Steric Hindrance in Substitution Reactions on Arsenic Acid by Pentaam(m)ine Complexes of Co^{III} and Cr^{III}

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Keywords: Reaction mechanisms / Kinetics / Arsenates / Acid catalysis

The kinetics of the substitution reaction of water by $H_2AsO_4^-$ in $[M(N)_5(H_2O)]^{3+}$ (M = Co^{III}, Cr^{III}) complexes have been studied at 25 °C for a series of $(N)_5$ groups, from monodentate $(NH_3)_5$ and $(CH_3NH_2)_5$ to macrocyclic 12-methyl-1,4,7,10-tetraazacyclotridecane-12-amine (L_{13}), 6-methyl-1,4,8,11-tetraazacyclotetradecane-6-amine (L_{14}), and 10-methyl-1,4,8,12-tetraazacyclopentadecane-10-amine (L_{15}) in their *cis* (L_{13} and L_{14}, Co^{III} and Cr; L_{15}, Co^{III}) and *trans* (L_{15}, Co^{III} and Cr^{III}) water-amino geometrical arrangements around the metal ion. Equilibration rate constants were found to be too large to be interpreted as occurring through the $M{-}OH_2$ bond scission that takes place in standard substitution processes on these t_{2g}^3 and t_{2g}^6 pentaamine complexes, and were also found to be highly dependent on the acidity of the medium. The results are interpreted in view of previously studied, similar reactions, where protonation played a very important role. This role was expected for reactions occurring via As–O bond scission; that is, the data fits well with that expected for oxygen exchange reactions of the labile tetrahedral $\{AsO_4\}$ moiety. The values found are a clear indication of the differences in steric requirements of the metal-bound water attacking the tetrahedral As^V centre [i.e. for M = Co^{III}, $k^+_{\text{non acid catalysed}}$ = 93, 1.9, 0.76, and 0.44 $M^{-1}s^{-1}$ for the $(NH_3)_5$, $(CH_3NH_2)_5$, *cis*-L_{13}, and *trans*-L_{15}, respectively], as well as of electronic influences of the amines of the cobalt complex on the As^V centre when attacked by the bulk water [i.e. for M = Co^{III}, $10^3k^-_{\text{non acid catalysed}}$ = 280, 5.7, 4.4, and 4.5 s^{-1} for the $(NH_3)_5$, $(CH_3NH_2)_5$, *cis*-L_{13}, and *trans*-L_{15} respectively].

Introduction

The kinetics and mechanisms for the substitution reactions on inert Co^{III} and Cr^{III} am(m)ine complexes have been thoroughly studied both from an anation[1] and a hydrolysis[2] approach; all the mechanistic implications have already been described, and only small differences due to fine tuning are still being carried out in view of the importance of their application to other systems.[3] On the other hand, substitution reactions on labile tetrahedral oxoanions are not as well known. Few oxygen exchange studies have been carried out,[4] and very little is known about the formal metal complex substitution reactions as shown in Equation (1).[5]

$$[M(L)_5(H_2O^*)]^{n+} + EO_x^{m-} \rightleftharpoons [M(L)_5(^*OEO_{(x-1)})]^{(n-m)+} + H_2O \quad (1)$$

We have already been involved in the study of this type of reaction with H_3AsO_4 in highly acidic media.[6] These reactions are traditionally avoided[7] because of the important $[H^+]$ acceleration of the reaction rate as well as the small equilibrium displacement in kinetically measurable conditions. In our previous study, a clear $[H^+]$-catalysed path was found, its quantification was achieved, in part, thanks to the ability of Cr^{III} to form fairly stable outer-sphere complexes.[8] More recently, a study on the oxygen exchange on H_3AsO_4 with bulk water in acidic media has also been carried out;[9] an $[H^+]$-catalysed path involving a pentacoordinated As^V species has been tentatively proposed as being responsible for the important acceleration of the interchange. This is in good agreement with our previous findings. The previously undetected reaction of $[Cr(NH_3)_5(H_2O)]^{3+}$ with the $H_3AsO_4/H_2AsO_4^-$ system,[6] has been revised in view of the new instrumentation available that allows us to measure the evolution, with time, of the full spectrum at 0.8 ms intervals, even at relative high concentrations. The results obtained are discussed in view of the complete information obtained in this study.

