text{-hmi-(taci)}_2]^{3+}$ (Scheme 2a, R = OH; taci = 1,3,5-***tri***a***mino-1,3,5-trideoxy-***cis***-***i***nositol) some years ago.[9]

Sargeson has already found that in complexes with sterically demanding diamine ligands such as *trans*-cyclohexane-1,2-diamine (*trans*-chxn), the capping reaction proceeds at a comparatively low rate.[10] Moreover, formation of a variety of by-products was noted. In particular, it was observed that some of the coordinated amino groups underwent methylation. It is thus apparent that, in general, the bridging process may be more complex than it appears at first glance.[11] After formation of the first two X–C bonds, additional deprotonation of XH can occur and the resultant anion could attack the electrophilic carbon atom of a third

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[‡] 1,3,5-Triamino-1,3,5-trideoxy-*cis*-inositol, a Ligand with Remarkable Versatility for Metal Ions, 15. Part 14: K. Hegetschweiler, P. J. Hagrman, J. Zubieta in *Advances in Coordination, Bioinorganic and Inorganic Chemistry* (Eds: M. Melník, J. Šima, M. Tatarko), Slovak Technical University Press, Bratislava, **2005**.

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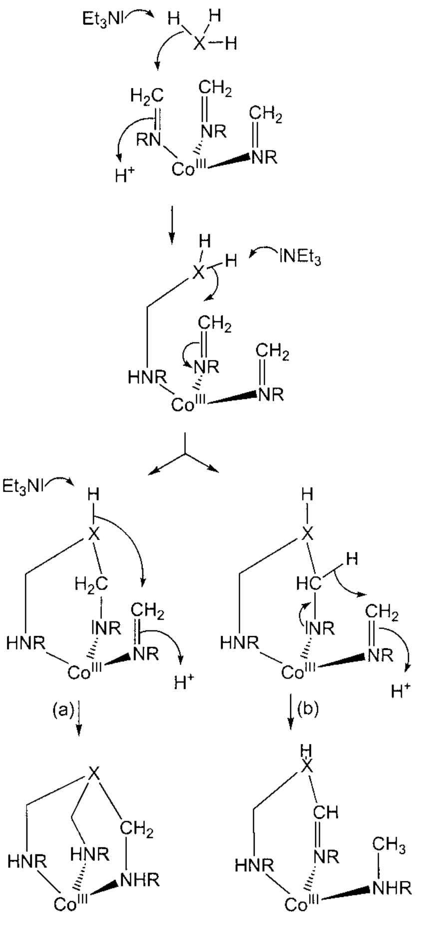
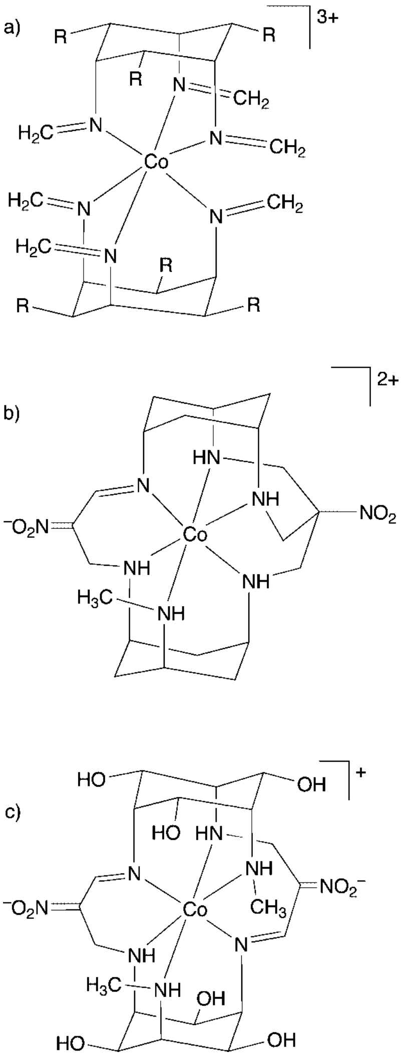


Scheme 1. Reaction of (hexaimine)Co^{III} complexes with a capping reagent H_3X; mechanistic details for the formation of a cap (a) or a strap (b, Cannizzaro type hydride shift). Some of the charges are omitted for clarity.



Scheme 2. a) Structures of [Co-hmi-(*cis*-tach)$_2$]$^{3+}$ (R = H) and [Co-hmi-(taci)$_2$]$^{3+}$ (R = OH).[9] b) and c): Major products isolated from the condensation reaction of the two (hmi)Co^{III} complexes with nitromethane. The reaction was carried out either in an alkaline aqueous medium (b)[12] or in acetonitrile using triethylamine as base (c)[9] (taci = 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol, *cis*-tach = all-*cis*-cyclohexane-1,3,5-triamine).

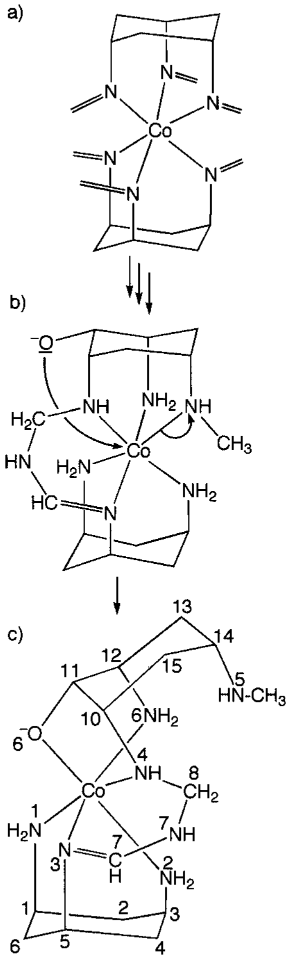
imino group (Scheme 1a). It is also possible at this stage, however, that an N=C double bond could reform within the NH–CH$_2$–XH–CH$_2$–N$^-$ bridge in conjunction with hydride transfer from the methylene carbon to an adjacent imino group (Scheme 1b). Such an intramolecular, Cannizzaro type hydride shift would explain formation of the *N*-methylated by-products observed in the capping reaction of [Co^{III}-(*trans*-chxn)$_3$]$^{3+}$. In the corresponding reaction of [Co^{III}(*cis*-tach)$_2$]$^{3+}$ with formaldehyde and two equiv. of nitromethane, both types of reaction were observed within the same molecule (Scheme 2b).[12] The addition of one of the nitromethane molecules yielded an $O_2N–C(CH_2–NH)_3$ cap whereas addition of the other resulted in the formation of an HN–CH$_2$–CH(NO$_2$)–CH=N strap. The hydrogen atom of the CH(NO$_2$) moiety was found to be strongly acidic and the complex was thus isolated as a dication with a carbanionic ligand having a delocalised O$_2$N=C–C=N π-system. Moreover, in the reaction of [Co^{III}-hmi-(taci)$_2$]$^{3+}$ with two equiv. of nitromethane, the resultant product was devoid of any $O_2N–C(CH_2–NH)_3$ cap (Scheme 2c). Both nitromethane entities were incorporated as HN–CH$_2$–C(NO$_2$)$^-$–CH=N straps.[9]

It is noteworthy that the rigidity of the ligand backbones increases in the order en < *trans*-chxn < *cis*-tach < taci. It appears, thus, that increasing the rigidity of the coordinated amine ligands tends to disfavour the capping reaction. Formation of such HN–CH$_2$–XH–CH=N straps has previously only been observed in the capping reaction with nitromethane.[9,12] It would be interesting to investigate the products formed when other types of nucleophiles are used. Such an investigation would not only shed light on the mechanism of this type of condensation processes but it could potentially open synthetic pathways to novel and interesting macrocyclic ligand systems. We therefore decided to extend our investigation of the capping of [Co^{III}-hmi-(taci)$_2$]$^{3+}$ using ammonia, aniline and cyanide as possible nucleophiles. In this paper, we describe the molecular structures of the products obtained and discuss the mechanism of the corresponding coupling reaction. We also carried out a series of molecular mechanics calculations to look for low-energy structures of the different possible stereoisomers.

Results

Reaction of [Co-hmi-(taci)$_2$]$^{3+}$ with Ammonia

Formation of the well known (sepulchrate)Co^{III} complex has been reported to occur readily upon mixing [Co^{III}-(en)$_3$]$^{3+}$ with formaldehyde and ammonia in an alkaline aqueous solution.[5] Consequently, initial attempts to carry out an analogous reaction of [Co^{III}-hmi-(taci)$_2$]$^{3+}$ (Scheme 2a, R = OH) with ammonia were performed in aqueous media. However, these experiments resulted in the complete hydrolysis of the imino groups, together with reduction of Co^{III} to Co^{II}. The protonated H$_3$taci^{3+} was the only product which could be isolated after acidification. Further experiments were therefore performed in acetonitrile. To achieve the required solubility, the chloride salt of [Co^{III}-hmi-(taci)$_2$]$^{3+}$ was converted into the corresponding triflate salt.[13] Reaction of [Co^{III}-hmi-(taci)$_2$](CF$_3$SO$_3$)$_3$ in acetonitrile with concentrated aqueous ammonia resulted in formation of a deep red solution containing a variety of different Co^{III} complexes. After hydrolysis of the remaining imines, two main products were isolated by chromatographic techniques. The major red component, [Co(HL^a)]Cl$_4$ (L^a = C$_{15}$H$_{33}$N$_7$O$_6$),[14] consisted of a complex in which the two taci-ligands are interlinked by an N=CH–NH–CH$_2$–NH bridge and where one of the coordinated amino group was methylated (Scheme 3). In a minor pink component, composed of [Co(H$_2$L^b)]Cl$_5$ (L^b = C$_{18}$H$_{36}$N$_8$O$_6$),[14] the taci moieties were connected by two such N=CH–NH–CH$_2$–NH bridges and two methylated amino groups were formed. Both compounds were characterised by FAB$^+$ mass spectrometry in which the pseudo-molecular ions [Co^{II}-(H$_{-1}$L^a)]$^+$ (m/z = 465) and [Co^{II}(H$_{-1}$L^b)]$^+$ (m/z = 518)[15,16] could be observed with high intensities.



Scheme 3. Formation of [Co(H$_{-1}$L^a)]$^{2+}$.[14] A part of the numbering scheme of this complex is shown in c). The non-coordinating OH-groups are omitted for clarity.

Characterisation of [Co(L^a)]$^{3+}$[14]

A ^{1}H-^{1}H COSY NMR spectrum exhibited two independent spin systems each with six resonances for the H(-C) ring protons of the two taci frameworks. Clearly no element of symmetry of the D_{3d} [Co^{III}-hmi-(taci)$_2$]$^{3+}$ precursor is retained in this complex. Four additional signals were indicative of one HC=N imino group, one N-CH$_3$ methyl group and one N–CH$_2$–N group. The ^{13}C{^{1}H} NMR spectrum was consistent with this analysis exhibiting fifteen signals which, on the basis of a DEPT experiment, could be assigned to one CH$_3$, one CH$_2$ and 13 CH-carbon resonances.[17] One of the CH signals was strongly deshielded (170–173 ppm, depending on pD) and clearly originated from the imino group.[6] The remaining 12 CH signals were assigned to the two taci backbones. They appeared in the range of 52–80 ppm. Eleven of them were located in a comparatively narrow range of 52–68 ppm, whereas one single CH-resonance was displaced to a particularly high frequency (δ = 80.0 ppm at pD 8). Such a significant low-field shift of a single cyclohexane carbon atom is indicative of asymmetric κ^3-*O*,*N*,*O* or κ^3-*N*,*O*,*N* coordination (formation of two five-membered chelate rings).[18–20] The additional ^{13}C-^{1}H HMQC and ^{13}C-^{1}H HMBC experiments[17] provided evidence that the imine portion of the N=CH–NH–CH$_2$–NH bridge and the N-CH$_3$ group are not bound to the same taci-unit. These structural assignments were subsequently confirmed by a single-crystal X-ray analysis of a hydrated [Co(HL^a)][ZnBr$_4$]$_2$ salt (Table 1, Figure 1). Although serious disorder was observed for one of the [ZnBr$_4$]$^{2-}$ anions (see experimental section), the structure proved to be of sufficient quality to establish unambiguously the formation of the novel ligand L^a. Significant structural properties are: (i) Different coordination modes[21] of the two taci fragments with a κ^3-*N*,*N*,*N* coordination for the moiety with the imino group and a κ^3-*N*,*O*,*N* coordination for the moiety with the N–CH$_3$ group (the N–CH$_3$ group itself is detached from Co); (ii) Different conformations for the two cyclohexane rings: the κ^3-*N*,*N*,*N*-coordinating fragment forms a regular chair, whereas the κ^3-*N*,*O*,*N*-coordinating unit has a twisted boat conformation.[22] (iii) A planar geometry around the atoms N3, C7 and N7 (the sums of bond angles are 360.0 ± 0.1°), indicative of sp^2 hybridisation for all the atoms of the amidine fragment.

