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Mechanistic behaviour of alkylcobaloximes and imino-oxime complexes related to vitamin B_{12}†

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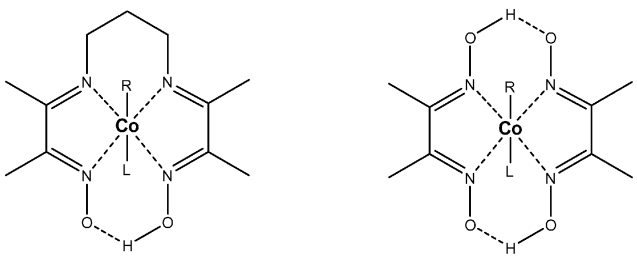
The ligand substitution reactions of complexes of the type *trans*-[(R)Co(Chel)S]$^{+/0}$ with L, where chel = (DO)(DOH)pn = 2,2′-(1,3-diaminopropanebis(2-methyl-3-butanone)oxime), R = CH_3, L = imidazole, pyrazole, 1,2,4-triazole and 1-methylimidazole, and S = water and MeOH, and chel = $(Hdmg)_2$ = bis(dimethylglyoximate), R = CH_2Cl, CH_2Br, and CH_2I, L = thiourea and pyridine, and S = water, were studied in detail as a function of temperature and pressure. The reported activation parameters ($\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$) support the operation of a dissociative interchange (I_d) mechanism. Complexes of the type *trans*-[RCo(Hdmg)$_2$L] (R = CH_2Cl, CH_2Br, and CH_2I; L = H_2O and Py) were fully optimized at the B3LYP/LANL2DZp level, and the structural data support the mechanistic assignment based on the reported activation parameters. For the reaction of *trans*-[$(CH_3)_2$Co((DO)(DOH)pn)] with acid, the activation parameters ($\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$) were found to be 37 ± 1 kJ mol^{-1}, −86 ± 3 J mol^{-1} K^{-1} and −18.9 ± 0.7 cm^3 mol^{-1}, respectively, and support a protonation mechanism.

Introduction

Since alkylcobaloximes have been proposed as model compounds[1] for vitamin B_{12}, a number of other cobalt complexes containing an equatorial chelating ring have been synthesised. Several reviews in this area have appeared.[2–7] Closely related complexes to the alkylcobaloximes are the imino-oxime[8–12] derivatives of the type *trans*-[(R)Co((DO)(DOH)pn)L]$^+$ (where R = alkyl group and L = neutral base) as shown in Fig. 1, which are formally derived from cobaloximes by displacement of an O–H–O$^-$ fragment by a propylene chain. Despite the close resemblance in structure, the two series of complexes exhibit considerable differences in their reactivity. In particular, the reaction of *trans*-[(CH_2Br)Co$(Hdmg)_2$L] with CH_3O^- gives the methoxymethyl derivative (eqn (1)) as follows:



trans-[(R)Co((DO)(DOH)pn)L]$^+$ *trans*-[(R)Co(Hdmg)$_2$L]

Fig. 1 Structures of *trans*-[(R)Co((DO)(DOH)pn)L]$^+$ and *trans*-[(R)-Co(Hdmg)$_2$L].

$$CoCH_2Br + CH_3O^- \rightarrow CoCH_2OCH_3 + Br^- \quad (1)$$

The reaction may be interpreted as a nucleophilic addition of the CH_3O^- fragment to the axial carbon.[13] In the attempt to reproduce the same reaction for *trans*-[(CH_2X)Co((DO)(DOH)pn)L]$^+$ (X = Cl, Br, I) derivatives, quite a different type of compound was isolated (in almost quantitative yield), which is characterized by the presence of a three-membered Co–N–C ring resulting from an interligand nucleophilic addition of an equatorial N donor to the ligated axial carbon.[14] In addition, the cobalt complexes of the type *trans*-[$(R)_2$Co((DO)(DOH)pn)] or *trans*-[(R′)(R″)Co((DO)(DOH)pn)][10,15–17] are well known. However, the synthesis of the corresponding *trans*-dialkylcobaloximes has not been reported so far.

It is of further interest to compare the kinetic properties of the above-mentioned complexes, since the availability of two series of complexes with an identical axial fragment R–Co–H_2O and different equatorial chelates, offers the opportunity to evaluate the relative effect of the equatorial moiety on the axial positions in terms of kinetic parameters for the substitution of coordinated water by different nucleophiles.

Two fundamental aspects emerge from these studies, *i.e.*, the strong *trans* effect due to the alkyl R group, as compared to inorganic groups (*viz.* NO_2^-), and the dissociative nature of the process. Based on activation volume data, we have recently shown that the activation mode is strongly affected by the R group. For the displacement of water by cysteine in a series of cobaloximes with R = CF_3CH_2, Ph, Me, Bz, Et and cyclo-C_5H_9, the corresponding $\Delta V^{\ddagger}$ were found to be: 0 ± 1, +4.5 ± 0.5, +5.5 ± 0.5, +5.9 ± 0.4, +6.6 ± 0.4 and +8.9 ± 0.7 cm^3 mol^{-1}, suggesting that a

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gradual mechanistic change over from I to D along the series of R groups from CF_3CH_2 to cyclo-C_5H_9 occurs.[18] In addition, we found that the mechanism is also affected by the nature of the entering ligand. This results from a study of the reactions of *trans*-[(R)Co(Hdmg)$_2$S] (where R = $PhCH_2$ or CF_3CH_2 and S = H_2O or MeOH) with 4-NH_2Py, Py and 4-CNPy.[19] By way of example for the reaction of the $PhCH_2$ derivative in methanol, the activation volumes +9.8 ± 0.1, +10.3 ± 0.3 and +13.0 ± 0.3 cm^3 mol^{-1} were found for the entering ligands 4-NH_2Py, Py and 4-CNPy, respectively. The same trend was also found for the reactions in water and for the reactions of the CF_3CH_2 derivative in both methanol and water.