In this paper we present the kinetic and mechanistic study of the substitution reactions shown in Equation (2).

$$[M(N)_5(H_2O)]^{3+} + H_2AsO_4^-/H_3AsO_4 \rightleftharpoons [M(N)_5(H_2AsO_4)]^{2+} + H_2O/H_3O^+ \quad (2)$$

M = Co^{III} and Cr^{III}, and $(N)_5$ = $(NH_3)_5$, $(CH_3NH_2)_5$, 12-methyl-1,4,7,10-tetraazacyclotridecane-12-amine (L_{13}), 6-methyl-1,4,8,11-tetraazacyclotetradecane-6-amine (L_{14}), and 10-methyl-1,4,8,12-tetraazacyclopentadecane-10-amine (L_{15}) (Scheme 1) in highly acidic media, where all the arsenic oxoanions are present in the form of H_3AsO_4 and $H_2AsO_4^-$. For all the Co^{III} systems, no build-up of outer-sphere encounter complexes was detected, while for some of the Cr^{III} pentaamine complexes limiting kinetics were observed. As a whole, important differences have been found both for the anation and aquation reactions that could be related to the steric demands on the M^{III} centre and the electronic differences of the $(N)_5$ skeleton, as expected for an associatively activated substitution on the tetrahedral As^V centre.

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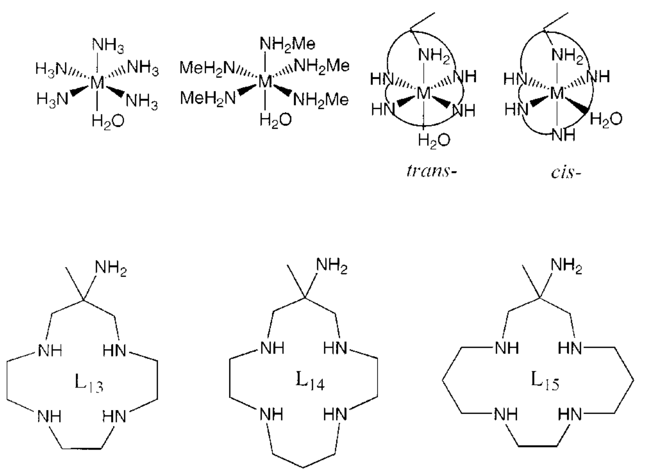


Scheme 1

Results and Discussion

All the values of k_{obs} as a function of the different M metals, $(N)_5$ groups, acidity, and total arsenic acid concentration, $[As]_T$ are collected in the Tables of the Supporting Information. Figure 1 shows some of the plots of k_{obs} versus $[As]_T$, as a function of the acidity, found in this study. No curvature is observed for any of the Co^{III} systems, indicating that there is no build-up of any outer-sphere complex in solution. As in other chromium(III) systems,[6,8] significant curvature of the above-mentioned plots for the $(N)_5$ monodentate systems is obtained, indicating that the amount of outer-sphere complex present in solution is measurable. Finally, for the macrocyclic Cr^{III} anation reactions, again, no build-up of outer-sphere complex is observed. Furthermore, with the exception of Cr^{III}/L_{15} system, an equilibrium of the substitution reaction is observed at this $[H^+]$, with a fairly unfavourable constant for the formation of the arsenato complexes. No second-order dependence on the value of $[As]_T$ has been found for the systems studied, indicating that the involvement of dimeric arsenic species is not present under the conditions used in this study.[4]

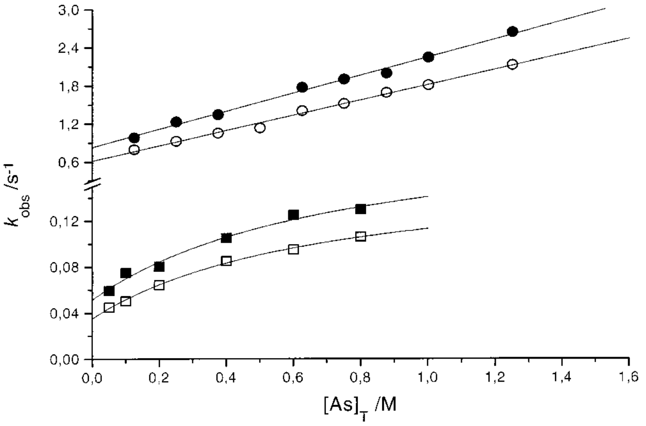
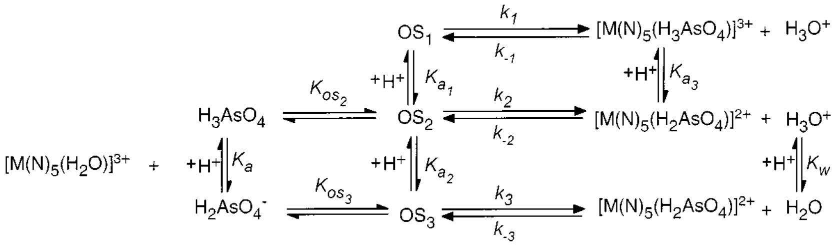