Table 1. Comparison between experimental[a] and calculated[b] bond lengths [Å] and bond angles [°] for $[Co(HL^a)]^{4+}$.

	Experimental	Calculated
Co–O(6)	1.931(6)	1.93
Co–N(3)	1.921(8)	1.93
Co–N(2)	1.944(7)	1.94
Co–N(1)	1.956(8)	1.96
Co–N(4)	1.974(8)	1.97
Co–N(6)	2.023(7)	1.97
C(7)–N(3)	1.299(12)	1.32
N(1)–Co–N(2)	91.4(3)	93
N(1)–Co–N(3)	90.4(4)	92
N(2)–Co–N(3)	90.2(3)	92
N(4)–Co–O(6)	82.4(3)	81
N(4)–Co–N(6)	84.1(3)	86
N(6)–Co–O(6)	83.4(3)	88
N(3)–C(7)–N(7)	122.8(10)	122

[a] Single-crystal X-ray structure analysis of $[Co(HL^a)][ZnBr_4]_2\cdot 5H_2O$. [b] Molecular mechanics calculations using the MOMEC force field[46,47] together with the extension listed in Table 4.

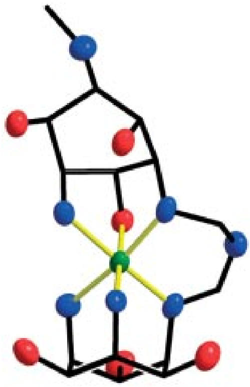


Figure 1. Molecular structure of $[Co(HL^a)]^{4+}$.[14] The carbon skeleton is shown as a stick model, other non-hydrogen atoms are shown as vibrational ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity. Colour code: Co green, O red, N blue. The numbering scheme is shown in Scheme 3c.

$[Co(HL^a)][ZnBr_4]_2\cdot 5H_2O$ was isolated from an acidic medium and, consequently, both the coordinated oxygen and the non-coordinating methylamino group are protonated as supported by charge balance considerations. In aqueous solution, however, the two sites could be deprotonated reversibly. Corresponding pK_a values of 2.0(1) and 5.28(1) were determined by potentiometric titration (25 °C, 0.1 M KCl). The first value (deprotonation of the coordinated hydroxy group) agrees nicely with the value of 2.0(2) observed for the model complex $[Co(\textit{cis}\text{-tach})(Htaci\text{-}\kappa^3\text{-}O^1,N^2,O^3)]^{4+}$ (Supporting Information, Scheme S1b, structure O7).[20] However, the pK_a of the methylammonium group is surprisingly low (the corresponding values for $[Co(\textit{cis}\text{-tach})(Htaci)]^{4+}$ are 7.23 and 8.84). An NMR titration experiment of $[Co(HL^a)]^{4+}$ (306 K, D_2O, no inert electrolyte) in the range $0.5 < pH < 8.5$ (Figure 2) revealed a characteristic pD-dependence of the individual ^1H resonances of the complex. The two protonation constants could be assigned as $pK_1 = 1.16$ and $pK_2 = 5.60$ which is in good agreement with the values determined by potentiometric measurements. In accord with a protonation of a nearby basic site, H(-C) resonances can be expected to shift to higher frequency upon protonation of this site and this effect should decrease with an increasing number of bonds between this site and the H(-C) group under consideration.[23] For the deprotonation of the coordinated hydroxy group, the resonances most affected (H10–H12) in the range $0.5 < pD < 2$ are all in close proximity to O6; and H11, which is located in the α position, did indeed exhibit the most significant shift (see Scheme 3c for the numbering scheme). However, for the deprotonation of the methylammonium group the most significant shift can be observed for the hydrogen atoms in the β positions (H13 and H15). The shift observed for the α hydrogen atom (H14) is almost negligible. Moreover, in the range $4.5 < pD < 6.5$, this signal is shifted to a higher frequency with increasing pD. This behaviour becomes understandable if a conformational change of the κ^3-*O*,*N*,*O*-coordinated cyclohexane residue takes place upon deprotonation of the methylammonium group. Below pD 4 the conformation of this ring corresponds to a twisted boat (Figure 1).[22] In terms of torsional strain, a corresponding chair conformation is expected to be of lower energy. However, as long as the non-coordinated nitrogen is protonated, such a geometry would give rise to dramatic repulsion between the three axial substituents (Scheme 4). This strain is released upon deprotonation because the methylamino group can act as a proton acceptor in an intramolecular hydrogen bond. A similar change in conformation has recently been described for a related complex with κ^3-*N*,*O*,*N*

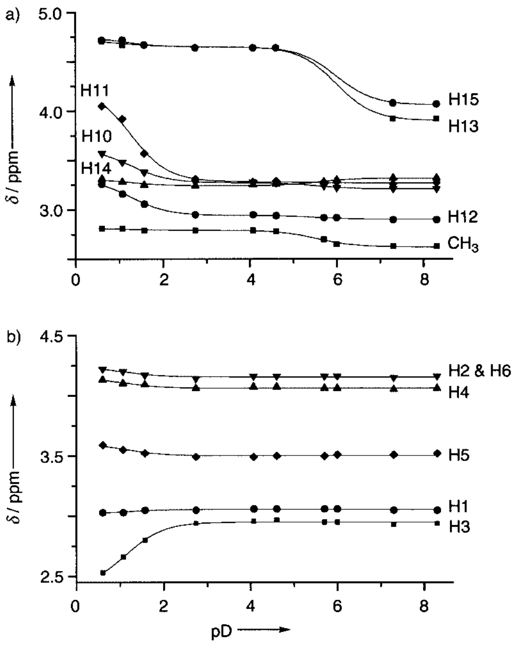
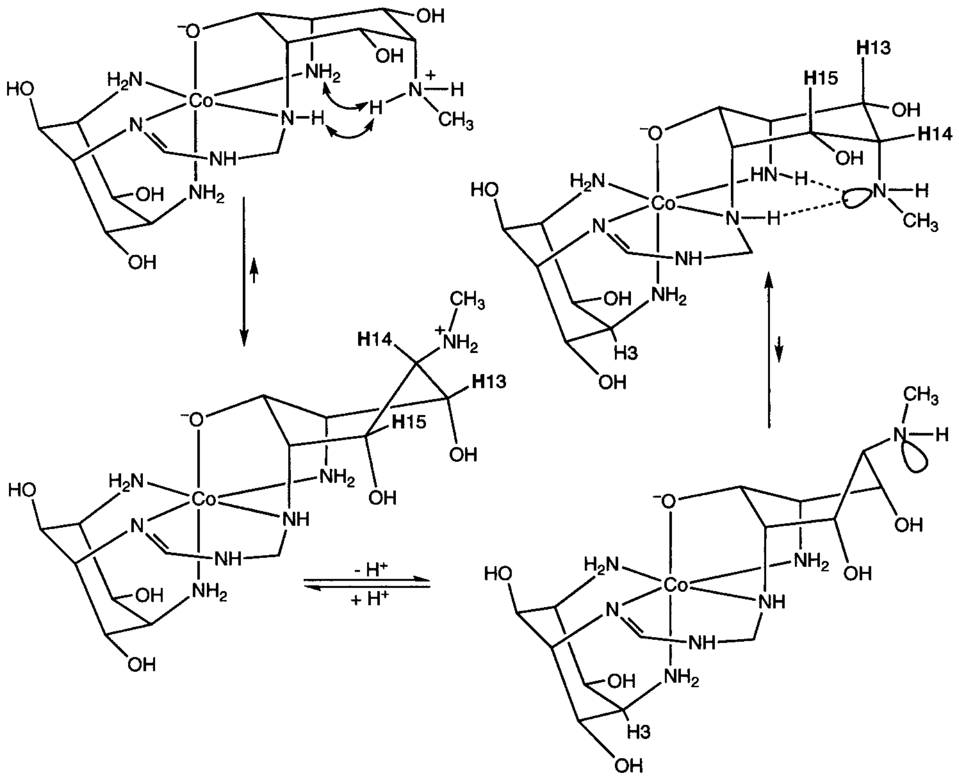


Figure 2. pD dependence of the ^1H NMR resonances of $[Co(HL^a)]^{4+}$ (D_2O, 33 °C, TSP = 0 ppm).[14] a) κ^3-*O*,*N*,*O*-coordinated taci ring b) κ^3-*N*,*N*,*N*-coordinated taci ring. Squares, triangles and circles correspond to the experimental values, the lines are calculated (minimisation of $\Sigma[\delta_{obs} - \delta_{calcd}]^2$. The numbering scheme shown in Scheme 3c has been used.



Scheme 4. The pH-dependent conformational equilibrium for the monobridged complex with a twisted boat conformation in acidic media ($[Co(HL^a)]^{4+}$ and $[Co(L^a)]^{3+}$) and a chair conformation at high pH ($[Co(H_{-1}L^a)]^{2+}$) as major species.[14] H–H Repulsion interactions are marked with arrows, possible hydrogen bonds are shown by dashed lines.

