Thermodynamic and Kinetic Studies on Complex-Formation Reactions of a Cobalt(II) Tripodal Tetraamine Complex

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Complex-formation constants were determined for the reaction of $[Co(Me_6tren)(H_2O)]^{2+}$ with different pyridine- and imidazole-based nucleophiles, and the kinetics of these reactions was studied as a function of entering ligand concentration, temperature, and pressure. The steric hindrance associated with the methyl substituents on the trigonal-bipyramidal complex induces a sensitive control over the substitution mechanism from dissociative for the weaker and more bulky entering nucleophiles, to associative for the stronger and less bulky nucleophiles. A changeover in mechanism can be observed as a function of nucleophile concentration, in the case of 2-MeImH as the entering ligand. The mechanistic assignments are based on the observed rate laws, and the activation parameters determined under limiting concentration conditions.

Introduction

The thermodynamics and kinetics of complex-formation and ligand-substitution reactions of octahedral transition metal complexes have been studied in much detail by many groups, and a number of reviews have appeared on this topic, of which a few typical examples are referenced.[1a−1d] In contrast, the formation, stability, and mechanistic behaviour of five-coordinate square-pyramidal or trigonal-bipyramidal first-row transition metal complexes have received significantly less attention.[2] Such five-coordinate complexes can exhibit significantly different ligand substitution behaviour since they are, in principle, able to coordinate an additional nucleophile in the transition state. In contrast, six-coordinate complexes usually undergo dissociative ligand substitution reactions. Thus, the study of their behaviour is of fundamental importance to the understanding of complex-formation and ligand-substitution reactions in general.

By way of a typical example, the introduction of a tripodal tetraamine ligand such as tren [tris(2-aminoethyl)amine] into the coordination sphere of copper(II) leads to the formation of a trigonal-bipyramidal complex, $[Cu(tren)(H_2O)]^{2+}$. This complex exhibits significantly slower water-exchange and complex-formation reactions than the parent $[Cu(H_2O)_6]^{2+}$ ion due to the absence of Jahn−Teller distortion.[3,4] Not only are the reactions much slower, their mechanism has also changed from the I_d to the I_a type as clearly indicated by the significantly different volumes of activation reported for these reactions.[3,4] Furthermore, the mechanistic behaviour of these complexes can be systematically tuned by the introduction of steric hindrance on the tripodal ligand, viz. tren, trimethylated (Me_3tren, i.e. one methylation per primary amine group of tren) and hexamethylated tren (Me_6tren, i.e. fully methylated primary amine groups).[5] The substitution reactions of $[Cu(Me_3tren)(H_2O)]^{2+}$ are more than two orders of magnitude slower than those of $[Cu(tren)(H_2O)]^{2+}$, but still follow an I_a mechanism. However, in the case of the $[Cu(Me_6tren)(H_2O)]^{2+}$ complex, a further decrease in the substitution rate and a changeover back to a dissociative reaction mechanism is observed. Only at high entering nucleophile concentrations, could evidence for a parallel associative reaction path be observed.[5] The introduction of steric hindrance on the tripodal tetraamine chelate controls the substitution behaviour of these complexes, and the extension of the chelate rings from ethyl to propyl causes a geometric changeover from trigonal-bipyramidal to square-pyramidal which is accompanied by a change in lability.[6]

Based on this experience, we have begun a study on the corresponding behaviour of cobalt(II) complexes. Our interest lies in the activation of dioxygen reported for the $[Co(tren)(H_2O)]^{2+}$ complex [7] and the details of the underlying reaction mechanism, which can then be compared with that previously found for an octahedral cobalt(II) complex.[8] However, since the activation of dioxygen in general involves the combination of ligand substitution and subsequent redox processes, it is at first essential to understand the ligand substitution behaviour of these systems. Due to the extreme oxygen sensitivity of the $[Co(tren)(H_2O)]^{2+}$ complex,[7] we first turned to the almost oxygen-insensitive $[Co(Me_6tren)(H_2O)]^{2+}$ complex and studied its complex-formation reactions in more detail. The

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results of this study show that the ligand-substitution mechanism can be controlled by the concentration and nucleophilicity of the entering ligand.

Results and Discussion

Determination of Complex-Formation Constants

The stability constant (log *K*) of the cobalt(II) complex with the chelate Me$_6$tren is 8.53, which is smaller than that of the corresponding copper(II) complex (viz. 15.65), and the pK_a of the corresponding aqua complex, $[Co(Me_6tren)(H_2O)]^{2+}$, is 8.6.[9]

The complex-formation constants for substitution of water on $[Co(Me_6tren)(H_2O)]^{2+}$ by pyridine, 4-methylpyridine, and imidazole were determined in the following manner. The complex concentration was kept constant at $3.4 \cdot 10^{-3}$ M and different concentrations of the ligands L were added.

$$[Co(Me_6tren)(H_2O)]^{2+} + L \rightleftharpoons [Co(Me_6tren)(L)]^{2+} + H_2O \quad K$$

On increasing the ligand concentration, the characteristic peak at 470 nm is incrementally reduced and almost disappears completely at high ligand concentrations. A typical example of the spectral changes observed for the substitution reaction with ImH is shown in Figure 1. The spectra in general show clean isosbestic points at low entering nucleophile concentrations, but a shift in isosbestic points occur at high added nucleophile concentrations. In the case of the reaction with ImH this effect is not very strong, but in the case of the reaction with 4-Mepy the deviations in isosbestic points are very significant. This indicates that different substitution products, in which the Me$_6$tren ligand is displaced in a stepwise manner by the entering nucleophile, can be formed depending on the concentration and nature of the added nucleophile. In fact it was possible to isolate and characterise $[Co(L)_4(H_2O)_2](ClO_4)_2$ (L = 4-MePy) and $[Co(L)_6](ClO_4)_2$ (L = ImH) as reaction products at high concentrations of 4-Mepy and ImH (see Experimental Section). From the molar conductivity measurements it is clear that the two isolated complexes are 2:1 electrolytes. The plot of absorbance at 470 nm versus ligand concentration for the reaction with ImH is shown in Figure 2. The latter data were used to estimate the complex-formation constant (*K*) in the usual manner.[10] Plots of log{($A_x - A_i$)/($A_\infty - A_x$)} versus log[nucleophile] showed a linear dependence with unity slope at low nucleophile concentrations, but deviations occurred at higher concentrations due to the formation of 1:2 and higher substituted complexes.