Kinetic studies pertinent to *trans*-[RCo((DO)(DOH)pn)H_2O]$^+$ are less in number.[20,21] However, specific studies aiming at a comparison of the kinetic properties of alkylcobalt imino-oxime complexes with those of alkylcobaloximes, have been reported.[22] Reactions studied are of the type shown in eqn (2):

$$\textit{trans}\text{-}[(R)Co(chel)Py]^n + P \rightarrow \textit{trans}\text{-}[(R)Co(chel)P]^n + Py \qquad (2)$$

where chel represents (DO)(DOH)pn (= 2,2′-(1,3-diaminopropanebis(2-methyl-3-butanone)oxime) with n = +1 or (Hdmg)$_2$ with n = 0, R represents nine different alkyl groups with varying electronic properties, and P represents tri-*n*-butylphosphine or trimethylphosphite. In the presence of an excess of the entering ligand, the observed rate constants were found to be independent of the nucleophile concentration, suggesting that eqn (2) follows a limiting dissociative (D) mechanism presented by eqn (3) and eqn (4).

$$\textit{trans}\text{-}\left[(R)Co(chel)Py\right]^n \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \left[(R)Co(chel)P\right]^n + Py \qquad (3)$$

$$\left[(R)Co(chel)\right]^n + P \xrightarrow{k_2} \textit{trans}\text{-}\left[(R)Co(chel)P\right]^n \qquad (4)$$

The dissociation rate constants k_1 (s^{-1}) could be obtained from the kinetic data and turned out to be virtually identical for the two series. Also the relative dependence on R was found to be quite similar for the two series of complexes.

In order to gain further understanding on this aspect, we report here kinetic parameters for the reaction of *trans*-[(CH_3)Co((DO)(DOH)pn)S]$^+$ (where S = H_2O or MeOH) with various azoles, *viz.* imidazole, pyrazole, 1,2,4-triazole and 1-methylimidazole. These data together with that previously reported for methylcobaloxime[23] and methylcobalt bisethylendiamine complexes,[24] enable a comparative analysis of three systems having different chelating rings, but the same CH_3–Co–H_2O axial fragment.

Furthermore, azoles as entering nucleophiles are interesting from a bioinorganic chemistry point of view. Recent structural results have shown that in some enzymes utilizing coenzyme B_{12}, the benzimidazole residue coordinated to the cobalt atom is replaced by the imidazole moiety of a histidine of the protein chain.[25–28]

In the present investigation we measured rate and activation parameters for substitution reactions of *trans*-[(R)Co(Hdmg)$_2H_2O$] (R = CH_2Cl, CH_2Br and CH_2I) with thiourea and pyridine, and supplemented it with structural data obtained from hybrid density functional theoretical calculations. In addition, we examined a further aspect related to the kinetic properties of imino-oxime complexes and in particular the demethylation of the complex *trans*-[$(CH_3)_2$Co((DO)(DOH)pn)] promoted by acids. This reaction is of particular interest since it represents a rare case of heterolytic cleavage of the cobalt–carbon bond.[29–31]

Experimental

Materials

All chemicals were of p.a. grade and used as received. Imidazole, pyrazole, 1,2,4-triazole and perchloric acid were purchased from Fluka, 1-methylimidazole from Acros, and taps buffer from Sigma. Ultra pure water was used in the preparation of all solutions for kinetic measurements. *Trans*-[CH_3Co((DO)(DOH)pn)-H_2O]ClO_4,[8] *trans*-[$(CH_3)_2$Co((DO)(DOH)pn)],[10] and *trans*-[RCo-(Hdmg)$_2H_2O$] (R = CH_2Cl, CH_2Br, and CH_2I)[32] were prepared as previously reported, and were characterized by elemental analysis, UV-vis and NMR spectroscopy. The results were in agreement with literature data. The preparation of solutions and all measurements were carried out in the dark because the investigated complexes are light sensitive.

Instrumentation

The pH of the solution was measured using a Mettler Delta 350 pH meter. The pH meter was calibrated with standard buffer solutions at pH 4.0, 7.0 and 10.0. UV-vis spectra were recorded on a Shimadzu UV-2101 spectrophotometer. Kinetic measurements were carried out on an Applied Photophysics SX 18MV stopped-flow instrument coupled to an online data acquisition system. At least eight kinetic runs were recorded under all conditions, and the reported rate constants represent the mean values. All kinetic measurements were carried out under pseudo-first order conditions, *i.e.* the ligand concentration was in at least a ten-fold excess. Measurements at high pressure were carried out using a home-made high pressure stopped-flow unit.[33] Kinetic data were analyzed with the OLIS KINFIT set of programs. All instruments used were thermostated to the desired temperature (± 0.1 °C).