Figure 1. Selected plots of the values of k_{obs} versus $[As]_T$ at different acidities for the anation reaction of some of the complexes (T = 25 °C; $[H^+]$, $HClO_4$; I = 1.0 M, $LiClO_4$); ○: $[Co(NH_3)_5(H_2O)]^{3+}$, $[H^+]$ = 0.125 M; ●: $[Co(NH_3)_5(H_2O)]^{3+}$, $[H^+]$ = 0.175 M; □: $[Cr(MeNH_2)_5(H_2O)]^{3+}$, $[H^+]$ = 0.40 M; ■: $[Cr(MeNH_2)_5(H_2O)]^{3+}$, $[H^+]$ = 0.57 M

It is important to note that, with the exception of the Cr^{III} macrocyclic systems, even at acidities where all the arsenic and arsenato complexes in the reaction medium are present as H_3AsO_4 and $[M(N)_5(H_2AsO_4)]^{2+}$, respectively, an acceleration in the equilibration reaction rate occurs on increasing the values of $[H^+]$. Taking this into account, as well as similar previously published studies,[6] a reaction scheme and a rate law such as those depicted in Scheme 2 and Equation (3) are proposed.

$$
\begin{aligned}
K_{obs} &= \frac{A[As]_T}{[H^+] + K_a + B[As]_T} + C \\
A &= k_1\left(\frac{K_{OS2}}{K_{a1}}\right)[H^+]^2\, k_2K_{OS2}[H^+] + k_3K_aK_{OS3} \qquad (3) \\
\mathrm{B} &= K_aK_{OS3} + K_{OS2}[H^+] + \left(\frac{K_{OS2}}{K_{a1}}\right)[H^+]^2 \\
C &= \left(\frac{k_{-1}}{K_{a3}}\right)[H^+]^2 + k_{-2}[H^+] + k_{-3}
\end{aligned}
$$

Figure 2 and Figure 3 show selected plots of A and C versus $[H^+]$ for some of the systems studied. The values found for the different terms in Equation (3) at 25 °C are collected in Table 1 and Table 2. Given the fact that most of the terms turn out to be composite of rate and equilibrium constants, no attempts to measure activation parameters have been carried out. Unlike the study with $[Cr(H_2O)_6]^{3+}$ under the same conditions (Table 1), where only acid-catalysed, **1**, and protic, **2**, paths were detected,[6] in this study, important differences exist depending on the metal centre and the nature of the $(N)_5$ group of ligands. Only in the case of the Co^{III} complexes was the non-protic path **3** detected, both for anation and hydrolysis reactions, while for all the Cr^{III} and Co^{III} systems rather important contributions to the observed equilibration rate constants are that of the acid-catalysed, **1**, and protic, **2**, paths. In all, the complete set of kinetic rate constants and active reaction paths (Scheme 2) is rather complex, and highly dependent on the nature of the metal centre, the mono- or polydentate nature of the $(N)_5$ skeleton, the size of the macrocycle, and the stereoisomery of the macrocyclic ligand. Nevertheless, in all cases, given the reaction rate constants obtained in this study as well as the available substitution data on analogous $[Co(N)_5Y]^{2/3+}$ and $[Cr(N)_5Y]^{2/3+}$ systems, it is clear that the substitution processes are taking place on the As^V centre as already described for other arsenate substitution reactions.[6][7b,9] Being a tetrahedral p-block element, this process is bound to be associatively activated in character with a transition state involving a direct attack of the M-bound oxygen to the As^V centre. Scheme 3 represents such a postulated transition state, where oxygen atoms labelled with ***i*** and ***ii*** indicate possible protonation sites for reaction paths **1** and **2**, respectively. In any of both cases, the As^V centre attains a lower electron density, allowing for the entrance of the oxygen from the water bound to the cobalt complex for the anation process, or for the entrance of a bulk water molecule for the aquation (reverse) reaction. In this respect,