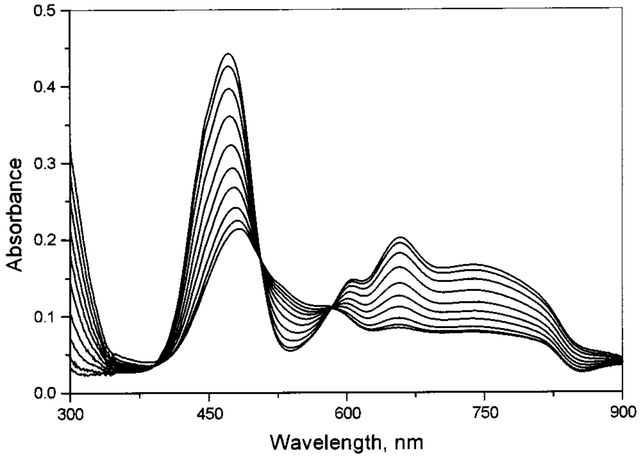


Figure 1. Absorption spectra for the complex formation between $[Co(Me_6tren)(H_2O)]^{2+}$ and ImH ([ImH] from 0.0 to 0.18 M) at 25.0 °C, pH = 7.92 ± 0.02, I = 0.2 M, 0.05 M Tris buffer, $[Co^{II}] = 3.21 \cdot 10^{-3}$ M

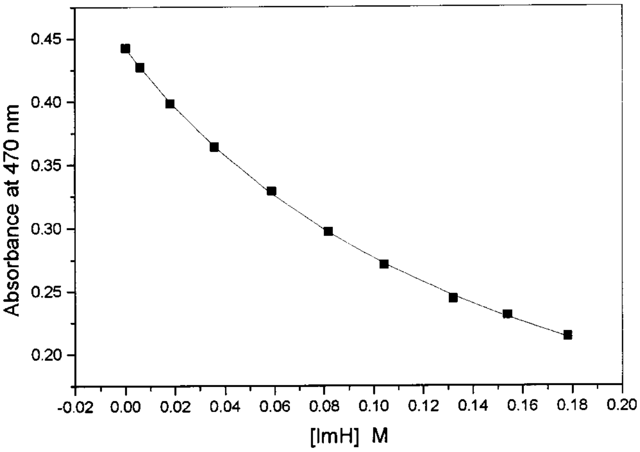


Figure 2. Absorbance at 470 nm versus concentration of ImH for the reaction of $[Co(Me_6tren)(H_2O)]^{2+}$ with ImH at 25.0 °C, pH = 7.92 ± 0.02, I = 1.0 M, 0.05 M Tris buffer, $[Co^{II}] = 3.21 \cdot 10^{-3}$ M

The 1:1 complex-formation constants for pyridine (py), 4-methylpyridine (4-Mepy), and imidazole (ImH) were found to be 1.0 ± 0.3 , 1.8 ± 0.4, and 7.4 ± 1.8 M^{-1} at 25 °C, respectively. A plot of the complex-formation constants (log *K*) versus the pK_a values of the ligands is shown in Figure 3. It can be seen that log *K* increases linearly with increasing pK_a, which is consistent with that expected in terms of the basicity of the entering nucleophiles. Such linear correlations between log *K* and pK_a have also been reported in the literature.[11]

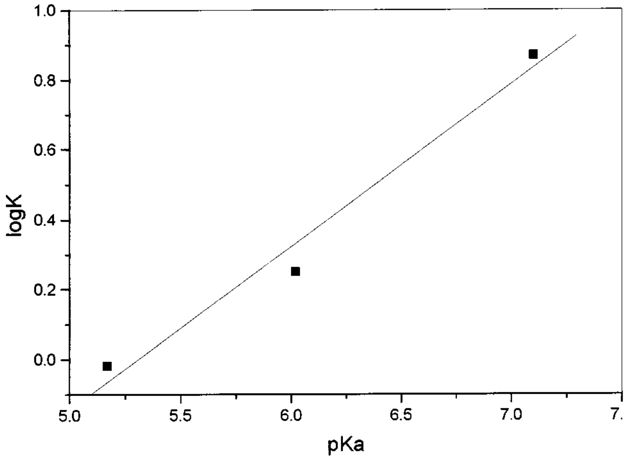


Figure 3. Plot of log *K* (from thermodynamic method) versus pK_a of the ligands for the reaction between $[Co(Me_6tren)(H_2O)]^{2+}$ and Py, 4-MePy, and ImH

A comparison of the K value for the formation of the pyridine complex, viz. 1.0 ± 0.3 M^{-1}, with that for the corresponding $[\mathrm{Cu(Me_6tren)(H_2O)}]^{2+}$ complex, viz. 6.6 ± 0.3 M^{-1},[5] indicates that the copper(II) complex is more stable. This is in agreement with the higher stability constant (log K) reported for $[\mathrm{Cu(Me_6tren)(H_2O)}]^{2+}$ as compared with that for $[\mathrm{Co(Me_6tren)(H_2O)}]^{2+}$, viz. 15.65 and 8.53, respectively.[9]

Kinetic Analysis

Preliminary Observations

Preliminary kinetic experiments for the reaction of $[\mathrm{Co(Me_6tren)(H_2O)^{2+}}]$ with the selected organic bases at a pH < 7.9, revealed kinetic traces in the absence of an added nucleophile as a result of the dilution of the complex solution in the stopped-flow instrument. This effect could be correlated with the dissociation of the complex on dilution. For this reason all kinetic measurements were performed at pH = 7.9 where this effect is negligible. Under this condition a small fraction of the complex exists in the inert hydroxo form due to the pK_a value of 8.6. Further experiments demonstrated that the observed pseudo first-order rate constants measured in the presence of an excess of the nucleophile also depended on the concentration of the cobalt(II) complex; the effect being much stronger at lower pH due to the partial dissociation of the complex under such conditions. All kinetic measurements were therefore performed at a fixed cobalt(II) concentration and a pH of 7.9.

Reactions of Pyridine and 4-Methylpyridine with $[\mathrm{Co(Me_6tren)(H_2O)}]^{2+}$

The reactions of pyridine and 4-methylpyridine with $[\mathrm{Co(Me_6tren)(H_2O)}]^{2+}$ are very similar. Kinetic measurements on the reaction were performed using total ligand concentrations in the range of 0.05−1.5 M at a pH = 7.92 and ionic strength of 1.0 M ($\mathrm{NaClO_4}$), and thus always at least in 10-fold excess of the $[\mathrm{Co(Me_6tren)(H_2O)}]^{2+}$ concentration. When k_{obs} is plotted versus the entering ligand concentration, k_{obs} decreases with increasing ligand concentration over the whole ligand concentration range (see Figure 4 and Figure 5). This is very characteristic for a dissociative mechanism involving an efficient back reaction. A similar nucleophile concentration dependence has been reported for several reversible dissociative ligand substitution reactions in the literature.[12a−12e] However, it should be noted that the observed trends differ significantly from that observed for the substitution reaction of $[\mathrm{Cu(Me_6tren)(H_2O)}]^{2+}$ with pyridine [4] (see further Discussion).