Quantum chemical methods

Trans-[(R)Co(Hdmg)$_2H_2O$] (R = CH_2Cl, CH_2Br and CH_2I) complexes were optimized at the B3LYP/LANL2DZp[34–36] hybrid functional with pseudo-potentials on the heavy elements and valence basis set augmented with polarisation functions. During the optimization of the structure no constrains other than symmetry were applied. In addition, the resulting structures were characterised as minima, transition structures, *etc.*, by computation of their vibrational frequencies. The relative energies were corrected for zero-point vibrational energies (ZPE). The Gaussian 03 program was used for all calculations.[37]

Results

The kinetics of the ligand substitution eqn (5) of *trans*-[(R)Co(Chel)S]$^{+/0}$ were studied for different nucleophiles L to form *trans*-[RCo(Chel)L]$^{+/0}$, where chel = (DO)(DOH)pn, R = CH_3, L = imidazole, pyrazole, 1,2,4-triazole, and 1-methylimidazole, and S = H_2O or MeOH, and chel = (Hdmg)$_2$, R = CH_2Cl, CH_2Br, and CH_2I, L = thiourea, and S = H_2O. Fig. 2 and 3, and Fig. S1, S2, S3 and S4 (ESI)† report plots of the pseudo-first-order rate constant k_{obs} *vs.* [L] for the reactions with imidazole,

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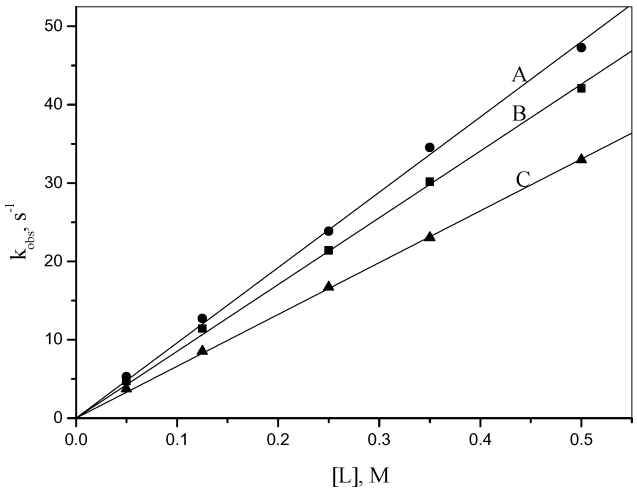

Fig. 2 Plots of k_{obs} *vs.* [pyrazole] (A), [imidazole] (B), and [1,2,4-triazole] (C) for the reaction with 1×10^{-4} M *trans*-$[(CH_3)Co((DO)(DOH)pn)H_2O]^+$ at 25.0 °C, pH 9 and $I = 0.1$ M $NaClO_4$.

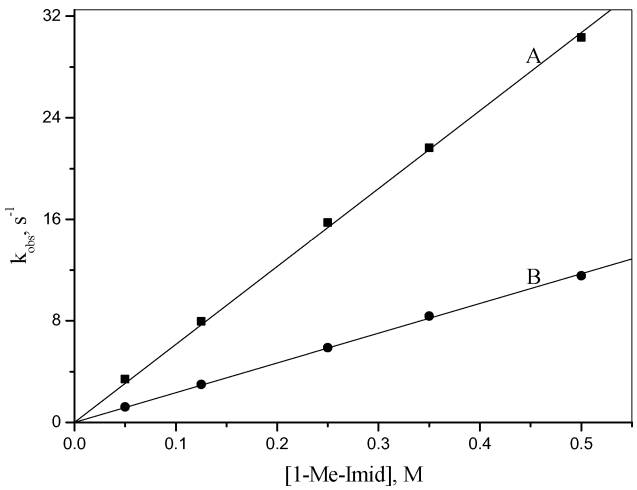

Fig. 3 Plots of k_{obs} *vs.* [1-methylimidazole] for the reaction with 1×10^{-4} M *trans*-$[(CH_3)Co((DO)(DOH)pn)H_2O]^+$ in H_2O (A) and MeOH (B) at 25.0 °C, pH 9 and $I = 0.1$ M $NaClO_4$ in aqueous solution.

pyrazole, 1,2,4-triazole, and 1-methylimidazole in H_2O and MeOH as solvents, and also thiourea in H_2O at 25 °C. The linear plots have negligible intercepts, indicating that a reverse or parallel reaction does not contribute significantly under the selected experimental conditions. This behaviour can be expressed by the dependence given in (6), where k_a represents the second order rate constant for the reaction.

$$trans\text{-}\left[\left(R\right)Co\left(chel\right)S\right]^{+/0} + L \xrightarrow{k_a} trans\text{-}\left[\left(R\right)Co\left(chel\right)L\right]^{+/0} + S \quad (5)$$

$$k_{obs} = k_a[L] \quad (6)$$

The reaction between *trans*-$[RCo(Hdmg)_2H_2O]$ (R = CH_2Cl, CH_2Br, and CH_2I) and pyridine was studied at different temperatures for which the results, presented in Fig. 4, and Fig. S5 and S6 (ESI),† show a significant deviation from linearity at high pyridine concentration. This behaviour can be explained in terms of an interchange mechanism presented in eqn (7) and (8), for which the rate law is given in eqn (9), where K represents the equilibrium