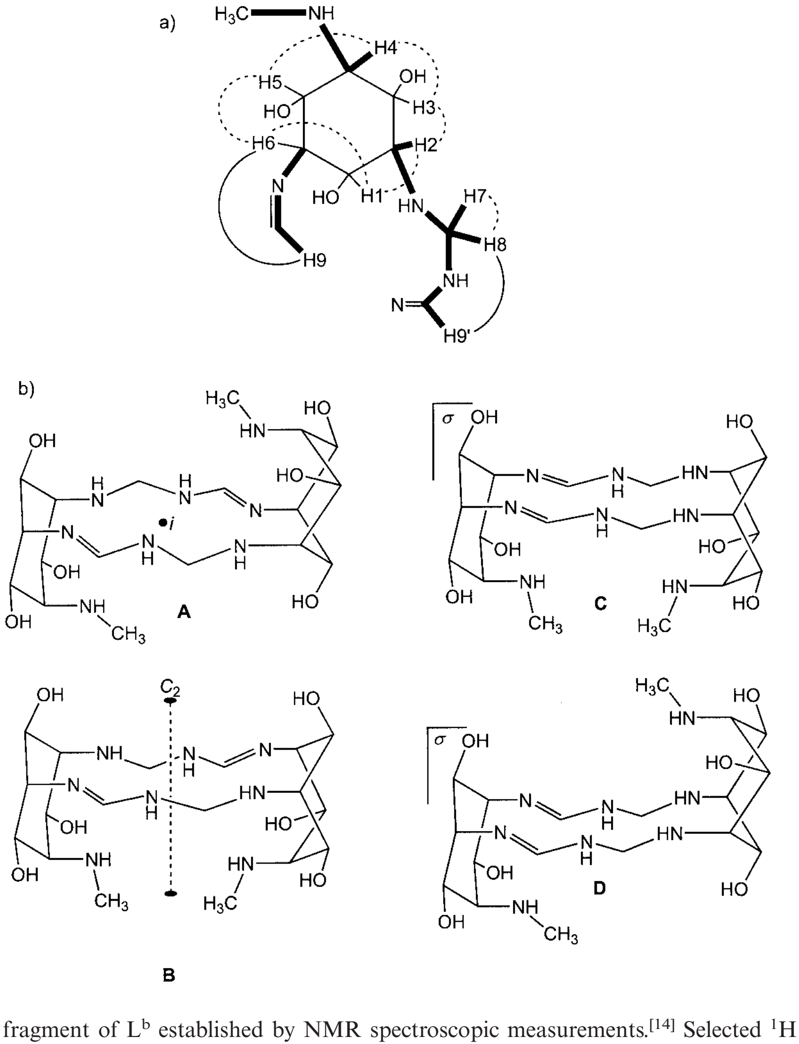
coordination in which hydrogen bonding to the non-coordinating amino group is suppressed by its conversion to an amide.[24] Molecular mechanics calculations support this interpretation, namely, for the fully deprotonated $[Co(H_{-1}L^a)]^{2+}$, the twisted boat conformer has a strain energy which is 17 kJ mol^{-1} higher than for the corresponding chair conformation. The change from the twisted boat to the chair conformation brings H14 into an equatorial and H13/H15 into an axial position. It is well known that equatorial hydrogens in a cyclohexane moiety generally appear at higher frequencies. Clearly the two effects (change from an axial to an equatorial position and shielding by deprotonation) tend to the same direction for the hydrogens in the β position but to opposite directions for the hydrogen in the α position of the methylamino group. Consequently, the resultant shift is almost zero for H14 and twice as much as expected for H13 and H15. The release of strain which is caused by this conformational change represents an additional driving force for the deprotonation of the methylammonium group and helps to explain the above-mentioned rather low value of 5.3 for this pK_a. A conformational change is further supported by the observation that the resonances of H13, H15 and of the methyl group exhibited strong line broadening in the range $4.5 \leq pD \leq 6$, indicative of some dynamic behaviour within the molecule.

The pD-dependence of most of the resonances of the κ^3-*N*,*N*,*N*-bonded moiety is relatively minor as expected (Figure 2b). There is one remarkable exception, however. H3, which is *trans* to the coordinated oxygen donor, exhibits a strong shift in the range $0.5 < pD < 2$ and even more interestingly, this signal is shifted to *higher* frequency with increasing pD. The observed pD behaviour clearly implies that this effect must be due to the deprotonation of the coordinated hydroxy group. We recently demonstrated that such a specific *trans* effect is very characteristic for the deprotonation of a coordinated oxygen in Co^{III} complexes with polyamino-polyalcohol ligands.[25]

The $^1A_{1g}$–$^1T_{1g}$ transition of the CoN_5O chromophore of $[Co(H_{-1}L^a)]^{2+}$ and $[Co(HL^a)]^{4+}$ can be observed at 508 nm (pH 12) and 513 nm (10 M HCl), respectively. These values are slightly higher than the corresponding values in the nonbridged [Co(*cis*-tach)(taci-κ^3-*N*,*O*,*N*)]$^{4+}$ (λ_{max} = 484 nm).[20] Cyclic voltammetry (Hg-electrode) revealed quasi-reversible redox behaviour with a reduction potential $E_{1/2}$ (Co^{III}/Co^{II}) of –0.12 V (vs. NHE).

Characterisation of $[Co(L^b)]^{3+}$[14]

The second pink coloured fraction was identified as a doubly bridged and dimethylated species.[15] The $^{13}C\{^1H\}$ NMR spectrum exhibited a total of nine signals for the 18 carbon atoms. They were assigned to one CH_3 resonance, one CH_2 resonance and seven CH resonances on the basis of DEPT experiments.[17] In the ^1H NMR spectrum two singlets, one of them at the low end and the other at the high end of the range observed for the chemical shifts, were assigned to the N–CH$_3$ methyl groups (6 H) and to the N=CH imine protons (2 H), respectively. The remaining eight resonances (each representing two hydrogen atoms) corresponded to the twelve cyclohexane ring protons and to the CH$_2$ groups of the bridges. Their mutual coupling pattern was established by a series of ^{1}H-^{1}H and ^{1}H-^{13}C correlation experiments (Scheme 5). The reduced number of signals is indicative of some symmetry. However, the C_s-symmetric forms **C** and **D** with the two imino groups attached to the same taci ring can be excluded from further consideration since a total of twelve rather than nine signals would be expected for such isomers in the ^{13}C NMR spectrum. The C_i and C_2 symmetric isomers **A** and **B** on the other hand are both consistent with the NMR characteristics. Further information about the structure of this complex can be obtained from the pD-dependence of the ^{1}H NMR resonances (Figure 3). The δ vs. pD curves could be modelled successfully using the four pK values pK_1 = 0.1, pK_2 = 2.4, pK_3 = 4.9 and pK_4 = 5.9. The exclusive and significant shift of H1 in the range $0 \leq \text{pD} \leq 2$ is again indicative of a deprotonation of the α hydroxy groups and the low values for the two corresponding pK_a values must be interpreted in terms of a coordination of these oxygen donors. pK_3 and pK_4 belong to the deprotonation of the non-coordinating methylammonium groups. Clearly, an asymmetric κ^3-*N*,*O*,*N*-binding mode, as already observed for [Co(HL^a)]$^{4+}$, has to be considered in the doubly bridged derivative and, based on symmetry arguments, both taci fragments must adopt such a coordination mode. As seen in the previous section, this type of coordination implies formation of five membered chelate rings and this is again clearly shown by the significant offset of C1 in the ^{13}C NMR spectrum.[18–20] Similar to [Co(L^a)]$^{3+}$, the resultant CoN$_4$O$_2$ chromophore exhibits a $\lambda_{\max}$ (525 nm in 12 M HCl, 517 nm at pH = 12) for the $^1A_{1g}$–$^1T_{2g}$ transition which is slightly higher than those of nonbridged analogues such as [Co(*cis*-tach)(taci-κ^3-*O*^{1},*N*^{2},*O*^{3})]$^{3+}$ ($\lambda_{\max}$ = 498) and [Co(taci-κ^3-*N*^{1},*N*^{3},*N*^{5})(taci-κ^3-*O*^{1},*N*^{2},*O*^{3})]$^{3+}$ ($\lambda_{\max}$ = 494).[20] The minor blue shift observed for this band upon an increase in pH is well established as an indicator for deprotonation of the coordinated ROH groups. The rearrange-



Scheme 5. a) The structural fragment of L^b established by NMR spectroscopic measurements.[14] Selected ^{1}H ^{13}C long range couplings are depicted in bold, geminal and vicinal ^{1}H ^{1}H coupling interactions and long range ^{1}H ^{1}H coupling interactions are marked with dashed and full lines, respectively. The carbon atoms are labelled with the same numbering scheme as shown for the corresponding hydrogen atoms. b) Representations for **A** (C_i), **B** (C_2), **C** (C_s), and **D** (C_s) showing possible structures of L^b as discussed in the text.

ment from a κ^3-*N,N,N* to a κ^3-*N,O,N* coordination mode appears to proceed in an analogous way to that of $[Co(L^a)]^{3+}$. However, it is worthy to note that in the mono-bridged complex only the moiety with three sp^3 nitrogen donors switches to a κ^3-*N,O,N*-mode (the moiety with the N=C group retains the adamantane-like triamine coordination), whereas in $[Co(L^b)]^{3+}$ both rings, although attached to an imine nitrogen, adopt a κ^3-*N,O,N* coordination.

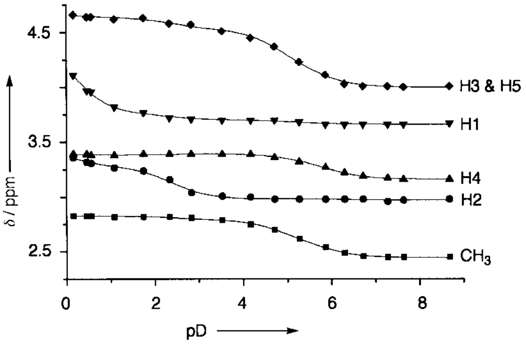
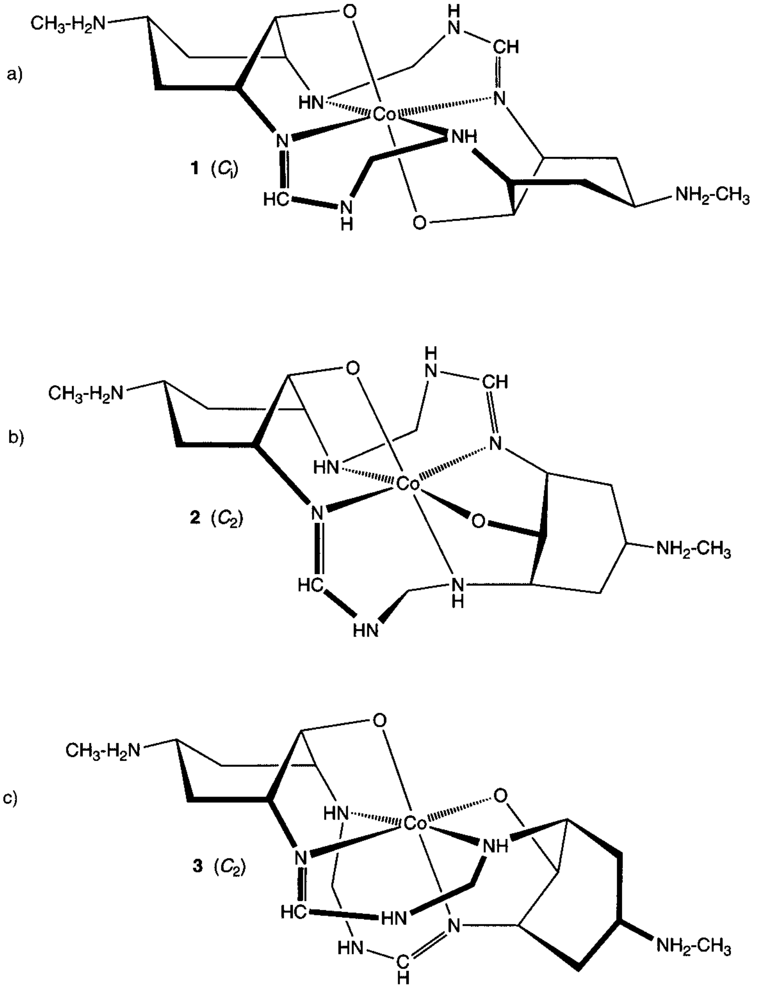


Figure 3. pD dependence of the ^{1}H NMR resonances of $[Co(H_2L^b)]^{5+}$ (D_2O, 33 °C, TSP = 0 ppm).[14] Squares, triangles and circles represent experimental values, the lines are calculated (minimisation of $\Sigma[\delta_{obs} - \delta_{calcd}]^2$. The numbering scheme of Scheme 5a has been used. The signal corresponding to H6 has been omitted due to pronounced line broadening around pD 5 (see text).