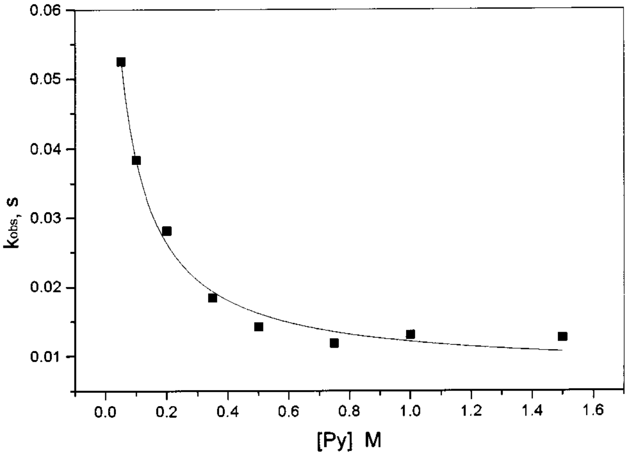


Figure 4. Kinetic data for the reaction of $[\mathrm{Co(Me_6tren)(H_2O)}]^{2+}$ with pyridine at 25°C, pH = 7.92 ± 0.02, I = 1.0 M, 0.05 M Tris buffer, $[\mathrm{Co^{II}}] = 3.61\cdot10^{-3}$ M

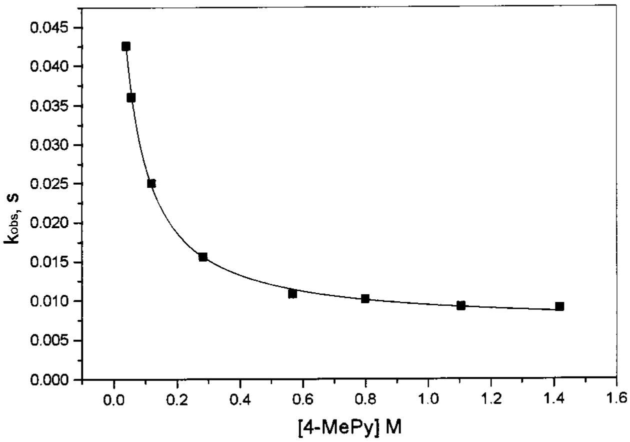


Figure 5. Kinetic data for the reaction of $[\mathrm{Co(Me_6tren)(H_2O)}]^{2+}$ with 4-MePy at 25.0 °C, pH = 7.92 ± 0.02, I = 1.0 M, 0.05 M Tris buffer, $[\mathrm{Co^{II}}] = 3.2\cdot10^{-3}$ M

On the basis of the observed kinetics, we propose the following reversible two-step mechanism [Equation (1) and Equation (2)].

$$[\mathrm{Co(Me_6tren)(H_2O)}]^{2+} \rightleftharpoons [\mathrm{Co(Me_6tren)}]^{2+} + \mathrm{H_2O} \quad k_1, k_{-1} \tag{1}$$

$$[\mathrm{Co(Me_6tren)}]^{2+} + \mathrm{L} \rightleftharpoons [\mathrm{Co(Me_6tren)(L)}]^{2+} \quad k_2, k_{-2} \tag{2}$$

(L = Py and 4-MePy) The rate law for this mechanism can be expressed as shown in Equation (3).

$$k_{\mathrm{obs}} = (k_1k_2[\mathrm{L}] + k_{-1}k_{-2})/(k_{-1} + k_2[\mathrm{L}]) \tag{3}$$

A non-linear least-squares fit of the data according to Equation (3) reveals that k_1 = 0.0076 ± 0.0025 s^{-1}, k_{-2} = 0.094 ± 0.015 s^{-1}, and k_2/k_{-1} = 18 ± 6 M^{-1} for pyridine, and those for 4-methylpyridine are k_1 = 0.0066 ± 0.0009 s^{-1}, k_{-2} = 0.077± 0.004 s^{-1}, and k_2/k_{-1} = 24 ± 2 M^{-1} at 25 °C. Thus the complex-formation constant K (= $k_1k_2/k_{-1}k_{-2}$) from the kinetic data for the reaction with pyridine is 1.5 ± 0.7 M^{-1} and that for 4-methylpyridine is 2.1 ± 0.3 M^{-1}, whereas the formation constant from the thermodynamic measurements are 1.0 ± 0.3 and 1.8 ± 0.4 M^{-1}, respectively. It follows that the data from the two independent methods are similar within the experimental error limits.

The temperature dependence of the substitution reactions of $[Co(Me_6tren)(H_2O)]^{2+}$ with pyridine and 4-methylpyridine was studied under limiting conditions at pyridine and 4-methylpyridine concentrations of 1.0 and 1.105 M, respectively, i.e. where k_{obs} reaches a minimum and $k_{obs} \approx k_1$. The results are summarised in Table 1, from which it follows that the activation enthalpy and activation entropy are 74 ± 4 kJ mol^{-1} and −35 ± 12 J K^{-1} mol^{-1} for the reaction with pyridine, and 71 ± 2 kJ mol^{-1} and −47 ± 5 J K^{-1} mol^{-1}, respectively, for substitution by 4-methylpyridine. Both the activation entropies are negative and are not in line with the concept of a limiting dissociative mechanism as suggested by the observed rate law. This is not unusual since activation entropies are inherently subjected to large error limits as a result of the way in which they are determined, viz. by extrapolation of rate constants measured over a limited temperature range to $1/T = 0$. For this reason the effect of pressure on the reaction with 4-methylpyridine was studied under similar experimental conditions. It was, however, difficult to obtain accurate data due to turbidity problems that occurred during mixing in the high-pressure stopped-flow system (see Experimental Section). For this reason the ionic strength of the solutions was decreased to almost zero and the temperature was raised to 45.0 ± 0.1 °C, which significantly improved the quality of the data. The results indicate that the observed rate constant (practically k_1) decreases with increasing pressure. The average activation volume calculated from the slope of ln(k) versus pressure ($= -\Delta V^{\neq}/RT$) for four series of measurements is +15 ± 7 cm^3 mol^{-1}. The large error limits is a result of the unfavourable time scale of the reaction and the small absorbance change associated with the reaction under these conditions. The value in principle supports the operation of a dissociative mechanism.