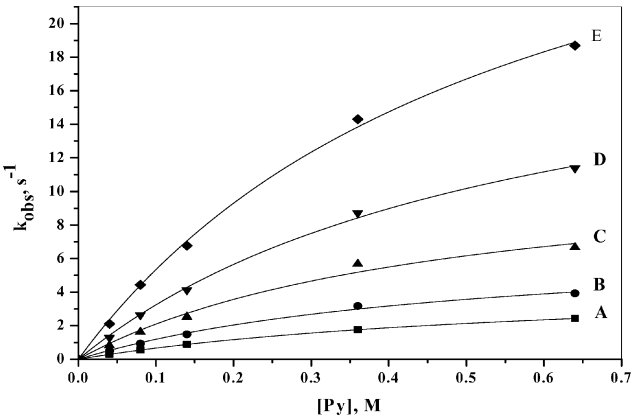

Fig. 4 Plots of k_{obs} *vs.* [pyridine] for the reaction with 1×10^{-3} M *trans*-$[(CH_2Cl)Co(Hdmg)_2H_2O]$ as a function of temperature. Experimental conditions: pH = 8, $I = 0.1$ M, and temperature 20 (A), 25 (B), 30 (C), 35 (D) and 40 (E) °C.

constant for precursor formation, and k the interchange rate constant.

$$\left[\left(R\right)Co\left(Hdmg\right)_2H_2O\right] + L \rightleftharpoons \left\{\left[\left(R\right)Co\left(Hdmg\right)_2H_2O\right].L\right\} \quad (7)$$

$$\left\{\left[\left(R\right)Co\left(Hdmg\right)_2H_2O\right].L\right\} \xrightarrow{k} \left[\left(R\right)Co\left(Hdmg\right)_2L\right] + H_2O \quad (8)$$

$$k_{obs} = kK[L]/(1+ K[L]) \quad (9)$$

The reaction of *trans*-$[(CH_3)_2Co((DO)(DOH)pn)]$ with acid was studied in a solution of MeOH and H_2O (1 : 1) to form *trans*-$[(CH_3)Co((DO)(DOH)pn)H_2O]^+$. Fig. 5 shows some curvature at high acid concentration and a zero intercept, which can be interpreted in terms of the protonation mechanism outlined in eqn (10) and (11), for which the $[H^+]$ dependence of k_{obs} can also be expressed by eqn (9), where $[L] = [H^+]$. The protonated intermediate formed in eqn (10) is formulated in a general way since it is uncertain on which site of the ligands the proton is located. The subsequent reaction step leads to the displacement of a methyl group accompanied by the release of methane.

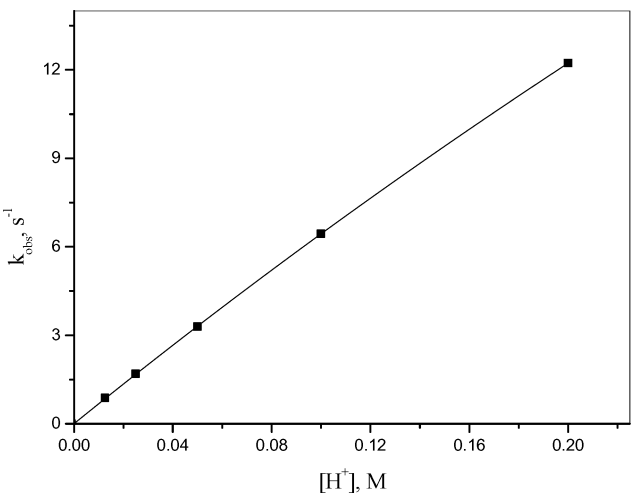

Fig. 5 Plot of k_{obs} *vs.* $[H^+]$ for the reaction with 3×10^{-5} M *trans*-$[(CH_3)_2Co((DO)(DOH)pn)]$ in H_2O and MeOH (1 : 1) at 25.0 °C and $I = 0.2$ M $NaClO_4$.

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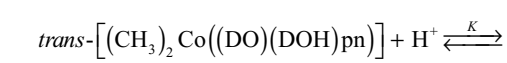
Table 1 Kinetic data and activation parameters for the reaction of *trans*-[(R)Co(Chel)S]$^{+/0}$ with various ligands

	trans-[(CH_3)Co((DO)(DOH)pn)S]$^+$							
Ligand	Imidazole		Pyrazole		1,2,4-Triazole		1-Methylimidazole	
Solvent	H_2O[a]	MeOH[b]	H_2O[a]	MeOH[b]	H_2O[a]	MeOH[b]	H_2O[a]	MeOH[b]
k_a/M^{-1} s^{-1}[c]	94.6 ± 1.4	26.0 ± 0.2	105.6 ± 1.8	21.0 ± 0.1	74.0 ± 0.6	20.2 ± 0.1	68.0 ± 0.4	24.3 ± 0.2
$\Delta H^{\ddagger}$/kJ mol^{-1}[d]	69 ± 2	70 ± 1	71 ± 2	72 ± 2	67 ± 2	70 ± 2	70 ± 2	67 ± 2
$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}[d]	+23 ± 6	+16 ± 4	+33 ± 6	+21 ± 5	+17 ± 7	+16 ± 5	+27 ± 5	+7 ± 8
$\Delta V^{\ddagger}$/cm^3 mol^{-1}[cd]	+2.7 ± 0.1	+3.4 ± 0.1	+3.7 ± 0.1	+4.1 ± 0.1	+3.4 ± 0.1	+4.4 ± 0.1	+2.9 ± 0.1	+4.3 ± 0.1