Scheme 2

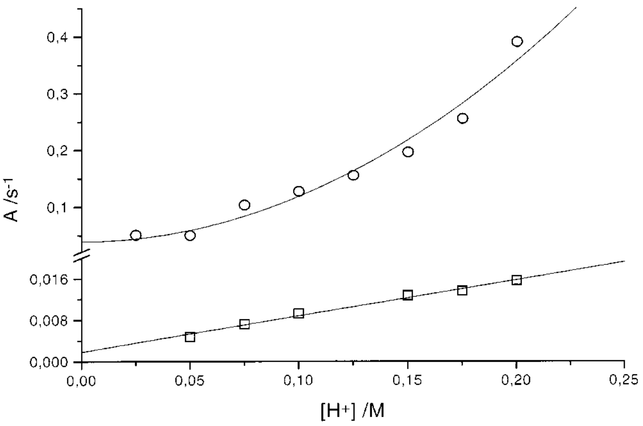


Figure 2. Plot of the values of A [Equation (3)] versus $[H^+]$ for the anation reactions of some of the complexes studied (T = 25 °C; $[H^+]$, $HClO_4$; I = 1.0 M, $LiClO_4$); ○: $[Co(NH_3)_5(H_2O)]^{3+}$; □: *trans*-$[CoL_{15}(H_2O)]^{3+}$

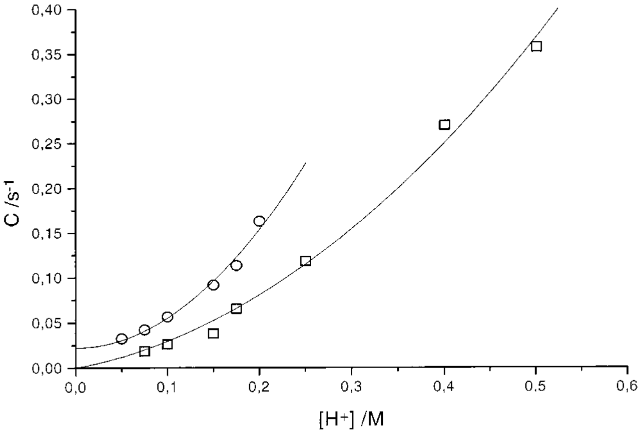
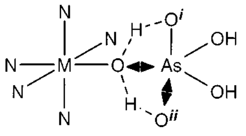


Figure 3. Plot of the values of C [Equation (3)] versus $[H^+]$ for the anation reactions of some of the complexes studied (T = 25 °C; $[H^+]$, $HClO_4$; I = 1.0 M $LiClO_4$); ○: *cis*-$[CoL_{15}(H_2O)]^{3+}$; □: $[Cr(NH_3)_5(H_2O)]^{3+}$

apart from obvious steric and electronic reasons affecting the magnitude of the reaction rate, the fact that some of the reaction pathways are selectively detected for some of the systems has to be looked into very carefully. Finally, the magnitude of the intrinsic errors involved due to the complex dependence of the equilibration rate constants on the acidity [Equation (2)], makes even small differences in the values very unreliable; factors of less than ca. two have to be taken with great caution specially when referring to paths **1** and **3**.



Scheme 3

Data in Table 1 indicates a clear-cut difference between chromium monodentate and macrocyclic systems. That is, while the observation of active forward path **2** and reverse path **3** in any of the substitutions studied at this $[H^+]$ is perfectly attributable to the major species existing in solution, namely H_3AsO_4 (90–98% of the total added arsenate at this $[H^+]$)[6] and *cis*-$[CrL_{13}(H_2AsO_4)]^{2+}$ (predominant at this pH, given the increase in acidity of coordinated ligands).[10] The observation of forward and reverse paths **1** and reverse path **2** seems to be a specific characteristic of monodentate pentaam(m)ine aqua complexes for these Cr^{III} derivatives {as for the already studied $[Cr(H_2O)_6]^{3+}$}.[6] In all, for the macrocyclic complexes, the active reaction paths are directly related to those involving the predominant species in solution at this pH range. Comparison of the monodentate pentaam(m)ine aqua systems clearly indicates, for the forward reaction, that the steric bulk of the entering chromium complex plays a very important role; a rate decrease of nearly one order of magnitude is observed on go-