Reaction of Imidazole with $[Co(Me_6tren)(H_2O)]^{2+}$

The kinetics of the substitution reaction of $[Co(Me_6tren)(H_2O)]^{2+}$ with imidazole differed significantly from that reported above for pyridine and 4-methylpyridine. When k_{obs} is plotted versus the ligand concentration (see Figure 6), it is clear that k_{obs} increases linearly with increasing imidazole concentration in the lower concentration range, but increases almost exponentially in the higher concentration range. The data can be interpreted in terms of a two-step associative substitution mechanism in which imidazole first displaces the coordinated water molecule in Equation (4), followed by either the binding of a second imidazole molecule to form a six-coordinate complex, or the stepwise dechelation of the Me_6tren ligand to form a five-coordinate disubstituted product in Equation (5).

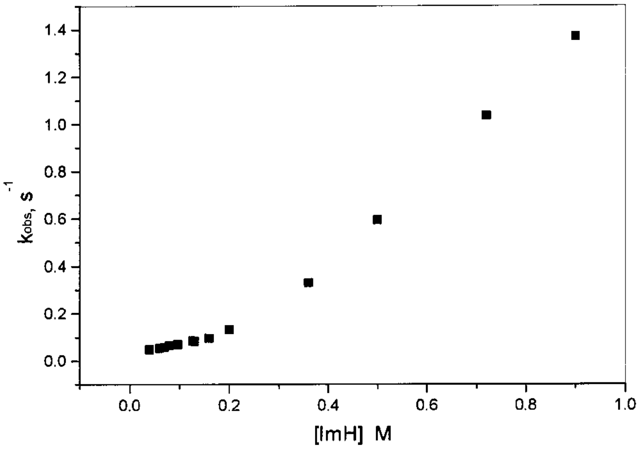


Figure 6. Kinetic data for the reaction of $[Co(Me_6tren)(H_2O)]^{2+}$ with ImH at 25.0 °C, pH = 7.92 ± 0.02, I = 0.2 M, 0.05 M Tris buffer, $[Co^{II}] = 3.21 \cdot 10^{-3}$ M

On the basis of these arguments we propose the following mechanism for the substitution of $[Co(Me_6tren)(H_2O)]^{2+}$ by imidazole (ImH).

Table 1. Kinetic data for the substitution of $[Co(Me_6tren)(H_2O)]^{2+}$ by an organic ligand L at pH = 7.92 ± 0.02, 0.05 M Tris buffer and I = 1.0 M

Ligand (L)	Temp. [°C]	k_{obs} [s^{-1}]	$\Delta H^{\neq}$ [kJ mol^{-1}] and $\Delta S^{\neq}$ [J mol^{-1} K^{-1}]
Pyridine	20.0	0.006 ± 3.0E−4	$\Delta H^{\neq} = 74 \pm 4$
[Py] = 1.0 M	25.0	0.01131 ± 2.9E−4	$\Delta S^{\neq} = -35 \pm 12$
	30.0	0.0158 ± 7.0E−4	
	35.0	0.0277 ± 2.0E−4	
	40.0	0.0471 ± 5.0E−4	
4-Methylpyridine	20.0	0.00575 ± 1.9E−4	$\Delta H^{\neq} = 71 \pm 2$
[4-MePy] = 1.105 M	25.0	0.009152 ± 3.1E−4	$\Delta S^{\neq} = -47 \pm 5$
	30.0	0.01536 ± 1.9E−4	
	35.0	0.02552 ± 7.6E−5	
	40.0	0.0378 ± 6.2E−4	
Imidazole[a]	15.0	0.02935 ± 1.0E−3	$\Delta H^{\neq} = 59 \pm 1$
[ImH] = 0.0964 M	20.0	0.04287 ± 3.2E−3	$\Delta S^{\neq} = -71 \pm 4$
	25.0	0.06872 ± 4.4E−4	
	30.0	0.09986 ± 3.6E−4	
	35.0	0.1524 ± 7.4E−4	
[ImH] = 0.5 M	15.0	0.3056 ± 1.0E−3	$\Delta H^{\neq} = 48 \pm 1$
	20.0	0.4311 ± 3.2E−3	$\Delta S^{\neq} = -87 \pm 4$
	25.0	0.5845 ± 3.8E−3	
	30.0	0.8404 ± 9.1E−3	
	35.0	1.224 ± 6.0E−2	

[a] I = 0.2 M.

$$[Co(Me_6tren)(H_2O)]^{2+} + ImH \rightleftharpoons [Co(Me_6tren)(ImH)]^{2+} + H_2O \quad k_3, k_{-3} \tag{4}$$

$$[Co(Me_6tren)(ImH)]^{2+} + ImH \rightarrow [Co(Me_6tren)(ImH)_2]^{2+} \quad k_4 \tag{5}$$

This leads to rate law (6) for the formation of the substitution products:

$$k_{obs} = k_{-3} + k_3[ImH] + (k_4k_3/k_{-3})[ImH]^2 \tag{6}$$

At lower concentrations of ImH, the rate law Equation (6) reduces to

$$k_{obs} = k_{-3} + k_3[ImH] \tag{7}$$

At higher concentrations of ImH, the rate law Equation (6) can be rewritten as

$$(k_{obs} - k_{-3})/[ImH] = k_3 + (k_4k_3/k_{-3})[ImH] \tag{8}$$

k_{-3} can be obtained directly from the plot of k_{obs} versus [ImH] at lower concentrations (Figure 6), and all other rate constants can then be obtained from the plot of $(k_{obs} - k_{-3})$/[ImH] versus [ImH] for all the data points (see Figure 7). This results in $k_{-3} = 0.031 \pm 0.002$ s^{-1}, $k_3 = 0.27 \pm 0.03$ M^{-1} s^{-1}, and $k_4(k_3/k_{-3}) = 1.46 \pm 0.08$ M^{-2} s^{-1}, from which it follows that $k_4 \approx 0.17 \pm 0.02$ M^{-1} s^{-1}, i.e. ca. two times as slow as k_3. These data account for the initial linear dependence of k_{obs} on the imidazole concentration in the lower concentration range and the exponential behaviour due to the contribution of the second-order term in imidazole concentration at higher concentrations.