	trans-[(R)Co(Hdmg)$_2H_2O$]					
R	CH_2Cl		CH_2Br		CH_2I	
Ligand	Thiourea	Pyridine	Thiourea	Pyridine	Thiourea	Pyridine
k_a/M^{-1} s^{-1}[e]	17.8 ± 0.3	13.7 ± 1.1[f]	7.3 ± 0.2	5.9 ± 0.8[f]	6.6 ± 0.1	4.9 ± 0.6[f]
$\Delta H^{\ddagger}$/kJ mol^{-1}	72 ± 1[d]	71 ± 1[d]	75 ± 1[d]	76 ± 2[d]	73 ± 3[d]	78 ± 2[d]
$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	+19 ± 3[d]	+14 ± 3[d]	+23 ± 4[d]	+25 ± 5[d]	+16 ± 10[d]	+31 ± 6[d]
$\Delta V^{\ddagger}$/cm^3 mol^{-1}[h]	+6.1 ± 0.4[d]	+5.2 ± 0.2[g]	+10.4 ± 0.5[d]	+6.0 ± 0.2[g]	+6.4 ± 0.2[d]	+4.9 ± 0.3[g]

[a] $[Co^{III}] = 1 \times 10^{-4}$ M, pH = 9, I = 0.1 M. [b] $[Co^{III}] = 1 \times 10^{-4}$ M. [c] T = 25 °C. [d] The activation parameters were calculated for the second-order rate constants. [e] $[Co^{III}] = 1 \times 10^{-3}$ M, pH = 8, I = 0.1 M, T = 25 °C. [f] This value represents the product kK. [g] The activation volumes were calculated for the limiting rate constant k reached at high nucleophile concentration, see Discussion. [h] $[Co^{III}] = 1 \times 10^{-3}$ M, pH = 8, I = 0.1 M, T = 25 °C, [TU] = 0.8 M, [Py] = 0.64 M.



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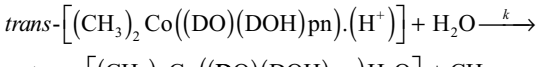

(11)

Tables 1 and 2, and Tables S1, S2, S3 and S4 (ESI)† summarize the kinetic data obtained as a function of temperature and pressure for the reaction of *trans*-[(R)Co(Chel)S]$^{+/0}$ with L, where chel = (DO)(DOH)pn, R = CH_3, L = imidazole, pyrazole, 1,2,4-triazole and 1-methylimidazole, and S = H_2O and MeOH, and where chel = $(Hdmg)_2$, R = CH_2Cl, CH_2Br, and CH_2I, L = thiourea and pyridine, and S = H_2O. Plots of lnk_{obs} *vs.* pressure gave good linear relationships for these reactions as shown in Fig. S7, S8, S9, S10 and S11 (ESI).† Kinetic data for the reaction of *trans*-[$(CH_3)_2$Co((DO)(DOH)pn)] with acid was studied in a mixture of MeOH and H_2O (1 : 1) and are summarized in Table 2. Fig. S12 (ESI)† shows the relationship between lnk_{obs} and pressure for the reaction of *trans*-[$(CH_3)_2$Co((DO)(DOH)pn)] with acid.

The B3LYP/LANL2DZp computed structures of *trans*-[(R)Co(Hdmg)$_2H_2O$], where R = CH_2Cl, CH_2Br and CH_2I, are shown in Fig. 6 and Fig. S13 (ESI),† and the bond lengths of *trans*-[(R)Co(Hdmg)$_2H_2O$] with different alkyl groups are summarized in Table 3.

Table 2 Kinetic data for the reaction of *trans*-[$(CH_3)_2$Co-((DO)(DOH)pn)] with acid as function of temperature and pressure

T/°C	kK/M^{-1} s^{-1}[ab]
5	20.1 ± 1.2
10	26.3 ± 0.8
15	35.1 ± 1.2
20	46.6 ± 1.2
25	63.4 ± 1.6
Pressure/MPa	
10	74 ± 2
50	95 ± 6
90	134 ± 4
130	181 ± 8
$\Delta H^{\ddagger}$/kJ mol^{-1}[c]	37 ± 1
$\Delta S^{\ddagger}$/J mol^{-1} K^{-1}[e]	−86 ± 3
$\Delta V^{\ddagger}$/cm^3 mol^{-1}[de]	−18.9 ± 0.7

[a] Overall second-order rate constant for eqn (10) and (11). [b] Solvent is H_2O and MeOH (1 : 1), I = 0.2 M. [c] $[H^+] = 2.5 \times 10^{-2}$ M. [d] $[H^+] = 1.25 \times 10^{-2}$ M. [e] T = 25 °C.