Table 1. Values for the different rate terms in Equation (3) for the anation reactions of complexes $[Cr(N)_5(H_2O)]^{3+}$ as a function of the $(N)_5$ group (T = 25 °C; $[H^+]$ = 0.05–0.2 M $HClO_4$; I = 1.0 M $LiClO_4$); $[Cr(H_2O)_6]^{3+}$ data from ref.[6] are included for comparative purposes

$(N)_5$	Path **1**			Path **2**		Path **3**	
	$k_1(K_{OS2}/K_{a1})$ /s^{-1}	K_{OS2}/K_{a1}	k_{-1}/K_{a3} /M s^{-1}	k_2K_{OS2} /M^{-1}s^{-1}	k_{-2} /s^{-1}	k_3K_{OS3} /M^{-1}s^{-1}	k_{-3} /s^{-1}
$(NH_3)_5$	$(7.3\pm1.0)\times10^{-1}$	4.9 ± 0.1	1.0 ± 0.1	$(7.5\pm0.4)+10^{-1}$	$(2.1\pm0.6)\times10^{-1}$	---	---
$(CH_3NH_2)_5$	$(1.3\pm0.2)\times10^{-1}$	2.6 ± 0.3	$(3.8\pm0.4)\times10^{-2}$	$(1.4\pm0.4)\times10^{-1}$	$(6.3\pm1.0)\times10^{-2}$	---	---
cis-L_{13}	---	---	---	$(1.1\pm0.3)\times10^{-1}$	---	---	$(1.3\pm0.2)\times10^{-1}$
trans-L_{15}	---	---	---	$(3.8\pm0.2)\times10^{-1}$	---	---	---
$(H_2O)_5$	2.3 ± 0.6	2.8 ± 0.5	$(9.6\pm2.1)\times10^{-1}$	1.1 ± 0.4	$(5.1\pm1.3)\times10^{-1}$	---	---

ing from ammine to methylamine. The electronic effect created for the more basic CH_3NH_2 ligands seems to be counterbalanced by the steric demands created on the substitution process; in this respect, the value found for K_{OS2}/K_{a1} agrees quite well with the latter assumption. A comparison of these monodentate $(N)_5$ systems with the hexaaquachromium(III) substitution studied, indicates that steric reasons have to be held responsible for the small differences in reactivity; the weaker Lewis acid character of the aqua ligand would point to the inverse of the observed effect.[11] When we move to the *cis*-L_{13} and *trans*-L_{15} $Cr^{III}/(N)_5$ systems, the most striking feature is the immediate disappearance of the acid catalysed path **1**, both for forward and reverse reactions. The values determined for k_2K_{OS2} for these two macrocyclic systems agree with the slight better steric availability of the chromium(III)-bound oxygen atom for the *trans*-L_{15} macrocyclic complex (see Scheme 1); electronic differences being at a minimum between the two macrocyclic complexes. On the one hand, it seems that the existence of a macrocyclic (including hydrogen bonding) wrapping of the Cr^{III} metal does not allow for protonation of the $[CrL_n(H_2AsO_4)]^{2+}$ final complex (Scheme 2). On the other hand, for OS_1 and OS_2, it is clear that we are not dealing with simple ion-pairing,[12] the existence of such aggregates with octahedral d^3 complexes showing larger stability constants than their d^6 analogues is a generally accepted fact.[8] Steric reasons that produce shorter $Cr–OH_2$ bond lengths for the macrocyclic systems, in spite of their shorter Cr–N bond lengths,[13] can be held responsible of a rather close approach of the arsenic acid species to the chromium-bound water oxygen. The presence of nitrogen-bound hydrogen atoms in the macrocycle are bound to produce hydrogen bonding with the available oxo groups in the H_3AsO_4 within the outer-sphere complex, deactivating protonation reaction K_{a1}. Finally, for the remarkable stability of the *trans*-$[CrL_{15}(H_2AsO_4)]^{2+}$ complex, the special capping geometry of the macrocycle (Scheme 1), with the possibility of hydrogen atoms directed to the oxo groups of the arsenate ligand, probably add up to an important increase in the stability of the complex when compared with *cis* arrangements.

With reference to cobalt data in Table 2, although monodentate and macrocyclic pentaam(m)ine complexes are still differentiable, striking differences are observed with the general trends obtained for the analogous Cr^{III} complexes, shown in Table 1. Paths **1** and **3** are operative for all the $[Co(N)_5H_2O]^{3+}/H_2AsO_4^-$ substitution processes, while path **2** is only detected for forward reactions with the macrocyclic complexes. The reactivity cannot be associated, in this case, to the dominant species in solution at this acidity (see above).