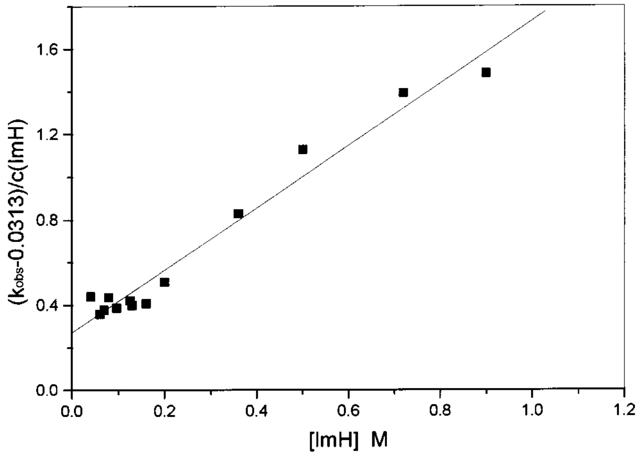


Figure 7. Fit of the kinetic data for the reaction of $[Co(Me_6tren)(H_2O)]^{2+}$ with ImH according to Equation (8) at 25.0 °C, pH = 7.92 ± 0.02, I = 0.2 M, 0.05 M Tris buffer, $[Co^{II}] = 3.21\cdot10^{-3}$ M

The temperature dependence of the reaction was studied at imidazole concentrations of 0.096 and 0.50 M, in order to cover the low and high concentration ranges, respectively. The results are included in Table 1 and the activation enthalpies are 48 ± 1 and 59 ± 1 kJ mol^{-1}, respectively. The significantly negative activation entropies of −87 ± 4 and −71 ± 4 J K^{-1} mol^{-1}, respectively, support the associative nature of the substitution process. The effect of pressure on the reaction was studied at an imidazole concentration of 0.16 M, and the pressure dependence of k_{obs} (see Figure 8) results in a $\Delta V^{\neq}$ value of −2.61 ± 0.07 cm^3 mol^{-1}. This small and negative value suggests that substitution by imidazole follows an associative interchange (I_a) mechanism.[3]

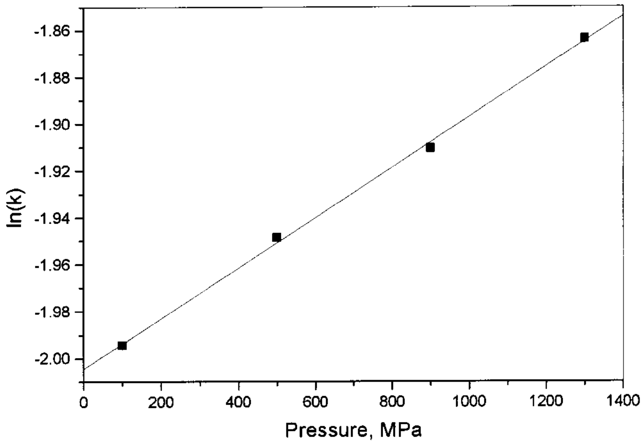


Figure 8. High pressure kinetic data for the reaction between $[Co(Me_6tren)(H_2O)]^{2+}$ and ImH at 25.0 °C, pH = 7.92 ± 0.02, I = 0.2 M, 0.05 M Tris buffer, $[Co^{II}] = 3.21\cdot10^{-3}$ M and [ImH] = 0.16 M

Reaction of 2-Methylimidazole with $[Co(Me_6tren)(H_2O)]^{2+}$

The reaction of 2-methylimidazole with $[Co(Me_6tren)(H_2O)]^{2+}$ is again different from that reported above for the reactions with pyridine, 4-methylpyridine and imidazole. In this case a combination of the dependencies reported in Figures 4 to 6 is observed. When k_{obs} is plotted versus the 2-methylimidazole concentration, it first decreases with increasing 2-methylimidazole concentration in the lower concentration range, and then increases with increasing concentration in the higher concentration range (see Figure 9). k_{obs} passes through a minimum at a 2-methylimidazole concentration of ca. 0.2 M and then depends linearly on the 2-methylimidazole concentration as shown in Figure 9. This concentration dependence is very similar to that reported for the substitution reaction of $[Cu(Me_6tren)(H_2O)]^{2+}$ with pyridine.[4] According to the literature and the results reported above, we propose the following mechanism for the substitution reaction of $[Co(Me_6tren)(H_2O)]^{2+}$ with 2-methylimidazole.

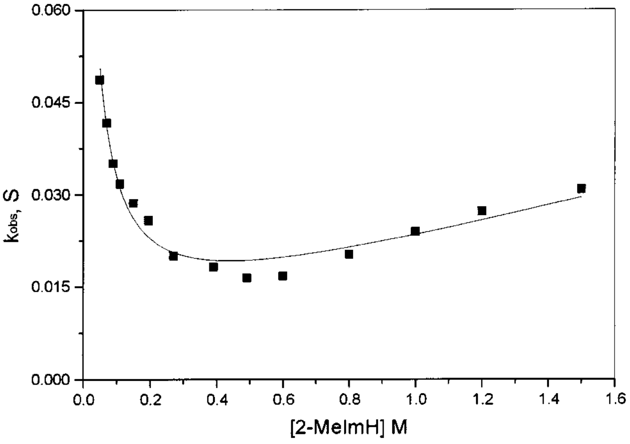


Figure 9. Kinetic data for the reaction of $[Co(Me_6tren)(H_2O)]^{2+}$ with 2-MeImH at 25.0 °C, pH = 7.92 ± 0.02, I = 1.0 M, 0.05 M Tris buffer, $[Co^{II}] = 3.23\cdot10^{-3}$ M

The mechanism consists of two parallel competing reaction paths. The displacement of coordinated water proceeds according to a dissociative mechanism that results in a rate law similar to Equation (3), and can account for the decrease in k_{obs} with increasing 2-methylimidazole concentration. The parallel dechelation reaction path can exhibit a linear dependence on the 2-methylimidazole concentration similar to Equation (7), with an intercept for the reverse reaction under conditions where dechelation is a pre-equilibrium step. The combination of these concentration dependencies will result in the curved dependence observed in Figure 9. At low 2-methylimidazole concentration the reaction will proceed mainly by the displacement of coordinated water, whereas at higher 2-methylimidazole concentration the parallel dechelation path will become more important since a linear concentration dependence is exhibited. The reactions can be summarised as described below.

At lower concentrations of 2-MeImH

$$[\mathrm{Co(Me_6tren)(H_2O)}]^{2+} \rightleftharpoons [\mathrm{Co(Me_6tren)}]^{2+} + \mathrm{H_2O} \quad k_1, k_{-1} \qquad (1)$$

$$[\mathrm{Co(Me_6tren)}]^{2+} + \mathrm{L} \rightleftharpoons [\mathrm{Co(Me_6tren)(L)}]^{2+} \quad k_2, k_{-2} \qquad (2)$$

(L = 2-MeImH)

The rate law is the same as given in Equation (3). At higher concentrations of 2-methylimidazole a significant contribution of the parallel associative displacement of the $\mathrm{Me_6tren}$ chelate, involving a dechelation pre-equilibrium, is suggested to account for the observed data [Equation (9) and Equation (10)].