For a further discussion of the stereochemistry of this complex, it should be kept in mind that the two NH bridge heads become stereogenic when coordinated to the Co^{III} centre and, consequently, different diastereomers must be taken into account. Based on symmetry arguments, the two nitrogen atoms must have related configurations (*R,S* in the C_i isomer **1** and *R,R* or *S,S* in the C_2 isomers **2** and **3** shown in Scheme 6). For the C_i symmetric ligand **A** (Scheme 5), only structure **1** (Scheme 6) is compatible with these considerations. However, the C_2 symmetric macrocycle **B** can be wrapped around the Co^{III} centre in two different ways resulting in distinct structures (**2** and **3**) where either the two sp^2 or the two sp^3 nitrogen donors have a *trans* orientation within the coordination sphere (for **B** the two oxygen donors of the C_2 symmetric ligand are always oriented *cis*). The observation that the deprotonation of the two coordinated hydroxy groups did not result in any reverse shift of any of the H(–C–N) ring protons (low-field shift upon in-



Scheme 6. Possible structures of $[Co(L^b)]^{3+}$ with C_i (a) or C_2 symmetry (b and c).[14] Non-coordinating hydroxy groups and charges are omitted for clarity.

creasing pD in the range $0 < pH < 2$, see the corresponding feature for H3 of $[Co(HL^a)]^{4+}$ in Figure 2) would exclude the presence of an O–Co–N–CH substructure with a *trans* O–Co–N orientation.[25] Consequently, the C_i symmetric structure **1** remains as the only stereoisomer which is compatible with all the NMR spectroscopic characteristics.

Further inspection of the pH dependence of the ^{1}H NMR signals in the range $2.5 \leq pD \leq 7.5$ revealed considerable line broadening. Similar behaviour has already been noted for the monobridged species $[Co(HL^a)]^{4+}$, although the line broadening observed for the doubly bridged complex is much more pronounced and some of the signals such as H5 and H6 disappear completely around pH 5. We interpret this line broadening again in terms of a changeover from a twisted boat to a chair conformation of the two cyclohexane back bones. These structural changes are a consequence of the deprotonation of the two non-coordinated methylammonium groups, allowing N–H···N hydrogen bonding in the deprotonated form. Molecular mechanics calculations for the fully deprotonated $[Co(H_{-2}L^b)]^+$ predict that among the various possible isomers the C_2 symmetric form **2** (Scheme 6) is of the lowest energy (Table S2, supporting information). The C_i symmetric isomer **1** has a slightly higher, and the C_2-symmetric isomer **3** a considerably higher strain energy. At first glance this result is in disagreement with the assignment of the centrosymmetric structure **1** for $[Co(L^b)]^{3+}$ as follows from the NMR spectroscopic data. However, it should be kept in mind that in analogy to the monobridged ion $[Co(L^a)]^{3+}$, the primary product of the condensation reaction is an N_6-coordinated complex and the N_4O_2-coordinated product is formed in a subsequent rearrangement (Scheme 3). Our calculations indeed revealed that the N_6-coordinated forms are all considerably more strained than the N_4O_2-coordinated species **1** and **2**. Furthermore, the N_6-coordinated complex with the C_i symmetric ligand **A** (Scheme 5) is about 9 kJ mol^{-1} less strained than the corresponding complex with ligand **B**. The calculations would thus be in full agreement with the experimental findings, if we assume formation of the N_6-coordinated species as the rate-limiting step in the entire reaction sequence.

Coupling with Aniline

Aniline was used as an alternative nitrogen nucleophile to study the influence of an aromatic substituent on the coupling reaction with $[Co^{III}\text{-hmi-}(taci)_2]^{3+}$. However, a noticeable conversion was only observed if an additional base such as triethylamine was added to the reaction mixture. Workup under acidic conditions yielded a very complex mixture with a $^{13}C\{^1H\}$ NMR spectrum exhibiting more than forty resonances. After further treatment of this product with aqueous NaOH (pH 11), a single red Co^{III} complex could be isolated as the major component by chromatographic methods. The FAB$^+$ mass spectrum showed an *m*/*z* value of 529 for the molecular ion which is consistent with the composition $[Co(C_{20}H_{36}N_7O_6)]^+$. The structure of this complex was again elucidated by NMR spectroscopy (Figure 4). Two independent spin systems were observed for the two cyclohexane rings. Additionally, one of the coordinated nitrogen donors bears a methyl group, another a C_7H_7N substituent. The latter clearly contains the aniline component in the form of a coordinated formamidine moiety. The monosubstituted phenyl ring of this substituent could be readily recognised by its ^{1}H and ^{13}C NMR spectroscopic characteristics and the amidine functionality was identified by a strong C=N stretch vibration at 1658 cm^{-1} and corresponding NMR resonances at δ = 8.74 ppm and 162.6 ppm in the ^{1}H and ^{13}C spectra.[6,26] Bridging of the two taci moieties was, however, not observed. The ^4J coupling between the H(–C)–imine proton and the cyclohexane proton H7 together with the $^3J_{C,H}$ coupling between H7 and the imine carbon atom enabled an unambiguous localisation of the amidine fragment. An additional long range coupling between H2 and the methyl group established that the amidine substituent and the methyl group are not attached to the same taci moiety. None of the ^{1}H resonances showed any pH dependence and we can therefore exclude a changeover from the CoN_6 to a CoN_5O coordination. This contention is also supported by the ^{13}C NMR characteristics whereby a resonance above 70 ppm, indicative of five-membered chelate rings,[18] was not observed. The relative orientation of the methyl group and the C_7H_7N substituent could not be deduced from experimental data. However, mechanistic considerations (hydride shift, see above) would clearly point to a *cis* arrangement of these two non-hydrogen substituents. Two different tautomers **I** and **II** are possible for the amidine moiety (Figure 4b) and, for each of them, a *Z* or *E* configuration of the C=N double bond and an *R* or *S* configuration of the stereogenic coordinated sp^3 amine donors must be taken into consideration. For the tautomers **I** with a coordinated imine, the methyl group of the NH–CH$_3$ donor can adopt a *syn* or *anti* orientation with respect to the amidine moiety. The reverse tautomers **II**, in which the C=N double bond is in conjugation with the phenyl ring, have two stereogenic nitrogen donors with either an *S*,*R*-, *R*,*S*-, *R*,*R*-, or *S*,*S* configuration. Once again, it was not possible to establish from experimental data which of the various isomers is predominantly formed. We therefore analysed the steric strain by means of molecular mechanics methods and these calculations established clearly that the tautomers with a coordinated imine (form **I**) are more stable (i.e. less strained) than the corresponding tautomers of the type **II** (Table 2). Moreover, form **I** enables the possibility for an extended π delocalisation within the N=C–NH–phenyl fragment which would not be possible in type **II**. A type **I** form is also in agreement with the structure observed for the organic analogue in which the Co centre and the taci subunit are replaced by two methyl groups.[27] Our calculations further revealed that the type **I** isomer with an *E* orientation for Co and NH-phenyl and a *syn* configuration of the amidine moiety and the methyl group is of lowest energy.[28] For this particular geometry, the calculations predicted Co^{III}–N bond lengths in the range of 1.95–1.99 Å (mean value 1.98 Å) with the 1.95 Å and the 1.99 Å distances corresponding to the bonds to the imine and methylamine nitrogen donor, respectively. For all possible isomers of $[Co(L^c)(L^d)]^{3+}$,[14] the increased strain is mainly caused by additional nonbonding interactions between the non-hydrogen substituents at the nitrogen donors and this is partially compensated for by an elongation of some of the Co–N bonds. As a matter of fact, it seems likely that these bonds are even somewhat longer than stated, since the calculations tend to slightly underestimate long Co^{III}–N distances.[29–31] The increased strain results in some weakening of the ligand field and this effect together with a possible conjugation between the 3d orbitals of Co and the extended π system of the amidine fragment supposedly contributes to the rather high λ_{max} value of 510 nm observed for the $^1A_{1g}$–$^1T_{2g}$ transition.[32,33]

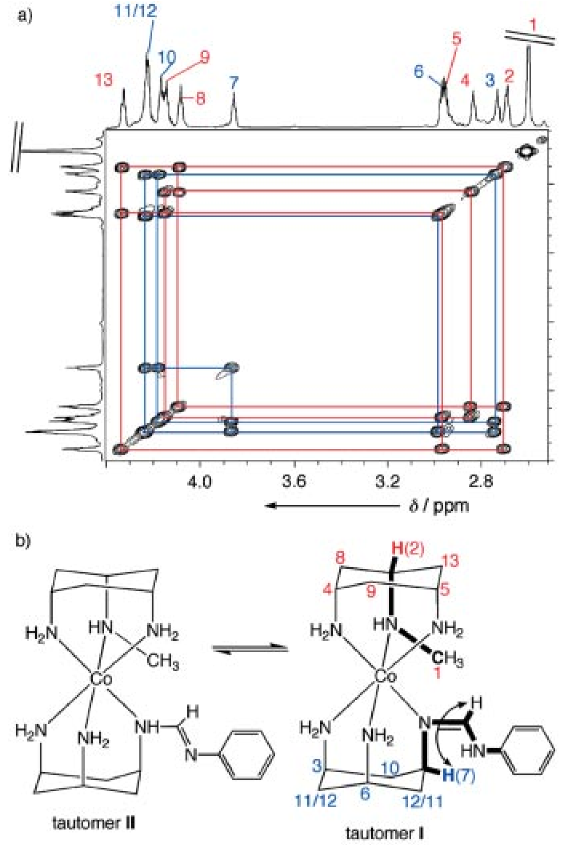


Figure 4. a) Section of the ^{1}H-^{1}H COSY NMR spectrum of $[Co(L^c)(L^d)]^{3+}$ with the two independent spin systems shown in blue and red.[14] b) Structural representation of the two possible types of tautomers of $[Co(L^c)(L^d)]^{3+}$ (OH groups omitted) with numbering scheme. C–H long-range and H–H long-range coupling interactions are shown by bold bonds and by an arrow, respectively.

Hydrogenation of $[Co(L^c)(L^d)]^{3+}$ in an aqueous acidic medium on Pd/C (5 atm) resulted in decomposition of the complex and complete hydrolysis of the amidine moiety. As a consequence, the reaction product consisted of a 1:1 mixture of taci and its monomethylated derivative.

Table 2. Calculated strain energies and Co–N bond lengths of possible isomers for $[Co(taci)_2]^{3+}$ and $[Co(L^c)(L^d)]^{3+}$.[a]

Complex	Relative strain energy [kJ mol^{-1}]	Co–N bond lengths [Å] range, mean
$[Co(taci)_2]^{3+}$		1.969
$[Co(L^c)(L^d)]^{3+}$, Tautomer **I**		
E/*syn* [b]	0	1.95–1.99, 1.975
E/*anti* [b]	6	1.96–1.99, 1.977
Z/*syn* [b]	25	1.96–2.00, 1.979
Z/*anti* [b]	20	1.97–1.99, 1.981
$[Co(L^c)(L^d)]^{3+}$, Tautomer **II**		
E/*S*,*S* [c]	25	1.97–2.00, 1.984
E/*S*,*R* [c]	34	1.97–2.00, 1.985
E/*R*,*S* [c]	24	1.98–1.99, 1.984
E/*R*,*R* [c]	25	1.97–2.00, 1.984
Z/*S*,*S* [c]	39	1.97–2.01, 1.985
Z/*S*,*R* [c]	51	1.97–2.01, 1.987
Z/*R*,*S* [c]	37	1.98–1.99, 1.984
Z/*R*,*R* [c]	38	1.97–2.00, 1.985

[a] Molecular mechanics calculations using the MOMEC force field[46,47] together with the extensions listed in Table 4. [b] *E* and *Z* refer to the NH and Co substituents at the C=N double bond. Note that the free ligand L^d and the complex $[Co(L^c)(L^d)]^{3+}$ have opposite stereo-descriptors: the *Z*-ligand[14] forms a complex with an *E* configuration and vice versa (Figure 4b). The descriptors *syn* and *anti* refer to the orientation of the methyl group with reference to the amidine moiety. [c] *E* and *Z* refer to the NH and C_6H_5 substituents at the C=N double bond, the two stereo-descriptors *R* and *S* refer to the configuration at the chiral amidine and methylamine nitrogen atoms, respectively, as shown in Figure 4b.