Table 3 Bond lengths (Å) in *trans*-[(R)Co(Hdmg)$_2H_2O$] and *trans*-[(R)Co(Hdmg)$_2$Py] complexes calculated by B3LYP/LANL2DZp

trans-[(R)Co(Hdmg)$_2H_2O$]		
R	Co–R/Å	Co–OH_2/Å
CI_3	2.09	2.11
CF_2H	1.94	2.15
CF_3	1.95	2.11
CCl_3	2.03	2.11
CBr_3	2.05	2.11
OH_2	—	1.96
CH_3	1.96	2.15
CH_2F	1.94	2.16
CH_2Cl	1.96	2.14
CH_2Br	1.96	2.14
CH_2I	1.96	2.13
trans-[(R)Co(Hdmg)$_2$Py]		
R	Co–R/Å	Co–Py/Å
CH_3	1.98	2.13
CH_2F	1.96	2.14
CH_2Cl	1.98	2.12
CH_2Br	1.99	2.11
CH_2I	1.99	2.11

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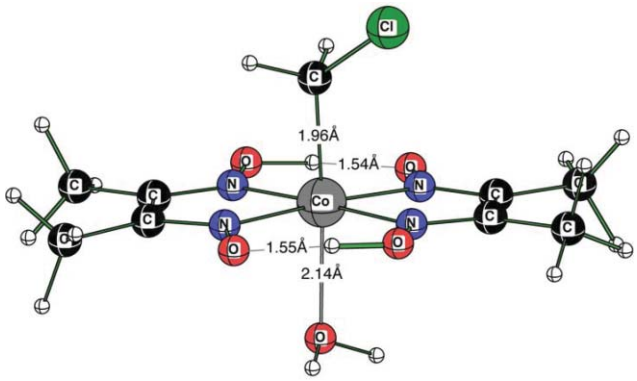

Fig. 6 DFT calculated B3LYP/LANL2DZp structure of *trans*-$[(CH_2Cl)Co(Hdmg)_2H_2O]$.

Discussion

Second order rate constants for substitution of *trans*-$[(CH_3)Co((DO)(DOH)pn)H_2O]^+$ by the series of entering ligands in Table 1 at 25 °C do not depend strongly on the nature of the entering ligand, although the pK_{BH+} values for imidazole, pyrazole, 1,2,4-triazole, and 1-methylimidazole are 7.2, 2.5, 2.3 and 7.2, respectively.[38–40] This is typical for a process that is dissociatively activated, either *via* a dissociative interchange (I_d) or limiting dissociative (D) mechanism. Thus, bond breakage in these reactions seems to largely control the rate and nature of the substitution mechanism. Moreover, it can be seen from the rather similar kinetic data for the reactions with imidazole and 1-methylimidazole that tautomerism present in the imidazole ligand but not in 1-methylimidazole, does not affect the coordination process. The activation volume data support in each case the operation of an I_d mechanism.

The kinetic data in Table 1 for substitution of *trans*-$[(R)Co(Hdmg)_2(H_2O)]$ (R = CH_2Cl, CH_2Br and CH_2I) by thiourea and pyridine show that the overall second order rate constants do not vary drastically on changing the nature of the halomethyl derivatives. This observation is opposite to that expected on the basis of the electronegativity of the halomethyl group. A comparison of other alkyl groups with the halomethyl group shows that the trend in the second order rate constants depends on the *trans* effect and steric influence as seen for the reactions of *trans*-$[(R)Co(Hdmg)_2(H_2O)]$ (R = C_2H_5, $CH_2C_6H_5$, CH_3, CH_2I and CH_2CF_3) for which the second rate constants are 2042, 1445, 132, 8.9 and 0.9 M^{-1} s^{-1}, respectively.[41,42] The second-order rate constant for the reaction of *trans*-$[(CH_2Cl)Rh(Hdmg)_2(H_2O)]$ with thiourea is higher than in the case of cobaloxime complexes, *viz.* 312 and 10.4 M^{-1} s^{-1} at 20 °C, respectively.[43]

The non-linear dependence of k_{obs} on the entering ligand concentration has before been reported for the reaction of *trans*-$[(R)Co(Hdmg)_2(H_2O)]$[19] and aqua-cobalamin[44] with substituted pyridines. The observed saturation kinetics was ascribed to the formation of a precursor adduct that involves both the attacking nucleophile and cobaloxime or cobalamin, in line with a dissociative interchange mechanism. The relatively strong precursor formation was ascribed to a π-interaction of the pyridine ligand with the coordination sphere of the metal complex. This results in the effective binding of the entering nucleophile close to the metal centre during precursor formation, which is followed by an interchange of ligands controlled by the breakage of the Co–H_2O bond *via* an I_d mechanism. The second-order rate constants for the substitution of H_2O in *trans*-$[(R)Co(Hdmg)_2H_2O]$ by pyridine follow the sequence 1.49×10^4 (isopropyl), 1.22×10^3 (phenylethyl), 1.17×10^3 (ethyl), 1.65×10^2 (2-methoxyethyl), 1.64×10^2 (3-cyanopropyl), 1.16×10^2 (methyl), 23.4 (1-propyl),[45] 13.7 (chloromethyl), 5.9 (bromomethyl), 4.9 (iodomethyl), 3.17×10^{-1} (2,2,2-trifluoroethyl)[19] and 5.59×10^{-2} M^{-1} s^{-1} (cyanomethyl)[45] at 25 °C. This sequence suggests that the *trans* effect of the R group decreases in the order isopropyl > phenylethyl > ethyl > 2-methoxyethyl > 3-cyanopropyl > methyl > 1-propyl > chloromethyl > bromomethyl > iodomethyl > trifluoroethyl > cyanomethyl.