Monodentate systems have the most homogeneous reactivity pattern, as with their Cr^{III} analogues. For the equilibrium reactions, both for the acid-catalysed and the non-protic paths, the steric effect of the increased size of the Co^{III} complex is clear, the difference between $(N)_5 = (NH_3)_5$ and $(MeNH_2)_5$ rate constants being even larger than with the Cr^{III} complexes. The usual differences in M–L bond lengths for cobalt and chromium pentaamine complexes can be held responsible for the enhanced hindrance of the Co^{III} systems.[13] The preference for path **3** versus path **2** for the cobalt complexes has to be considered much more carefully. For the reverse reaction, the attack of a protonated water molecule on an As^V centre would be much less favoured for the electronically richer t_{2g}^6 Co^{III} complexes; in fact, acidity of coordinated water is higher for the $[Cr(NH_5)_5H_2O]^{3+}$ than for the $[Co(NH_5)_5H_2O]^{3+}$ complexes.[10][11a] Consequently, while attack of H_3O^+ on the tetrahedral As^V is only possible once protonation has taken place (path **1**), its attack on the non-protonated arsenato complex (path **2**) is suppressed. For the forward reactivity, the rationalisation is not so straightforward; a plausible explanation involves the (possibly complex) hydrogen bonded nature of the postulated transition state depicted in Scheme 3. Given the less positive character of the hydrogen atoms from the cobalt-bound water, the proton-receiving oxygen atoms bound to the arsenic centre must be very sensitive to the existing degree of protonation. That is, while the presence of two protons attached to oxygen atoms ***i*** and ***ii*** in Scheme 3 accelerates the reaction by enhancement of the good leaving character of one of them, the attachment of only one of such proton is not enough. Furthermore, in the latter situation,

Table 2. Values for the different rate terms in Equation (2) for the anation reactions of complexes $[Co(N)_5(H_2O)]^{3+}$ as a function of the $(N)_5$ group {T = 25 °C; $[H^+]$ = 0.05–0.2 M ($HClO_4$); I = 1.0 M $LiClO_4$}

$(N)_5$	Path **1**		Path **2**		Path **3**	
	$k_1(K_{OS2}/K_{a1})$ /s^{-1}	k_{-1}/K_{a3} /M s^{-1}	k_2K_{OS2} /M^{-1}s^{-1}	k_{-2} /s^{-1}	k_3K_{OS3} /M^{-1}s^{-1}	k_{-3} /s^{-1}
$(NH_3)_5$	8.0±0.6	(2.1±1.4)×10	---	---	(9.3±3.0)×10	(2.8±0.3)×10^{-1}
$(CH_3NH_2)_5$	1.6±0.2	1.5±0.1	---	---	1.9±0.9	(5.7±3.3)×10^{-3}
cis-L_{13}	---	(9.5±1.2)×10^{-1}	(1.3±0.1)×10^{-1}	---	(7.6±2.9)×10^{-1}	(4.4±2.7)×10^{-3}
cis-L_{14}	---	(1.3±0.1)×10^{-1}	(1.4±0.1)×10^{-1}	---	---	(6.4±2.5)×10^{-3}
cis-L_{15}	---	3.3±0.2	1.1±0.1	---	---	(2.2±0.5)×10^{-2}
trans-L_{15}	---	(4.2±0.5)×10^{-1}	(6.9±0.4)×10^{-2}	---	(4.4±0.2)×10^{-1}	(4.5±1.1)×10^{-3}

the depicted hydrogen bonding between metal-bound water and arsenate is not enough for good attack of the cobalt-bound oxygen atom on the As^V centre, only the loss of the last proton restores the reaction rate by a best hydrogen bonding interaction in the transition state.