Coupling with Cyanide

The reaction of CN^- with $[Co^{III}\text{-hmi-}(taci)_2]^{3+}$ in aqueous solution again yielded a complex reaction mixture. Several different fractions could be separated on a Sephadex column but only the major red component could be identified unequivocally by means of MS and NMR spectroscopic measurements as a monobridged derivative $[Co^{III}(L^e)]^{3+}$ (Figure 5).[14] The FAB$^+$ spectrum exhibited signals of the pseudo-molecular ions $[Co^{II}(H_{-1}L^e)]^+$ and $[Co^{II}(L^e)Cl]^+$ ($L^e = C_{14}H_{31}N_7O_6$) with intensities of 100% and 13%, respectively. $[Co(L^e)]^{3+}$ is completely asymmetric as indicated by the ^{1}H and ^{13}C NMR spectra which contained a total of 10 and 11 signals for the two taci rings, respectively (one signal in the ^{13}C NMR and two signals in the ^{1}H NMR spectrum with double intensity corresponded to the resonances of two atoms). The ^{1}H-^{1}H correlated 2D spectrum showed two independent spin system each consisting of six hydrogen atoms. The corresponding carbon atoms, which were identified as CH groups from a DEPT experiment,[17] were assigned by a ^{1}H-^{13}C correlated spectrum. An additional CH_2 group with two diastereotopic hydrogen atoms was located and the ^{13}C spectrum also exhibited a strongly deshielded signal at δ = 176 ppm, indicative of the formation of an imino group. Formation of a C=N double bond was further confirmed by a strong, sharp band at 1647 cm^{-1} in the IR spectrum.[26] However, the DEPT experiment together with the ^{1}H characteristics clearly show that, in contrast to the products obtained in the reaction with ammonia or aniline, the amidine-C is not bonded to any hydrogen atoms. Furthermore, the NMR spectroscopic data gave no indication of the presence of an N–CH_3 group. The bridging position of the N=C(NH_2)–CH_2–NH moiety was finally established from a long-range 2D C-H correlated experiment in which long range interactions from the bridging moiety to both cyclohexane entities could be observed. In analogy to [Co(L^c)(L^d)]$^{3+}$, it was not possible to conclude from the experimental data as to which of the two possible tautomers is formed. However, as outlined in the previous section it seems highly probable that the form with the imine nitrogen donor bonded to Co^{III} is more stable. Indications for a κ^3-*N*,*O*,*N* coordination mode as described above for [Co(HL^a)]$^{4+}$ and [Co(H_2L^b)]$^{5+}$ have not been detected.

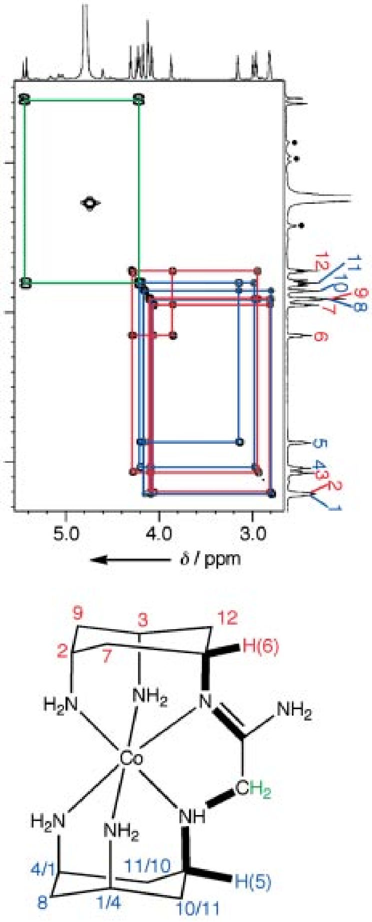


Figure 5. a) Section of the ^{1}H-^{1}H COSY NMR spectrum of [Co(L^e)]$^{3+}$;[14] H(–N) protons of the coordinated amino groups are marked with black circles. b) structural representation of [Co(L^e)]$^{3+}$ with numbering scheme.[14] C–H long-range coupling interactions are shown in bold. The hydroxy groups in positions 7,9,12 and 8,10,11 are omitted for clarity.

The two doublets of the methylene group exhibited a rather large $^2J_{H,H}$ coupling constant of 18 Hz. Such unusually large coupling constants are known for spin systems with a π electron system attached to the CH_2 group as observed in cyclopentene-1,4-dione and it has been proposed that this enhancement is particularly large if the vector between the two protons is oriented parallel to the π orbitals[34] which is clearly the case for the N=C(NH_2)–CH_2–NH bridge of [Co^{III}(L^e)]$^{3+}$. The CH_2-groups are weakly acidic and, if a solution of [Co^{III}(L^e)]$^{3+}$ in D_2O is brought to a pD of about 11, the signals of the methylene group disappear in the ^{1}H NMR spectrum and they do not reappear after addition of DCl. However, the DEPT spectrum still showed the presence of a methylene group indicative of H/D exchange. It is clear that the corresponding carbanion which is formed above pD 10 is stabilised by significant electron delocalisation.

The entire structure of [Co^{III}(L^e)]$^{3+}$ was again modelled by molecular mechanics calculations. In this model, the Co^{III}–N_{imine} bond length proved to be relatively short (1.92 Å), whereas the remaining Co^{III}–N_{amine} bonds lengths (1.96–1.97 Å) are consistent with the values reported in the literature for X-ray structures of a range of (hexaamine)-Co^{III} complexes.[33] The high rigidity of the amidine-bridge resulted in some distortion of the octahedral coordination geometry with N–Co–N angles between 84° and 99°. The $^1A_{1g}$–$^1T_{2g}$ transition appeared at 497 nm which again indicates some weakening of the ligand field. Cyclic voltammetry showed a quasi-reversible redox process with a redox potential of –0.35 V (vs. NHE). A similar value has been observed for the parent system [Co$^{II/III}$(taci)$_2$]$^{2+/3+}$.[20,35]

Discussion

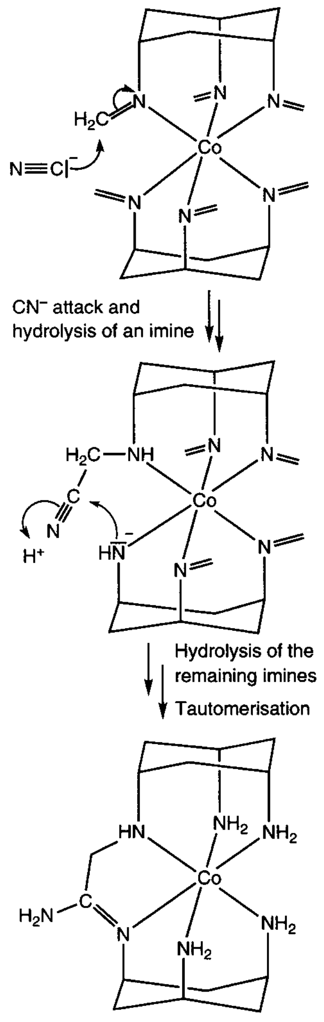
The reaction of [Co^{III}-hmi-(taci)$_2$]$^{3+}$ with the three nucleophiles NH_3, aniline and CN^- yielded three considerably different types of products. The reaction with NH_3 resembles the previously reported reaction with nitromethane insofar as formation of NH–CH_2–XH–CH=N bridges [XH = NH, C(H)-NO_2], connecting the two taci frames, coincides with methylation of an adjacent primary amino group.[9] The mechanism of this reaction has been discussed in terms of an intramolecular Cannizzaro reaction (Scheme 1, b) whereby a hydride is transferred from the methylene group of the initially formed NH–CH_2–XH–CH_2–N^- bridge to an imino group. However, some characteristic differences are evident: (i) In the reaction with nitromethane (X = C-NO_2), the XH proton is finally abstracted by NEt_3 and the ligand appears in a carbanionic form, whereas in the reaction with NH_3, the nitrogen atom in the bridge (X = N) retains its proton. (ii) In the reaction with nitromethane, the doubly bridged complex was isolated as the main product while in the reaction with ammonia, the monobridged species was formed as the major product and the doubly bridged complex was only obtained as a very minor component. (iii) The bridging process with NH_3 was generally followed by a rearrangement of the coordination sphere of the Co^{III} centre, i.e. the taci-moiety which becomes methylated switches from a κ^3-*N*,*N*,*N* to a κ^3-*N*,*O*,*N* coordination mode (Scheme 3). Consequently, an alkoxopentaamine coordination was observed for the monobridged complex and the doubly bridged derivative exhibits a dialkoxo-tetraamine coordination mode (Scheme 6). In the reaction with nitromethane, such a rearrangement of the coordination sphere was not observed. The isolated product retains its hexaamine coordination. It has, however, been noted that the nitromethane adduct undergoes a characteristic structural rearrangement in strongly alkaline solutions and re-acidification leads to a species which was not identical with the initial condensation product. It is particularly interesting to note that in the initial product a total of 30 signals were observed in the ^{13}C NMR spectrum and that this number was reduced to a total of 10 at high pH. Moreover, in the initial reaction product, no resonance was observed above 70 ppm for the cyclohexane carbon atoms, whereas at high pH one of these signals shifted to 76 ppm. Based on the results presented in this paper, it thus appears highly probable that the previously observed[9] "low-energy isomer" has a doubly bridged structure with an analogous CoN_4O_2-coordination mode as reported here for $[CoL^b]^{3+}$.

For $[Co^{III}(cis\text{-tach})(H_{-1}ino)]^{2+}$ (ino = *cis*-inositol, Structure O6 in Scheme S1b), an equilibrium between two different stereoisomers has been observed in aqueous solution.[36] In the first isomer, the metal is bound to the three axial hydroxy groups of *cis*-inositol whereas in the second isomer the binding occurred by means of three hydroxy groups having a subsequent axial-equatorial-axial orientation. The kinetics of the isomerisation reaction have been investigated in detail and it has been found that (i) this reaction occurs at a considerably higher rate than complete dissociation of the inositol ligand, (ii) the isomerisation reaction becomes dramatically accelerated at high pH and (iii) the equilibrium between the triaxial and the axial-equatorial-axial coordination mode is influenced by the possibility of intramolecular O···H–O hydrogen bond formation. The higher rate of isomerisation compared with ligand dissociation was interpreted in terms of a mechanism in which the inositol ligand remains partially coordinated. For $[Co(L^a)]^{3+}$ and $[Co(L^b)]^{3+}$ with a hypothetical hexaamine coordination, the presence of an $N–CH_3$ group would generate significant strain due to nonbonding interactions between the methyl group and a hydrogen atom of a primary amino group of the neighbouring taci frame.[9] This strain is clearly responsible for the change to the κ^3-*N*,*O*,*N* axial-equatorial-axial coordination mode. By analogy with $[Co^{III}(cis\text{-tach})(ino)]^{3+}$, the rearrangement can occur without dissociation of the ligand (Scheme 3) and it is particularly fast in an alkaline medium. Similar to $[Co^{III}(cis\text{-tach})(ino)]^{3+}$, the pH has a significant influence on the possibility of intramolecular hydrogen bond formation: As long as the methylamino group remains deprotonated, it can act as a proton acceptor and can thus stabilise the corresponding cyclohexane chair. However, after protonation, significant nonbonding N–H···H–N repulsive interactions would arise. In contrast to $[Co^{III}(cis\text{-tach})(ino)]^{3+}$, this conflict cannot be resolved by a return to the double-adamantane-type structure and the only way for strain to be minimised is by the adoption of a twisted boat conformation (Scheme 4).