The temperature and pressure dependence of the substitution of *trans*-$[(R)Co(Hdmg)_2(H_2O)]$ (R = CH_2Cl, CH_2Br and CH_2I) by thiourea and pyridine for which the data are summarized in Table 1, and Tables S3 and S4 (ESI),† indicate that the second-order rate constants for the reaction with thiourea are characterized by small positive activation entropy and volume data. These support the operation of a dissociative interchange (I_d) substitution mechanism. For the reactions with pyridine, the precursor formation constants K for eqn (7) (see Tables S4 and S5†) are relatively small, approx. 1 M^{-1}, and the thermodynamic parameters indicate that in all three cases precursor formation is an exothermic process, *i.e.* K decreases with increasing temperature. The values of $\Delta S°$ are significantly negative, especially for R = CH_2Cl and CH_2I, indicating the higher order of the intermediate, which is ascribed to weak π-interaction of the pyridine nucleophile with the ligand sphere prior to substitution of water by pyridine. The pressure dependence of this reaction measured at a high pyridine concentration, *i.e.* where eqn (9) simplifies to $k_{obs} = k$, the rate constant for the interchange process (eqn (8)), reveals activation volumes between 5 and 6 cm^3 mol^{-1}, typical for the operation of an I_d mechanism.

The solvent has a significant effect on the second-order rate constant of the ligand substitution reaction. The second order rate constant for substitution of the solvent in *trans*-$[(CH_3)Co((DO)(DOH)pn)S]^+$ by imidazole, pyrazole, 1,2,4-triazole, and 1-methylimidazole were found to fall in the range 68–106 and 20–26 M^{-1} s^{-1} at 25 °C for S = H_2O and MeOH, respectively. The slower reaction in methanol could be due to the partial protonation of an imidazole nitrogen in methanol as solvent,[19,23] and the fact that we are dealing with a totally different leaving group. The values of the second-order rate constants in MeOH are all independent of the nature of the entering nucleophile.

In terms of rate constants and mechanism, the reaction of *trans*-$[(CH_3)Co(Hdmg)_2S]$ with imidazole (S = H_2O and MeOH), pyrazole and 1,2,4-tiazole (S = H_2O),[23] exhibits a well correlated behaviour with the data for the corresponding reactions with *trans*-$[(CH_3)Co((DO)(DOH)pn)S]^+$ as summarized in Table 4. For both *trans*-$[(CH_3)Co(en)_2H_2O]^{2+}$ and aqua-cobalamin, the reactions with certain azoles are more complicated, *viz.* the reaction with 1,2,4-triazole occurs in a biphasic process, where the second slower step was found to be independent of the triazole concentration. It was suggested that in both cases 1,2,4-triazole coordinates to the Co centre through N-1 or N-2 donors in a fast step, followed by a linkage isomerization to bind through N-4.[24,46] In addition, kinetic data for *N*-acetylimidazole binding in both

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Table 4 Kinetic data and activation parameters for the reaction of *trans*-[$(CH_3)Co(Hdmg)_2S$] with imidazole, pyrazole, and 1,2,4-triazole for S = H_2O and MeOH[a]

Ligand	Imidazole[b]	Pyrazole[b]	1,2,4-Triazole[b]	Imidazole[c]
$k_a/M^{-1}\ s^{-1}$	70 ± 1	91 ± 2	71 ± 1	23.6 ± 0.2
$\Delta H^{\ddagger}/kJ\ mol^{-1}$	74 ± 2	79 ± 2	72 ± 3	74 ± 2
$\Delta S^{\ddagger}/J\ mol^{-1}\ K^{-1}$	+40 ± 8	+56 ± 7	+31 ± 9	+29 ± 5
$\Delta V^{\ddagger}/cm^3\ mol^{-1}$	+3.7 ± 0.2	+4.5 ± 0.4	+4.0 ± 0.1	+7.3 ± 0.1

[a] Data taken from ref. 23. [b] S = H_2O. [c] S = MeOH.