With respect to the macrocyclic systems the situation is dramatically different. While reverse paths are the same as those found for the monodentate systems, forward path **1** is never observed, and the forward reactivity of path **3** is now shared with that from path **2**. The reasoning mentioned for the reactivity for the aquation reactions through path **1** and **3** remains valid; nevertheless, the value of the rate constants determined for the *cis*-$[CoL_{15}H_2AsO_4]^{2+}$ complex is surprisingly high. We can speculate about the fact that the increased size of the macrocycle, with shorter Co–N bond lengths than in the Cr^{III} analogues,[14] can produce a "back-folded" geometry of the macrocycle when a rather large $\{AsO_4\}$ tetrahedral centre is attached. Furthermore, this has to be more possible for Co^{III}, given the richer electron density of the complex that does not favour hydrogen bonding between amine protons and arsenic-bound oxygen atoms. This is contrarily to what has been said for the chromium derivatives. As for the forward reaction paths, the change in reactivity from path **1** to path **2** has to be related to the preferential nature of the interaction in the outer-sphere complex OS_2 that does not allow for reactive protonation. Thus, protonation of the OS_2 complex is prevented, even when hydrogen bonding should be less important than for the Cr^{III} analogues.[10] The value found for k_2K_{OS2} for the largest *cis*-L_{15} metal complex is definitively larger, again suggesting the possibility of a certain degree of "back-folded" effect in the preferential outer-sphere interaction,[12] producing a much more efficient attack on the As^V centre. With respect to the forward path **3**, the rate constant values for the *cis*-L_{13} and *trans*-L_{15} are rather important. At the moment we are not able to understand this fact, nevertheless the two systems for which k_3K_{OS3} have a definite value are those which are bound to be the less sterically demanding by themselves, and their forward rate constants are larger than those for the protic path, **2**.

Conclusions

The study carried out on the formal substitution reactions on pentaam(m)ine Cr^{III} and Co^{III} shows the "oppressive" array of terms typical for substitution processes taking place on tetrahedral As^V species, where the importance of protonation is evident. For the monodentate metal complexes studied, an acid catalysed path is always present, which enhances the reaction rate by the formation of a good protonated leaving group. The operation of a path with fully protonated species is only found for the chromium complexes, where fewer electrons present in the systems allows even the entrance of weak Lewis bases, as fully protonated species are, without the assistance of a good leaving group. With reference to the macrocyclic systems studied, although the same reasoning can be used for some of the reactivity, an increased influence of the steric effects are evident. In this case, not only size, but hydrogen bonding and differences in Cr^{III} and Co^{III} bond lengths, seem to be responsible for the trends observed. In all, the reactivity has proven to be extremely complex, with many factors to be accounted for. Substitution processes on p-block elements have been traditionally avoided; therefore, further studies in this field have to be carried out in order to have a good overview of the processes taking place in their reactions.

Experimental Section

Materials: $[Co(NH_3)_5(H_2O)](ClO_4)_3$, $[Cr(NH_3)_5(H_2O)](ClO_4)_3$, $[Co(CH_3NH_2)_5(H_2O)](ClO_4)_3$, $[Cr(CH_3NH_2)_5(H_2O)](ClO_4)_3$, *cis*-$[CoL_{13}(H_2O)](ClO_4)_3$, *cis*-$[CoL_{14}(H_2O)](ClO_4)_3$, *cis*-$[CoL_{15}(H_2O)](ClO_4)_3$, *trans*-$[CoL_{15}(H_2O)](ClO_4)_3$, $[Co(NH_3)_5(H_2AsO_4)](H_2AsO_4)_2$, and $[Cr(NH_3)_5(H_2AsO_4)](ClO_4)_2$ were prepared as described in the literature.[7b,12,15] $LiClO_4$ was prepared from Li_2CO_3 and recrystallized three times before use. Arsenic acid was prepared by nitric acid oxidation of As_2O_3;[16] commercially available Aldrich As_2O_5 was too impure to be used (a solution of commercial Aldrich As_2O_5 was found to produce a brown precipitate that was very difficult to eliminate, making all kinetic runs impossible).