The reaction of $[Co^{III}\text{-hmi-(taci)}_2]^{3+}$ with aniline is remarkable because the resultant structure is devoid of any bridge between the two taci-frames. Formation of an amidine moiety together with *N*-methylation must again be interpreted in terms of a Cannizzaro type hydride shift. The lack of observation of a bridge is, however, a clear sign that the hydride shift already occurs after the first condensation step (bridge formation would require a double attack of the nucleophile to two adjacent imino groups, see Scheme 1). At present, it is still not clear why the hydride shift already occurs here at an earlier stage. Either electronic properties (reduced nucleophilicity of the aniline nitrogen) or steric reasons (increased repulsion due to the larger aromatic substituent) may account for this behaviour.

The reaction of the hexaimine complex with cyanide is special because CN^- cannot undergo multiple binding to adjacent $H_2C=N(R)–Co$ groups. In a nonaqueous medium, the reaction of CN^- with an imine would simply generate a $Co–N(R)^-–CH_2–CN$ moiety. Such a product could then become protonated to give $Co–N(R)H–CH_2–CN$. It would, however, remain in equilibrium with the initial components.[37] In an aqueous environment, CN^- binding and hydrolysis may occur simultaneously as competing processes. It is possible to control the reaction in such a way that one imino group reacts with OH^- reforming the deprotonated, coordinated amine, whereas at the same time, an adjacent imino group reacts with CN^- (Scheme 7). The nitrile-carbon atom can now react as an electrophilic centre,[26,38] being able to accept the adjacent, negative nitrogen donor. In organic chemistry, the reaction of a nitrile RCN with an amine to give a corresponding amidine is only known for nitriles which are activated either by a strongly electron-withdrawing substituent R or by coordination of a Lewis acid.[39] The situation is different in coordination chemistry in which the generation of a metal-bound amidine by an intramolecular reaction between a deprotonated, coordinated amine and a nitrilo group has been documented with a few examples.[37,40]

Owing to the reversible addition of CN^- to the imine, successful formation of $[Co(L^e)]^{3+}$ requires a well balanced ratio of the two reaction rates. This ratio can be influenced by varying either the CN^- or the OH^- concentration. We obtained reasonable yields of the mono-bridged species in aqueous solution around pH 10–12. Even at this relatively moderate OH^- concentration, complete hydrolysis of the hexaimine represents a significant side reaction as indicated by the isolation of considerable amounts of $[Co(taci)_2]^{3+}$ from the reaction mixture. Further lowering of the pH should, however, be avoided, due to possible HCN formation. We have not yet succeeded in the isolation of any doubly bridged product and it appears that the formation of a second bridge would occur at a significantly lower rate. Since the reaction of a coordinated imine with CN^- is reversible, all of the remaining imino groups are hydrolysed and the final product was found to be devoid of any *N*-methylidene-imino groups. The reaction of $[Co\text{-hmi-(taci)}_2]^{3+}$ with CN^- in aqueous media thus represents a promising route for connecting two taci-rings by one N–C–C–N bridge. However, we have not yet established whether reduction of the amidine to the amine and de-metallation can be readily achieved. Similar to the reaction of $[Co^{III}\text{-hmi-(taci)}_2]^{3+}$ with aniline and with nitromethane, the hexaamine coordination appears to be retained in $[Co(L^e)]^{3+}$,



Scheme 7. Proposed mechanism for the formation of $[Co(L^e)]^{3+}$.[14] The non-coordinating OH-groups are omitted for clarity.

although molecular mechanics calculation indicated some distortion from regular octahedral geometry. $[Co(L^e)]^{3+}$ is the only example in this study in which the coupling reaction does not result in formation of a methylamino group. Clearly a hydride shift from the $Co–N(R)^-–CH_2–CN$ methylene group to an adjacent imino group is not possible.

In conclusion, our study has fully confirmed that the successful capping reaction observed for $[Co(en)_3]^{3+}$ cannot be applied to (hexaamine)Co^{III} complexes with rigid cyclic amine ligands. Sargeson proposed that the lack of observation of the capping process in such systems is a consequence of the slow exchange rate of the amine protons.[10] Such an assumption is plausible because condensation with the aldehyde and addition of the capping reagent can be performed in a single reaction with N–H deprotonation as the first step. In our investigation, we have used the hexamethylideneimine derivative as a starting material and it has thus become evident that other factors must be responsible for the different behaviour of the cyclic ligands. We attribute the slow rate or indeed the failure to observe bridge formation to be mainly due to steric constraints. The molecular mechanics calculations provided unambiguous evidence that in general, bridging of two taci moieties by means of two nitrogen donors of the hexaamine coordination implies a significant increase of strain and that this strain increases with an increasing number of bridges.

Experimental Section

Physical Measurements and Analyses: ^1H and ^{13}C NMR spectra were recorded in D_2O at 306 K with a Bruker Avance DRX 500 spectrometer at frequencies of 500.13 MHz and 125.9 MHz, respectively. Chemical shifts (in ppm) are given relative to $[D_4]$sodium (trimethylsilyl)propionate (0 ppm) as the internal standard. The pD values of the NMR samples were adjusted with NaOD and DCl and were determined as described previously.[41] Multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. The gradient-selected (gs) ^1H-^1H COSY, gs ^1H-^{13}C COSY and gs ^1H-^{13}C HMBQ experiments were performed as described in the literature.[42] CH_3, CH_2 and CH carbon atoms were assigned using ^{13}C DEPT experiments.[17] IR spectra were recorded on a Perkin-Elmer 883 IR spectrometer (KBr wafer) and UV/Vis spectra were measured on a Uvikon 940 spectrometer at 25 ± 1 °C. FAB^+ mass spectra were recorded on a VG ZAB VSEQ instrument. The samples were measured as aqueous solutions using a glycerol matrix. Cyclic voltammetry was performed at ambient temperature (23 ± 2 °C) on a BAS C2 cell equipped with an Hg or Au electrode, a platinum counter electrode and an Ag/AgCl reference electrode with a BAS 100B/W potentiostat. The measurements were performed in an aqueous borax buffer (pH 9) with 1-mM sample concentrations and NaCl (1 M) as a supporting electrolyte. pK_a values were determined by potentiometric titrations as described previously[41] (25.0 °C, 0.10 M KCl) and evaluated using a fixed value of 13.78 for pK_w. C, H and N analyses were performed by H. Feuerhake (Universität des Saarlandes).

Materials: Et_3N, CH_3CN, aniline, aqueous NH_3 (≈ 25%), KCN and trisodium citrate dihydrate were commercially available products from Fluka. CH_3CN was dried with P_4O_{10}. Aniline was freshly distilled prior to use. CF_3SO_3H (>98%) was purchased from Lancaster Synthesis and stored under N_2. $[Co(taci)_2](NO_3)_3·2H_2O$[31] and its hexamethylideneimino (hmi) derivative $[Co\text{-hmi-}(taci)_2]Cl_3·6H_2O$[9] were prepared according to published procedures. Dowex 50 W-X2 cation-exchange resin (100–200 mesh, H^+ form) was obtained from Fluka. SP-Sephadex C-25 cation exchange resin (200 mesh, from Pharmacia Biotech) was converted into the Na^+ form by elution with NaCl (2 M) prior to use and sufficient rinsing with H_2O until the eluent was free of chloride (checked with $AgNO_3$).

$[Co\text{-hmi-}(taci)_2](CF_3SO_3)_3·2H_2O$: $[Co\text{-hmi-}(taci)_2]Cl_3·6H_2O$ (500 mg, 0.71 mmol) was dissolved in CF_3SO_3H (20 mL). The clear yellow solution was heated to 80 °C and a stream of dry N_2 was passed through the mixture for 3 h. The clear, dark yellow solution was cooled to room temperature and was then cautiously poured into Et_2O (750 mL). A solid precipitated which was removed by filtration, washed six times carefully with Et_2O (portions of 100 mL) and dried in air. Yield: 636 mg (92%) of a pale yellow solid. $C_{21}H_{34}CoF_9N_6O_{17}S_3$ (968.6): calcd. C 26.04, H 3.54, N 8.68; found C 26.22, H 3.34, N 8.71. IR (KBr): $\tilde{\nu}$ = 1618 (s) cm^{-1}. ^1H NMR (D_2O, pD < 1): δ = 4.07 (t, J = 3.0 Hz, 6 H), 4.62 (t, J = 3.0 Hz, 6 H), 7.91 (d, J = 7.5 Hz, 6 H), 8.13 (d, J = 7.5 Hz, 6 H) ppm. $^{13}C\{^1H\}$ NMR (D_2O, pD < 1): δ = 68.5 (CH), 76.7 (CH), 122.6 (q, $J_{C,F}$ = 317 Hz), 187.2 (C) ppm.

Reaction of $[Co\text{-hmi-}(taci)_2](CF_3SO_3)_3·2H_2O$ with NH_3: $[Co\text{-hmi-}(taci)_2](CF_3SO_3)_3·2H_2O$ (1.0 g, 1.03 mmol) was dissolved in dry

CH_3CN (100 mL). To the yellow solution was rapidly added concentrated aqueous NH_3 (10 mL). An immediate colour change to dark green was noted and the reaction mixture turned to a reddish brown within a few minutes. A brownish solid finally precipitated. The suspension was stirred for 24 h at room temperature giving a bright red solution together with a yellow solid. The entire mixture was poured into a solution of aqueous H_2SO_4 (30 g of conc. H_2SO_4 dissolved in 600 mL of H_2O). The solution was further diluted with H_2O to a total volume of 1 L (pH $\approx$ 1) and adsorbed on Dowex 50. The column was washed with H_2O until the eluent was neutral and then elution with aqueous HCl (0.5 M) was carried out. Further elution with HCl (3 M) yielded a red fraction which was evaporated to dryness and redissolved in H_2O (100 mL). Traces of acid were neutralised by adding small portions of NaOH (1 M). The solution was then adsorbed on Sephadex. Elution with trisodium citrate (0.2 M) resulted in the separation of three bands: A pink fast moving minor fraction (F1) followed by a major red fraction (F2) and a slower moving badly resolved third fraction (F3). The yellow front part of F3 was identified as $[Co(taci)_2]^{3+}$ by ^1H and ^{13}C NMR spectroscopy. According to NMR and MS measurements, the purple coloured tailing part of F3 was a mixture of several components which could be neither separated nor identified. Each fraction was desalted on Dowex 50, (elution with 0.5 M HCl and 3 M HCl). The products which were obtained in the 3-M HCl fractions were evaporated under reduced pressure and dried in air.

Analytical Data of Fraction F1 {$[Co(H_2L^b)]Cl_5$}:[14] Yield: 5 mg of pink brittle flakes. ^1H NMR (D_2O, pD = 0.2): δ = 2.83 (s, 6 H), 3.36 (m, 2 H), 3.39 (t, J = 5 Hz, 2 H), 3.71 and 3.98 (AB-system, J = 12 Hz, 4 H), 4.11 (t, J = 4 Hz, 2 H), 4.33 (m, 2 H), 4.66 (m,4 H), 8.53 (s, 2 H) ppm. $^{13}C\{^1H\}$ NMR (D_2O, pD = 1): δ = 35.7 (CH_3), 60.0 (CH), 61.0 (CH_2), 62.2 (CH), 62.9 (CH), 63.2 (CH), 64.9 (CH), 76.4 (CH), 174.1 (CH) ppm. MS-FAB$^+$ m/z (%) = 518 (36) $[Co(H_{-1}L^b)]^+$,[15] 554 (6) $[Co(L^b)Cl]^+$. UV/Vis: λ_{max} = 525 nm (12 M HCl), λ_{max} = 517 nm (pH = 12).