$$[\mathrm{Co(Me_6tren)(H_2O)}]^{2+} \rightleftharpoons [\mathrm{Co(Me_6tren')(H_2O)}]^{2+} \quad K_5 \qquad (9)$$

$$[\mathrm{Co(Me_6tren')(H_2O)}]^{2+} + \mathrm{L} \rightarrow [\mathrm{Co(Me_6tren')(H_2O)(L)}]^{2+} \quad k_6 \qquad (10)$$

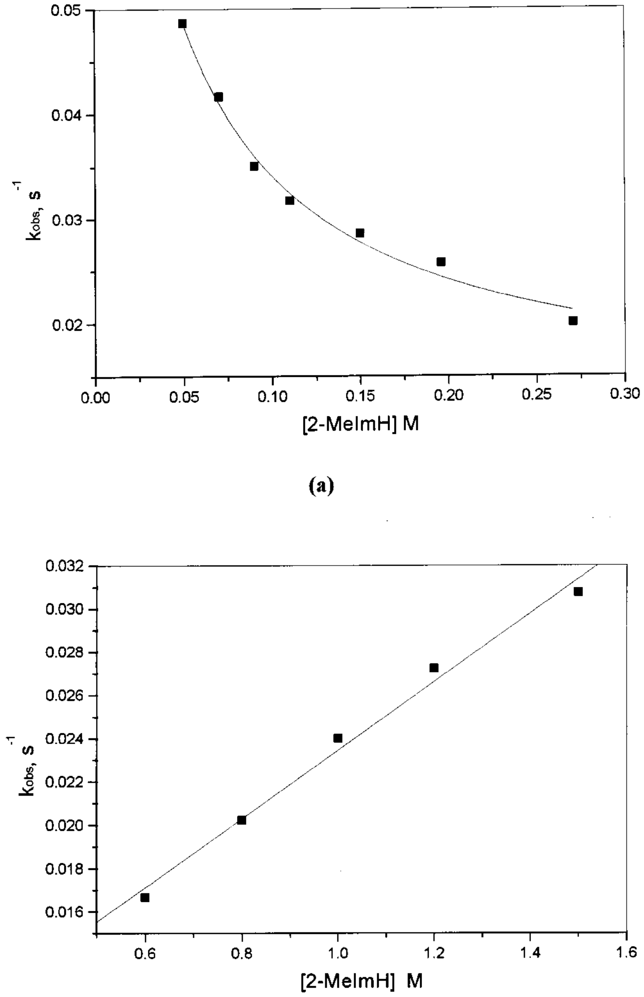
($\mathrm{Me_6tren'}$ represents 3-coordinated $\mathrm{Me_6tren}$; L = 2-MeImH) This mechanism leads to the rate law $k_{obs} = k_6K_5[\mathrm{L}]$, and combined with Equation (3) results in the combined rate law

$$k_{obs} = (k_1k_2[\mathrm{L}] + k_{-1}k_{-2})/(k_{-1} + k_2[\mathrm{L}]) + k_6K_5[\mathrm{L}] \qquad (11)$$

At high concentrations of 2-MeImH, Equation (11) reduces to

$$k_{obs} = k_1 + k_6K_5[\mathrm{L}] \qquad (12)$$

From a fit of the data in Figure 10 (a) using Equation (3), $k_1 = 0.012 \pm 0.006\ \mathrm{s^{-1}}$, $k_{-2} = 0.12 \pm 0.04\ \mathrm{s^{-1}}$ and $k_2/k_{-1} = 37 \pm 23\ \mathrm{M}4^1$. With these values and using $k_1k_2/k_{-1} = 0.42\ \mathrm{M^{-1}\ s^{-1}}$, the experimental data in Figure 9 were fitted to Equation (11), which resulted in $k_1 = 0.007 \pm 0.001\ \mathrm{s^{-1}}$, $k_{-2} = 0.18 \pm 0.03\ \mathrm{M^{-1}\ s^{-1}}$, $k_2/k_{-1} = 60 \pm 10\ \mathrm{M^{-1}}$, and $k_6K_5 = 0.014 \pm 0.001\ \mathrm{M^{-1}\ s^{-1}}$. From a fit of the higher concentration data in Figure 10 (b) using Equation (12), $k_1 = 0.0076 \pm 0.0010\ \mathrm{s^{-1}}$ and $k_6K_5 = 0.0158 \pm 0.001\ \mathrm{M^{-1}\ s^{-1}}$. It follows that the experimental data reported in Figure 9 is well described by the mechanism outlined in the reactions represented by Equations (1), (2), (9), and (10).



(a)

(b)

Figure 10. Fit of the kinetic data reported for the reaction of $[\mathrm{Co(Me_6tren)(H_2O)}]^{2+}$ with 2-MeImH in Figure 9; (a) for data at [2-MeImH] < 0.3 M; (b) for data at [2-MeImH] from 0.5 to 1.6 M

Overall Comparison of Kinetic Data

According to the kinetic data for the substitution reaction of $[\mathrm{Co(Me_6tren)(H_2O)^{2+}}]$ with pyridine and 4-methylpyridine, the reactions proceed according to a dissociative mechanism, which is controlled by the release of $\mathrm{H_2O}$, i.e. k_1. The limiting rate constants reached at high nucleophile concentrations represent k_1 and are indeed close for the two ligands studied ($0.0076\ \mathrm{s^{-1}}$ for pyridine as compared with $0.0066\ \mathrm{s^{-1}}$ for 4-methylpyridine). On increasing the nucleophilicity, the substitution reaction with imidazole shows an associative character, and a second imidazole ligand can enter the coordination sphere at high ligand concentration.

The steric hindrance associated with 2-methylimidazole prevents an associative reaction at low ligand concentration, and evidence for a dissociative reaction is observed. On increasing the ligand concentration further, a concentration range is reached where an associative process contributes to the overall reaction sequence. Again it can be seen that the limiting (minimum) value reached is that for k_1

(viz. 0.008 s^{-1}), which is close to that found for pyridine and 4-methylpyridine, and is consistent with the same rate-determining step.

For the substitution reaction with imidazole, k_3 (viz. 0.27 M^{-1} s^{-1}) is larger than k_4 (viz. 0.17 M^{-1} s^{-1}), which is in agreement with the difficulty of the second imidazole molecule in entering the coordination sphere. By way of comparison, the second-order rate constant for the reaction with 2-methylimidazole, viz. $k_6K_5 = 0.014$ M^{-1} s^{-1}, is significantly smaller presumably due to steric reasons.

Within the context of a limiting dissociative mechanism, the entering nucleophile must compete with the solvent for the intermediate [Co(Me$_6$tren)] species, as expressed by the ratio k_2/k_{-1}. This ratio increases from pyridine (18 M^{-1}), to 4-methylpyridine (24 M^{-1}), to 2-methylimidazole (60 M^{-1}), which follows the order of the increase in nucleophilicity of the ligands.