cis-$[CrL_{13}(H_2O)](CF_3SO_3)_3$ and *trans*-$[CrL_{15}(H_2O)](ClO_4)_3$ were prepared in a similar manner to their cobalt analogues from the corresponding $[CrL_nCl](ClO_4)_2$ precursors.[15] In these cases, the base hydrolyses were carried out at pH = 9–10, and once acidified with perchloric or triflic acid, the stoichiometric amount of $AgClO_4$ was added to remove all existing chlorides in the reaction medium. On standing, the complexes are collected as orange-red solids. Occasionally, the isolated complexes were contaminated with $NaClO_4$, their recrystallisation from diluted $HClO_4$ produced analytically pure samples. The aqua complexes were characterised by their elemental analyses and UV/Vis spectra in 0.1 M $HClO_4$. – Analyses (calcd./found): *cis*-$[CrL_{13}(H_2O)](CF_3SO_3)_3 \cdot 3.5\ H_2O$: C 19.6/19.2, N 8.8/9.0; *trans*-$[CrL_{15}(H_2O)](ClO_4)_3 \cdot 2\ H_2O$: C 22.3/22.4, N 10.8/10.5. – UV/Vis (λ/nm, $\varepsilon/M^{-1}cm^{-1}$): *cis*-$[CrL_{13}(H_2O)](CF_3SO_3)_3 \cdot 3.5\ H_2O$: 486 (137), 362 (79) and *trans*-$[CrL_{15}(H_2O)](ClO_4)_3 \cdot 2\ H_2O$: 486 (61), 450 (sh), 356 (81).

cis-$[CoL_{13}(H_2AsO_4)](ClO_4)_2$, *trans*-$[CoL_{15}(H_2AsO_4)](ClO_4)_2 \cdot H_2O$, and *trans*-$[CrL_{15}(H_2AsO_4)](H_2AsO_4)_2$ were prepared as their pentaammine analogues.[17] The aqua complexes were dissolved in 3–4 M H_3AsO_4, the cherry red solution formed immediately was concentrated to a syrupy consistency. Addition of ethanol produced a red solid on standing at –30 °C. The complexes were characterised by their elemental analyses and UV/Vis spectra in solid (to avoid the fast aquation reaction) or in 2 M H_3AsO_4. – Analyses (calcd./found): *cis*-$[CoL_{13}(H_2AsO_4)](ClO_4)_2$: C 19.6/19.0, N 11.4/11.7; *cis*-$[CoL_{15}(H_2AsO_4)](ClO_4)_2 \cdot H_2O$: C 21.8/21.8, N 10.6/10.8; *trans*-$[CrL_{15}(H_2AsO_4)](H_2AsO_4)_2$: C 20.1/19.9, N 9.8/9.5. – UV/Vis in solid (λ/nm): *trans*-$[CoL_{15}(H_2AsO_4)](ClO_4)_2 \cdot H_2O$: 507; *trans*-$[CrL_{15}(H_2AsO_4)](H_2AsO_4)_2$: 509, 368. – UV/Vis in 2 M H_3AsO_4 (λ/nm, $\varepsilon/M^{-1}cm^{-1}$): *cis*-$[CoL_{13}(H_2AsO_4)](ClO_4)_2$: 500 (sh), 454 (145), 346 (132); *cis*-$[CoL_{15}(H_2AsO_4)](ClO_4)_2 \cdot H_2O$: 528 (100), 354 (139); *trans*-$[CrL_{15}(H_2AsO_4)](H_2AsO_4)_2$: 514 (73), 372 (100).

All UV/Vis spectra were recorded with an HP8452A instrument. The spectra of the final $[M(N)_5(H_2AsO_4)]^{2+}$ complexes were determined, as done[17] for the similar $[Cr(NH_3)_5(H_2AsO_4)]^{2+}$ by solution of the corresponding aqua complexes in 2 M H_3AsO_4 (the known spectra of the characterised arsenato derivatives were used as a reference of the validity of the method).

Kinetics: The general kinetic technique has already been described.[6] All kinetic measurements were performed under pseudo-first-order conditions, with the total concentration of arsenic acid in excess over the cobalt complex. Typical M^{III} complex concentrations were within the $1–5\cdot10^{-3}$ M range. Solutions for the kinetic runs were made up from the corresponding stock solutions of $HClO_4$, metal complex, H_3AsO_4, and $LiClO_4$. Runs were carried out in a Durrum D-110 stopped-flow instrument at the desired wavelength, determined from the differences between initial and final products. Alternatively, the instrument was connected to a J&M Tidas instrument and the complete spectra were recorded and analysed; this technique allowed us to revise the anation reaction of the $[Cr(NH_3)_5(H_2O)]^{3+}$ complex, obtaining reasonable results. All the k_{obs} values were derived from the obtained absorbance versus time exponential traces using a nonlinear least-squares fitting method. All post run data fitting were done by unweighted least-squares fit to the desired equations.

Acknowledgments

Financial support from the CIRIT of the Generalitat de Catalunya (to E. R.) and the Ministerio de Educación y Cultura is gratefully acknowledged.

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Received July 7, 1999
[I99246]