Analytical Data of Fraction F2 {$[Co(HL^a)]Cl_4\cdot H_2O$}:[14] Yield: 283 mg (0.45 mmol, 44%) of a deep red solid. $C_{15}H_{36}CoCl_4N_7O_7$ (627.2): calcd. C 28.72, H 5.79, N 15.63; found C 28.84, H 5.83, N 15.70. IR (KBr): $\tilde{\nu}$ = 1628 (s) cm^{-1}. ^1H NMR (D_2O, pD = 1): δ = 2.55 (t, J = 3.5 Hz, 1 H), 2.82 (s, 3 H), 3.04 (t, J = 3.5 Hz, 1 H), 3.28 (m, 1 H), 3.32 (m,1 H), 3.58 (m, 1 H), 3.60 (t, J = 3.5 Hz, 1 H), 3.84 and 3.96 (AB-system, J = 11.5 Hz, 2 H), 4.04 (m, 1 H), 4.13 (t, J = 3.5 Hz, 1 H), 4.22 (t, J = 3.5 Hz, 1 H), 4.23 (t, J = 3.5 Hz, 1 H), 4.71 (m, obscured by HDO, δ taken from ^1H ^1H-COSY, 1 H) 4.75 (m, obscured by HDO, δ taken from ^1H ^1H-COSY, 1 H), 8.15 (s, 1 H) ppm. $^{13}C\{^1H\}$ NMR (D_2O, pD = 1): δ = 33.2 (CH_3), 52.0 (CH), 52.1 (CH), 54.8 (CH), 57.9 (CH), 59.7 (CH), 61.4 (CH_2), 62.2 (CH), 62.7 (CH), 64.1 (CH), 65.8 (CH), 65.9 (CH), 66.7 (CH), 75.7 (CH), 172.8 (CH); (pD = 8): 40.2, 52.5, 53.2, 60.5, 61.7, 65.1, 65.5, 66.0, 66.85, 66.94, 67.3, 68.1, 68.3, 80.0, 170 ppm. MS-FAB$^+$ m/z (%): 465 (100) $[Co(H_{-1}L^a)]^+$, 501 (13) $[Co(L^a)Cl]^+$. UV/Vis (12 M HCl): λ_{max} = 383 nm (ε = 289 M^{-1}cm^{-1}), λ_{max} = 513 nm (ε = 120 M^{-1}cm^{-1}); (NaOH, pH = 12) λ_{max} = 386 nm (ε = 170 M^{-1}cm^{-1}), λ_{max} = 508 nm (ε = 90 M^{-1}cm^{-1}). Crystals of composition $[Co(HL^a)][ZnBr_4]_2\cdot 5H_2O$ suitable for X-ray analysis were grown by slow diffusion of EtOH into an acidified (HBr) aqueous solution of $[Co(HL^a)]Cl_4$ saturated with $ZnBr_2$ at 4 °C.

Reaction of $[Co\text{-}hmi\text{-}(taci)_2](CF_3SO_3)_3\cdot 2H_2O$ with Aniline: Aniline (3.3 mL, 36 mmol) and $[Co\text{-}hmi\text{-}(taci)_2](CF_3SO_3)_3\cdot 2H_2O$ (520 mg, 0.54 mmol) were dissolved in dry CH_3CN (150 mL). NEt_3 (6.6 mL, 47 mmol) was added to the resultant light yellow solution which caused an immediate colour change to dark green. The mixture was stirred for 30 min at room temperature and then poured into aqueous H_2SO_4 (18 g of H_2SO_4 in 400 mL of H_2O). The reddish orange solution was further diluted with H_2O to a total volume of 1 L and sorbed on Dowex 50. The column was eluted with aqueous HCl (0.5 M and 4 M). The 4-M HCl fraction was evaporated to dryness and the residue redissolved in H_2O (50 mL). NaOH (1.5 M) was added carefully in small portions until the pH reached a value of 11 (checked using a glass electrode). During this addition, the colour changed to violet and precipitation of a solid was observed. The suspension was stirred at room temperature for 24 h, acidified with dilute HCl to pH 7 and sorbed onto Sephadex. Elution with Na_2SO_4 (0.28 M) resulted in the separation of three bands: a very small fast moving light red band which was discarded, a yellow band of $[Co(taci)_2]^{3+}$, and a strong red band of $[Co(L^c)(L^d)]^{3+}$. The last red fraction was desalted on Dowex 50, evaporated to dryness and dried in vacuo. Yield: 177 mg (0.26 mmol, 49%) of red $[Co(L^c)(L^d)]Cl_3\cdot 2H_2O$.[14] $C_{20}H_{41}CoCl_3N_7O_8$ (672.9): calcd. C 35.70, H 6.14, N 14.57; found C 35.94; H 5.77; N 14.54. IR (KBr): $\tilde{\nu}$ = 1658 (s) cm^{-1}. ^1H NMR (D_2O): δ = 2.60 (s, 3 H), 2.69 (t, J = 3.5 Hz, 1 H), 2.72 (t, J = 3.5 Hz, 1 H), 2.83 (t, J = 3.5 Hz, 1 H), 2.95 (t, J = 3.5 Hz, 1 H), 2.96 (t, J = 3.5 Hz, 1 H), 3.84 (t, J = 3.5 Hz, 1 H), 4.07 (t, J = 3.5 Hz, 1 H), 4.13 (t, J = 3.5 Hz, 1 H), 4.16 (t, J = 3.5 Hz, 1 H), 4.21 (m, 2 H), 4.32 (t, J = 3.5 Hz, 1 H), 7.29 (m, 3 H), 7.47 (m, 2 H), 8.74 (s, 1 H) ppm. $^{13}C\{^1H\}$ NMR (D_2O): δ = 44.3 (CH_3), 52.3 (CH), 52.4 (CH), 52.8 (CH), 53.5 (CH), 55.5 (CH), 61.6 (CH), 65.3 (CH), 65.6 (CH), 65.8 (CH), 66.7 (CH), 67.6 (CH), 68.9 (CH), 120.7 (CH_{arom}), 128.1 (CH_{arom}), 132.5 (CH_{arom}), 141.0 (C_{arom}), 162.6 (CH) ppm. MS-FAB$^+$ m/z (%): 529 (97) $[H_{-1}\{Co(L^c)(L^d)\}]^+$, 565 (9) $[Co(L^c)(L^d)]Cl^+$. UV/Vis (H_2O): λ_{max} = 368 nm (ε = 147 M^{-1}cm^{-1}), λ_{max} = 510 nm (ε = 44 M^{-1}cm^{-1}).

Reaction of $[Co\text{-}hmi\text{-}(taci)_2]Cl_3\cdot 6H_2O$ with KCN: Caution! KCN and HCN are strong poisons. All manipulations must be performed in a well ventilated fume hood. HCN must be destroyed by passing any evolving gas through an NaOCl solution. A solution of KCN (250 mg, 3.84 mmol) in H_2O (250 mL) was added to a solution of $[Co\text{-}hmi\text{-}(taci)_2]Cl_3\cdot 6H_2O$ (1.05 g, 1.50 mmol) in H_2O (250 mL). The first 50 mL of the KCN solution were added dropwise whereas the remaining 200 mL were added in one portion. The solution, which by this time showed a red colour, was stirred at room temperature for 30 min and then poured into aqueous sulfuric acid (15 g of conc. H_2SO_4 in 500 mL of H_2O). **Caution!** Formation of HCN. The solution was further diluted with H_2O until a pH of 2 was reached and was then sorbed on Dowex 50. The resin was eluted with H_2O and with aqueous HCl (0.5 M). Further elution with HCl (3 M) gave a major broad band with a yellow front ($[Co(taci)_2]^{3+}$) and a red tail. The red portion was collected. However, complete separation from the yellow part was not possible. The resultant solution was evaporated to dryness, redissolved in 250 mL of H_2O and sorbed on Sephadex. Elution with trisodium citrate (0.2 M) gave four bands: a fast moving, very weak pink band which was discarded, a yellow band of $[Co(taci)_2]^{3+}$, a major red band and a violet band. NMR measurements showed that the violet band consisted of several unidentified Co^{III} complexes. The red and the yellow bands again showed some overlap and could not be separated completely. The entire red fraction was collected, desalted on Dowex 50 and the solvents evaporated to dryness. Remaining traces of $[Co(taci)_2]^{3+}$ could be removed by crystallisation: The solid was dissolved in H_2O (5 mL). $ZnBr_2$ (500 mg, dissolved in 4 mL of H_2O) and HBr (5 mL 48% in H_2O) were added and the solution was allowed to stand at 4 °C for 12 h. $[Co(taci)_2]^{3+}$ precipitated quantitatively as the $[ZnBr_4]^{2-}$ salt which was removed by filtration. The remaining red solution was then sorbed again on Dowex 50. The column was washed with H_2O and eluted with aqueous HCl (0.5 M and 1.0 M). Further elution with HCl (3 M) gave a red solution of the pure $[Co(L^e)]^{3+}$. This solution was evaporated to dryness and dried in vacuo. Yield: 261 mg (28%) of red $[Co(L^e)]Cl_3\cdot 3.5H_2O$.[14] $C_{14}H_{38}CoCl_3N_7O_{9.5}$ (621.8): calcd. C 27.04, H 6.16, N 15.77; found C 26.89, H 6.22, N 15.99. IR (KBr): $\tilde{\nu}$ = 1647 (s) cm^{-1}. ^1H NMR (D_2O): δ = 2.78 (m, 2 H), 2.93 (t, J = 4.0 Hz, 1 H), 2.96 (t, J = 4.0 Hz, 1 H), 3.13 (t, J = 3.0 Hz, 1 H), 3.84 (t, J = 4.0 Hz, 1 H), 4.05 (t, J = 4.0 Hz, 1 H), 4.09 (m, 2 H), 4.14 (t, J = 3.0 Hz, 1 H), 4.19 (t, J = 4.0 Hz, 1 H), 4.19 (d, J = 18.0 Hz, 1 H), 4.27 (t, J = 4.0 Hz, 1 H), 5.41 (d, J = 18.0 Hz, 1 H) ppm. $^{13}C\{^1H\}$ NMR (D_2O): δ = 51.3 (CH), 51.6 (CH), 53.3 (CH), 54.3 (CH), 57.5 (2 CH), 58.2 (CH_2), 65.6 (CH), 65.9 (CH), 67.0 (CH), 67.2 (CH), 68.3 (CH), 68.6 (CH), 175.9 (C) ppm. MS-FAB$^+$ *m/z* (%): 451 (100) $[Co(H_{-1}L^e)]^+$, 487 (13) $[Co(L^e)Cl]^+$. UV/Vis (H_2O): λ_{max} = 345 nm (ε = 343 M^{-1}cm^{-1}), λ_{max} = 497 nm (ε = 198 M^{-1}cm^{-1}).