For the aquation of the substituted complex, it can be seen that k_{-2} for pyridine (viz. 0.09 s^{-1}) is similar to that for 4-methylpyridine (viz. 0.08 s^{-1}), and both are larger than the corresponding data (k_{-3}) for imidazole (viz. 0.031 s^{-1}), which is again consistent with the order of nucleophilicity of the ligands. These values are all smaller than that for 2-methylimidazole (viz. 0.18 s^{-1}), which can be ascribed to the steric hindrance associated with the 2-methylimidazole ligand which will accelerate the aquation of the complex.

For the complex-formation constants K, there is a small difference between the thermodynamically and kinetically determined values. For the ligands pyridine, 4-methylpyridine and imidazole, K_{td} is 1.0, 1.8, and 7.4 M^{-1}, respectively, whereas K_{kin} for these ligands is 1.5, 2.1, and 8.7 M^{-1}, respectively. It can be seen that the values of K from the thermodynamic analysis are slightly smaller than those from the kinetic treatment, but are in good agreement considering the error limits involved.

Conclusions

The results of this study have demonstrated how the nature and mechanism of ligand substitution reactions of $[Co(Me_6tren)(H_2O)]^{2+}$ can be controlled in a rather sensitive manner by the nature, concentration, and nucleophilicity of the entering ligand. We are presently in the process of extending this study systematically to the substitution behaviour of the sterically less hindered and more oxygen-sensitive $[Co(Me_3tren)(H_2O)]^{2+}$ and $[Co(tren)(H_2O)]^{2+}$ complexes. Finally, we plan to investigate the activation of dioxygen by both complexes in more detail.

Experimental Section

Materials: The compounds used were of commercially available reagent quality (Acros), except for the preparation reported below. Ultra pure water was used for the preparation of the aqueous solutions. *WARNING: Perchlorate salts are potentially explosive; they should be handled in small amounts and with caution!* − The ligand Me$_6$tren was prepared according to a literature method and characterised by ^{13}C and ^{1}H NMR spectroscopy.[13] The spectra were in agreement with those reported in the literature.[13] $[Co(Me_6tren)](ClO_4)_2$ was prepared according to the literature and characterised by elemental analysis and spectral data.[14] Solutions of the complex for the thermodynamic and kinetic studies were prepared by dissolving the solid product in the buffer (0.05 M Tris and pH ≈ 7.9) [$I = 1.0$ M for reactions with pyridine, 4-methylpyridine and 2-methylimidazole; and $I = 0.2$ M for imidazole ($NaClO_4$)], adding 50% excess of the Me$_6$tren chelate to stabilise the complex, and adjusting the final pH of the solution with 1.0 M $HClO_4$ to 7.92 ± 0.02.

Physical Measurements: Conductance measurements were made with a HANNA instrument HI1281 at room temperature. − Electronic spectra were measured with a Shimadzu 240 spectrophotometer. − IR spectra were recorded with an ATJ Mattson FT-IR 60 AR spectrophotometer in KBr pellets in the 4000−400 cm^{-1} range. − ESR spectra were recorded with a Bruker DXP 300 AVANCE spectrometer.

Characterisation of $[Co(L)_4(H_2O)_2](ClO_4)_2$ (L = 4-MePy) and $[Co(L)_6](ClO_4)_2$ (L = ImH): In the study of the complex-formation reactions in the presence of a large excess of entering nucleophile, precipitates were formed during the reaction of $[Co(Me_6tren)(H_2O)]^{2+}$ with 4-methylpyridine and imidazole. These were isolated and characterised.

$[Co(4\text{-}MePy)_4(H_2O)_2](ClO_4)_2$: $C_{24}H_{32}Cl_2CoN_4O_{10}$ (666.4): calcd. C 43.26, H 4.84, N 8.41; found C 43.11; H 4.49, N 8.07. − Molar conductivity: 124 cm^2/ohm mol (DMF, $1.03\cdot10^{-3}$ M, 25 °C). − 151 cm^2/ohm mol [$CH_3CH_2NO_2$, $4.4\cdot10^{-3}$ M, 25 °C, ref.[15] 157−201 cm^2/ohm mol for $Co(4\text{-}MePy)_4(ClO_4)_2$]. − Electronic spectrum (in $CHCl_2/CHCl_3$, 1:1): λ (ε) = 20700 (sh), 19700 (600) [ref.[15] 18000−23000 cm^{-1} two peaks in CH_2Cl_2 for $Co(4\text{-}MePy)_4(ClO_4)_2$; 18900 (sh), 17900 (611) in $CHCl_2/CHCL_3$ (1:1) for $Co(4\text{-}MePy)_4(PF_6)_2$[16]]. − IR ($cm^{-1}$): ṽ = 630, 935, 1018, 1092, 1111, 1141 [for ν(ClO_4^-), ref.[17] 625, 925, 1020, 11371]; 1231, 1505, 1618 [for ν(4-MePy), ref.[16] 1240, 1511, 1622]; 3434 [br. for ν(H_2O)]. − ESR: $g = 4.25$.

$[Co(ImH)_6](ClO_4)_2$: $C_{18}H_{24}Cl_2CoN_{12}O_8$ (666.3): calcd. C 32.47, H 3.63, N 25.25; found C 32.47, H 3.50, N 25.42. − Molar conductivity: 154 cm^2/ohm mol (DMF, $1.0\cdot10^{-3}$ M, 25 °C); 150 cm^2/ohm mol ($CH_3CH_2NO_2$, $6.0\cdot10^{-3}$ M, 25 °C, ref.[18] 180 cm^2/ohm mol, 23 °C). − Electronic spectrum (in DMF with 10% excess ImH): λ (ε) = 20120 (25), 18940 (sh) cm^{-1} [ref.[18] 20230 (20), 18900 (sh) cm^{-1}]. − IR (cm^{-1}): ṽ = 1057, 1089, 1115 [for ν(ClO_4^-), ref.[18] 1000−1120 vs)]; 938, 1537, 3149, 3368 [for ν(NH), ref.[18] 935, 1530, 3100, 3300]. − ESR: $g = 4.15$ {ref.[19] 4.20 for $[Co(ImH)_6](NO_3)_2$}.