X-ray Diffraction Analysis:[43] Diffraction data of $[Co(HL^a)][ZnBr_4]_2\cdot 5H_2O$ were collected at room temperature on a Siemens CCD Platform using monochromated Mo-K_α radiation and a crystal of dimensions 0.24 × 0.16 × 0.14 mm (Table 3). 21887 reflections were collected in the range of $1.49° < \theta < 23.24°$. An empirical absorption correction was performed (SADABS). Of a total of 5572 unique reflections 3217 were observed with $2\sigma(I)$. The structure was solved by direct methods and refined using full-matrix least-squares calculations on F^2.[44] One of the two counter-anions (Zn2) proved to be disordered and was modelled using a superposition of three discrete positions with occupancies of 50%, 38% and 12%. The Zn2 centre was located on two split positions (Zn2a and Zn2b) with a Zn2a–Zn2b separation of 0.753 Å. Both of these positions had an occupancy of 50%. The four Br$^-$ ligands (Br21–Br24) which are bound to Zn2a could be unambiguously located. They were also refined with occupancies of 50%. The Zn2a–Br distances and Br–Zn2a–Br angles are as expected. For each of the four Br$^-$ ligands bound to Zn2b, a major (Br31–Br34, 38%) and a minor (Br41–Br44, 12%) position was assigned. The major component refined well again but the minor component, which corresponds to a relatively small amount of electron density, was rather poorly defined (Zn2b–Br distances: 2.12–2.64 Å, mean value: 2.37 Å, and Br–Zn2b–Br angles of 89–133°, mean value: 108.5 °). Five additional peaks (O1S–O5S) were interpreted as H_2O molecules. The distances O1···O3S···O4S···O5S and O4···O2S fall between 2.7–2.8 Å which is the range expected for normal O–H···O hydrogen bonds. The O4S···O6 distance of 2.50 Å is rather short and indicative of a strong hydrogen bond. This is consistent with the high acidity of the coordinated hydroxy group (see Characterisation of $[Co(L^a)]^{3+}$ in the Results section above). O2S was found to be distributed over two positions with an O2Sa···O2Sb separation of 0.98 Å and occupancy factors of 60 and 40%. O1S and O5S were located in proximity to the disordered $[Zn2Br_4]^{2-}$ counterion and some of the corresponding O···Br separations were considerably shorter than the sum of the van der Waals radii. A split model was again used for O5S with occupancies of 20% for O5Sa (which is in conflict with Br24) and 80% for O5Sb. O1S was found to be in conflict with Br43. Since Br43 itself has an occupancy of only 12%, the occupancy of O1S was set to 88%. Although the remaining 12% of this H_2O molecule could not be located, a search for free voids[45] clearly indicated that sufficient empty space would be available for accommodation of this H_2O molecule within the Zn2bBr41–Br44 variant of the structure. Anisotropic displacement parameters were refined for all nonhydrogen atomic positions except for the two split positions of the disordered H_2O oxygen O5S. Hydrogen atoms of the complex cation were placed in calculated sites (riding model) and isotropic displacement parameters were used which were fixed at $1.5 \times U_{eq}$ of the pivot atom of hydroxy, amino, and methyl groups and $1.2 \times U_{eq}$ for all other C atoms. Owing to the isolation from an acidic medium (HBr), the meaningful hydrogen bonding scheme and based on charge balance considerations, N5 and O6 were both considered as being protonated. A total of 495 parameters were used in the final refinement, yielding a residual electron density with a minimum and a maximum of –0.58 and +1.07 e Å^{-3}. Puckering parameters of the two cyclohexane rings were calculated using the computer program PLATON.[45]

Table 3. Crystallographic data for $[Co(HL^a)][ZnBr_4]_2\cdot 5H_2O$ and $[Co(taci)_2][NO_3]_3\cdot 2H_2O$.

Empirical formula	$C_{15}H_{44}Br_8CoN_7O_{11}Zn_2$	$C_{12}H_{34}CoN_9O_{17}$
Formula mass [g mol^{-1}]	1327.52	635.41
Crystal size [mm]	0.24 × 0.16 × 0.14	0.20 × 0.15 × 0.15
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$ (No. 14)	$I2/a$ (No. 15)
a [Å]	9.0419(2)	14.696(3)
b [Å]	27.1800(6)	8.9090(18)
c [Å]	16.0600(4)	17.875(4)
β [°]	98.8170(10)	91.27(3)
V [Å^3]	3900.25(16)	2339.7(8)
Z	4	4
T [K]	298(2)	298(2)
λ [Å]	0.71073 (Mo-K_α)	0.71073 (Mo-K_α)
$\rho_{calcd.}$ [g cm^{-3}]	2.261	1.804
μ [mm^{-1}]	9.889	0.837
R [$I > 2\sigma(I)$]	0.0500	0.0282
wR_2 (all data)	0.1438	0.0692

Diffraction data of $[Co(taci)_2](NO_3)_3\cdot 2H_2O$ were collected at 25(2) °C on a Stoe Stadi 4 diffractometer using monochromated Mo-K_α radiation and a crystal of dimensions 0.20 × 0.15 × 0.15 mm. Of a total of 3975 reflections which were collected in the range $2.28° < \theta < 25.00°$, 2066 were unique and 1742 were observed with $I > 2\sigma(I)$. An empirical absorption correction was applied to the data. The structure was solved by direct methods and was refined using full-matrix least-squares calculations on F^2 (259 parameters).[44] All non-hydrogen atoms were refined in the anisotropic mode. The hydrogen atoms (including H_2O) were all located in a difference Fourier map and were refined using variable isotropic displacement parameters. One of the NO_3^- counterions was found to be slightly disordered. Its nitrogen atomic position (N5) was located on a two fold rotational axis and each of the oxygen atoms were equally distributed over two positions. The minimum and maximum in the final residual electron density map were –0.21 and +0.29 e Å^{-3}.

Molecular Modelling: The commercially available program MOMEC97 was used for the calculations.[46,47] Since the structures of the complexes investigated in this paper contain a variety of fragments which were not considered in MOMEC97, additional parameters had to be added to the force field. These parameters were derived from a total of 30 related structures with their geometries obtained from the Cambridge Structural Data Base (see Scheme S1, and Table S1 in the Supporting Information). The required parameters were estimated and systematically varied until the calculated bond lengths could reproduce the experimental values within ± 0.02 Å and the bond angles within ± 5°. This additional data set is listed in Table 4. In the course of geometry optimisation, it became obvious that three of the already supplied parameters (CI–NI bond-stretch, CI–NI–CT valence angle and **–NI–CT–** torsion angle) also had to be adjusted slightly in order to get better consistency during the parametrisation procedure. In all calculations, the N=C–N portion of the amidine moieties was modelled using the atom types NI–CI–NT. The structures were refined using the geometry optimization procedure with the full-matrix Newton Rapson algorithm. Convergence was reached in all calculations. As exemplified in Table 1 for $[Co(HL^a)]^{4+}$, the new parameter set allowed accurate reproduction of the structural parameters.

Table 4. New MOMEC force-field parameters.[a]

Bond-stretch parameters

Atom 1	Atom 2	k_b [mdyn Å^{-1}][b]	r_o [Å]
CO3	NI	1.750	1.870
CO3	OW	3.000	1.900
CI	NT	6.700	1.317
CI	CT	5.000	1.500
CI	NI	7.200	1.290
CT	NI	6.000	1.480
CA	NI	5.940	1.399
NI	H	6.030	0.910

Torsional angle parameters[c]

Atom	Atom	Atom	Atom	k_φ [mdyn Å]	m	φ_{offset} [rad]
**	CA	NI	**	0.0100	6	1.571
**	CI	NT	**	0.0005	6	0.524
**	CI	CT	**	0.0005	6	0.524
**	OR	CT	**	0.0080	3	0.000
**	NI	CI	**	0.0250	2	1.571
**	NI	CT	**	0.0001	2	1.571

Valence-angle parameters

Atom 1	Atom 2	Atom 3	k_θ [mdyn Å rad^{-2}]	θ_0 [rad]
CO3	NI	CT	0.200	1.920
CO3	NI	CI	0.400	2.150
CO3	NT	CI	0.200	1.920
CO3	OW	CT	0.050	1.915
CO3	OW	H	0.100	1.915
OW	CO3	OW	0.040	1.571
OW	CO3	NI	0.150	1.650
NI	CO3	NI	0.050	1.571
NI	CI	NT	0.015	2.094
CT	CI	H	0.450	2.094
CT	OW	H	0.360	1.909
CT	CI	NI	0.450	2.094
CT	CT	OR	0.450	1.909
CA	CA	NI	0.970	2.094
CA	NI	CI	0.490	2.030
CA	NI	H	0.490	2.059
OR	CT	H	0.360	1.909
H	CI	H	0.450	2.094
NI	CI	CT	0.450	2.094
NI	CT	CT	0.450	1.911
NI	CT	H	0.450	1.911
NT	CO3	OW	0.040	1.571
NT	CO3	NI	0.050	1.571
NT	CI	CT	0.450	2.094
NT	CT	CI	0.450	1.911
NT	CI	H	0.450	2.094
NT	CT	OR	0.450	1.911
NT	CT	NI	0.450	1.911
CI	NT	CT	0.450	1.911
CI	NT	CA	0.450	1.911
CI	CT	CT	0.450	1.911
CI	NI	CT	0.970	2.094
CI	NI	H	0.490	2.059
CI	NT	H	0.450	2.050
CI	CT	H	0.360	1.909

[a] For atom-type labels, see ref.[46] [b] 1 dyn = 10^{-5} N. [c] ** = any atom.

Supporting Information (see footnote on the first page of this article): Comments on the parametrisation procedure. Table S1 and Scheme S1: Structures (CCDC) considered for parametrisation. Table S2: Strain energies for the isomers **1**–**3** of $[Co(H_{-2}L^b)]^+$ and $[Co(\kappa^6\text{-}N_6\text{-}L^b)]^{3+}$.

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[14] Systematic names L^a = (1*E*)-*N*-({[*all-cis*-3-amino-2,4,6-trihydroxy-5-(methylamino)cyclohexyl]amino}methyl)-*N′*-(*all-cis*-3,5-diamino-2,4,6-trihydroxycyclohexyl)imidoformamide, L^b = *all-cis*-(2*E*,12*E*)-9,19-bis(methylamino)-2,4,6,12,14,16-hexaazatricyclo[15.3.1.1^{7,11}]docosa-2,12-diene-8,10,18,20,21,22-hexol, L^c = 1,3-diamino-1,3,5-trideoxy-5-(methylamino)-*cis*-inositol, L^d = (1*Z*)-*N′*-(3,5-diamino-2,4,6-trihydroxycyclohexyl)-*N*-phenylimidoformamide, L^e = (1*Z*)-*N′*-(*all-cis*-3,5-diamino-2,4,6-trihydroxycyclohexyl)-2-[*all-cis*-

(3,5-diamino-2,4,6-trihydroxycyclohexyl)amino]ethanimidamide.

[15] The multi-peak signal in the range of $515 \leq m/z \leq 520$ was interpreted in terms of a superposition of $[Co^{III}(H_{-4}L^b)]^+$ (5%), $[Co^{II}(H_{-3}L^b)]^+$ (8%), $[Co^{III}(H_{-2}L^b)]^+$ (19%), $[Co^{II}(H_{-1}L^b)]^+$ (55%) and $[Co^I(L^b)]^+$ (13%). This assignment was established by least-squares calculations R^2 = min, with $R = \Sigma|I_{calc}-I_{obs}|/\Sigma I_{obs} = 0.016$ for all possible isotopomers. The different types of ions postulated for the interpretation of this signal are in line with well established processes observed in a glycerol matrix under FAB conditions, where the bombarding of the matrix with fast atoms results in the generation of organic radicals which can either abstract H_2 from the NH–CH_3 single bond (generation of a corresponding imine) or reduce the central metal cation (generation of Co^{II} and Co^I).[16]

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[29] For $[Co(taci)_2]^{3+}$, the calculated Co–N bond length is 1.97 Å, whereas the value obtained from X-ray diffraction analysis is 1.99 Å.[30] Similarly, the Co–N6 distance in $[Co(HL^a)]^{4+}$ was calculated as 1.97 Å instead of 2.02 Å as observed in the crystal structure (Table 1). The slight underestimation of long Co–N distances might be due to the use of a harmonic potential for the Co^{III}–N bond, see: P. Comba, A. F. Sickmüller, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2006.

[30] The crystal structure of $[Co(taci)_2](NO_3)_3\cdot 2H_2O$ was determined several years ago.[31] Because of the moderate quality of the data, we decided to determine this structure again. Consequently we now possess a data set of significantly higher accuracy. The Co–N bond lengths changed from 1.991(6) Å–2.009(5) Å (mean value: 2.000 Å)[31] to 1.9854(18) Å–2.0057(18) Å (mean value 1.994 Å).

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