Methods

Thermodynamic Studies: Spectral and thermodynamic measurements were carried out at 25.0 ± 0.1 °C in 0.05 M Tris buffer and 1.0 M $NaClO_4$ for pyridine and 4-methylpyridine, and 0.2 M $NaClO_4$ for imidazole. UV/Vis spectra were recorded with a Varian Cary 5 spectrophotometer using a 1-cm quartz cuvette. The pH of the solutions was measured by employing a Mettler Delta pH meter with a Mettler Toledo Inlab 412 combined glass electrode. The electrode calibration for the H^+ concentration was such that pH is defined as $-\log[H^+]$. All test solutions were kept under nitrogen. Details on the experimental method and treatment of the data have been reported before.[20,21]

Kinetic Studies: An Applied Photophysics, Model SX 18MV, stopped-flow spectrophotometer with an observation path length of 1.0 cm was used to monitor the kinetics of the substitution reaction of $[Co(Me_6tren)](ClO_4)_2$ with organic bases at ambient pressure. In each case the pH values of the complex and ligand solutions were adjusted to 7.92 ± 0.02 using 0.05 M Tris and $HClO_4$. The ionic strength was kept constant at 1.0 M ($NaClO_4$) for the reactions with pyridine, 4-methylpyridine, and 2-methylimidazole, and at 0.2 M for the reaction with imidazole. Temperature control was achieved by circulation of a thermostated fluid (25.0 ± 0.1 °C). The substitution kinetics were monitored at 470 nm, and kinetic traces as a function of concentration and temperature were recorded with an online computer and subsequently processed to yield kinetic parameters using the OLIS KINFIT program (Bogart, GA). A minimum of at least five kinetic traces were recorded for each set of experimental conditions. The kinetic traces fitted well to a single exponential function. − Kinetic measurements at elevated pressure for the substitution reactions of $[Co(Me_6tren)(H_2O)]^{2+}$ with imidazole and 4-methylpyridine were performed with a home-built stopped-flow unit which can be immersed in a high-pressure chamber.[22] For the reaction with imidazole, the solutions were identical to those used in the ambient pressure experiments and the monitoring wavelength was 470 nm. The temperature was controlled by circulation of a thermostated fluid at 25.0 ± 0.1 °C. For the reaction with 4-methylpyridine, the ionic strength of the solutions was reduced to almost zero and the temperature was increased to 45.0 ± 0.1 °C in order to prevent turbidity problems encountered during the mixing of concentrated solutions. The kinetic data was also checked under ambient conditions at low ionic strength, in order to justify the selected conditions.

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[1] [1a] S. F Lincoln, A. E. Merbach, *Adv. Inorg. Chem.* **1995**, *42*, 1−88. [1b] A. Roodt, A. Abou-Hamdan, H. P. Engelbrecht, A. E. Merbach, *Adv. Inorg. Chem.* **1999**, *49*, 60−126. [1c] R. van Eldik, C. Dücker-Benfer, F. Thaler, *Adv. Inorg. Chem.* **1999**, *49*, 1−58. [1d] H. Elias, *Coord. Chem. Rev.* **1999**, *187*, 37−73.

[2] E. A. Ambundo, M. V. Deydier, A. J. Grall, N. Aguera-Vega, L. T. Dressel, T. H. Cooper, M. J. Heeg, L. A. Ochrymowycz, D. B. Rorabacher, *Inorg. Chem.* **1999**, *38*, 4233−4242, and references cited therein.

[3] D. H. Powell, A. E. Merbach, I. Fabian, S. Schindler, R. van Eldik, *Inorg. Chem.* **1994**, *33*, 4468−4473.

[4] D. H. Powell, P. Furrer, P. A. Pittet, A. E. Merbach, *J. Phys. Chem.* **1995**, *99*, 16622−16629.

[5] F. Thaler, C. D. Hubbard, F. W. Heinemann, R. van Eldik, S. Schindler, I. Fabian, A. M. Dittler-Klingemann, F. E. Hahn, C. Orvig, *Inorg. Chem.* **1998**, *37*, 4022−4029.

[6] A. M. Dittler-Klingemann, C. Orvig, F. E. Hahn, F. Thaler, C. D. Hubbard, R. van Eldik, S. Schindler, I. Fabian, *Inorg. Chem.* **1996**, *35*, 7798−7803.

[7] H. Mäcke, *Helv. Chim. Acta* **1981**, *64*, 1579−1598.

[8] M. Zhang, R. van Eldik, J. H. Espenson, A. Bakac, *Inorg. Chem.* **1994**, *33*, 130−133.

[9] G. Anderegg, V. Gramlich, *Helv. Chim. Acta* **1994**, *77*, 685−689.

[10] H. M. Marques, J. C. Bradley, K. L. Brown, H. Brooks, *Inorg. Chim. Acta* **1993**, *209*, 161−169.

[11] M. S. A. Hamza, J. M. Pratt, *J. Chem. Soc., Dalton Trans.* **1994**, 1367−1371.

[12] [12a] H. E. Toma, J. M. Malin, E. Giesbrecht, *Inorg. Chem.* **1973**, *12*, 2084−2089. [12b] J. M. Malin, H. E. Toma, E. Giesbrecht, *J. Chem. Educ.* **1977**, *54*, 385−386.[12c] W. Byers, J. A. Cossham, J. O. Edwards, A. T. Gordon, J. G. Jones, E. T. P. Kenny, A. Mahamed, J. McKnight, D. A. Sweigart, G. A. Tondreau, T. Wright, *Inorg. Chem.* **1986**, *25*, 4767−4774. [12d] K. J. Schneider, R. van Eldik, *Organometallics* **1990**, *9*, 92−96. [12e] R. A. Henderson, K.E. Oglieve, *J. Chem. Soc., Chem. Commun.* **1994**, 1961−1962.

[13] J. H. Coates, P. R. Collins, S. F. Lincoln, *Aust. J. Chem.* **1980**, *33*, 1381−1389.

[14] M. Clampolini, N. Nardi, *Inorg. Chem.* **1966**, *5*, 41−44.

[15] W. C. Jones, W. E. Bull, *J. Chem. Soc. A* **1968**, 1849−1852.

[16] R. M. Morrison, R. C. Thompson, *Can. J. Chem.* **1978**, *56*, 985−991.

[17] D. H. Brown, R. H. Nuttall, J. Mcavoy, D. W. A. Sharp, *J. Chem. Soc. A* **1966**, 892−896.

[18] W. J. Davis, J. Smith, *J. Chem. Soc. A* **1971**, 317−324.

[19] A. Bencini, C. Benelli, D. Gatteschi, C. Zanchini, *Inorg. Chem* **1983**, *22*, 2123−2126.

[20] S. F. Lincoln, C. D. Hubbard, *J. Chem. Soc., Dalton. Trans.* **1974**, 2513−2516.

[21] I. Fábián, H. Diebler, *Inorg. Chem.* **1987**, *26*, 925−928.

[22] R. van Eldik, W. Gaede, S. Wieland, J. Kraft, M. Spitzer, D. A. Palmer, *Rev. Sci. Instrum.* **1993**, *64*, 1335−1357.

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