Table 5 Comparison of structural, pK_a and $E_{1/2}$ data for *trans*-[$(CH_3)Co((DO)(DOH)pn)H_2O]^+$ and *trans*-[$(CH_3)Co(Hdmg)_2H_2O$]

	trans-[$(CH_3)Co((DO)(DOH)pn)H_2O]^+$	*trans*-[$(CH_3)Co(Hdmg)_2H_2O$]
Co–C/Å[a]	1.977(4)	1.990(5)
Co–O/Å[a]	2.103(3)	2.058(3)
$\alpha/°$[a,b]	+2.0	−4.0
d/Å[a,b]	0.01	0.00
pK_a	12.31[c]	12.68[d]
$E_{1/2}$ *vs.* SCE[e]	−1.30	−2.2

[a] Taken from ref. 61. [b] α is the bending angle between the two equatorial halves and d the displacement of the Co out of the four N-donor plane; positive values for α and d indicate bending towards methyl group and displacement towards H_2O, respectively. [c] From ref. 21. [d] From ref. 62. [e] Values for the half-wave potential *vs.* SCE for the Co(III)–Co(II) reduction at −26 °C, solvent CH_3CN, data taken from ref. 63.

trans-[$(CH_3)Co(en)_2H_2O]^{2+}$ and aqua-cobalamin are consistent with the presence of precursor formation preceding the slow coordination step. In *trans*-[$(CH_3)Co(en)_2H_2O]^{2+}$, the intermediate is suggested to involves hydrogen bonding between *N*-acetylimidazole and equatorial ethylenediamine. In aqua-cobalamin, hydrogen bonding involves the amide side-chain.

To gain further information on the *cis* effect of the equatorial ligand, we examined the axial substitution rates. The *cis* effect is well documented in the case of non-organometallic complexes and generally correlated with the extent of unsaturation of the equatorial ring. For instance, it has been found that the rate constants for the hydrolysis of $Co^{III}(N_4)$ complexes increase as the extent of unsaturation of the equatorial ligand is increased along the series 1,4,8,11-tetraazacyclotetradecane < 1,4,8,11-tetraazacyclotetradecane-1,7-diene < cobaloxime.[47] The substitution reaction of water in *trans*-[$Co^{III}(salen)(H_2O)_2]^+$ represents a case of extreme labilisation of the non-organometallic complexes. The second order rate constants for water substitution in *trans*-[$Co^{III}(salen)(H_2O)_2]^+$ by various nucleophiles,[48] viz. HSO_3^-, $S_2O_3^{2-}$, Py, NCO^- and thiourea, all fall in the range (5–32) × 10^3 $M^{-1}\ s^{-1}$, that is one order of magnitude faster than those of aquacobalamin. This enhancement in the rate constants was attributed not only to the extensive unsaturation of the equatorial ring causing cobalt to lose its d^6 character, but also to a possible deviation of the planarity of the equatorial ring, which is a characteristic feature of the Co-salen complexes.[49] The idea is also accepted that a co-operative effect due to the simultaneous presence of an unsaturated chelating system and a strong activating axial ligand may lead to five-coordinate species as in the case of alkyl cobalt salen and acacen (bis(acetylacetone)ethylenediimine) complexes.[50] These complexes in the presence of strong nucleophiles produce six-coordinate species, probably formed in a diffusion-controlled reaction.

Data from the present study permit a comparison of the *cis* effect for three hexa-coordinate aqua complexes with different equatorial chelates and the same strong *trans* activating group, *viz.* *trans*-[$(CH_3)Co((DO)(DOH)pn)H_2O]^+$, *trans*-[$(CH_3)Co(Hdmg)_2H_2O$] and *trans*-[$(CH_3)Co(en)_2H_2O]^{2+}$. Second order rate constants for the substitution of water by azoles in *trans*-[$(CH_3)Co(Hdmg)_2H_2O$] were found to be 91, 71 and 70 $M^{-1}\ s^{-1}$ at 25 °C for pyrazole, 1,2,4-triazole and imidazole, respectively.[24] These values are very close to those found for the reactions of the corresponding nucleophiles with *trans*-[$(CH_3)Co((DO)(DOH)pn)H_2O]^+$, *viz.* 106, 75 and 95 $M^{-1}\ s^{-1}$, respectively. These values indicate a similar contribution of the two different equatorial ligands in assisting the axial substitution and are in agreement with earlier observations.[22] Available thermodynamic and structural data are collected in Table 5. In this case, neither the pK_a values nor the Co(III/II) half-wave potentials are of much benefit to interpret the kinetic behaviour. This is due to the different formal charges of the two complexes. Thus, the lower pK_a of the imino-oxime mono-cation with respect to the neutral cobaloxime complex may be due to electrostatic repulsion that is larger in the former complex, and consequently these values cannot be taken as a measure of the cobalt-water bond strength. Moreover, it has been shown that the Co(III/II) half-wave potential is strongly affected by the formal charge of the complex.[50]

The bond lengths depend on the nature of the alkyl group and the equatorial ligands, the hybridization of the carbon atom attached to the cobalt centre, steric interactions between the axial alkyl and the equatorial ligands (steric *cis* influence), and the nature of the equatorial ligands.[3,51] The X-ray structure data show that the bond lengths of Co–OH_2 are 1.955(11),[3] 2.058(3),[52] 2.14(2)[53] and 2.153(6) Å[23] for *trans*-[(Br)Co(Hdmg)$_2H_2O$], *trans*-[$(CH_3)Co(Hdmg)_2H_2O$], *trans*-[$(CH_3)Co((DO)(DOH)pn)H_2O]^+$, and *trans*-[$(CH_3)Co(en)_2H_2O]^{2+}$, respectively. The structural data suggest a greater flexibility of the ((DO)(DOH)pn) moiety with respect to $(Hdmg)_2$. However, the expected enhancement in the rate constants of the imino-oxime complexes over the cobaloximes was not experimentally confirmed. The only difference in the two series of complexes lies in their activation volumes. The values for the reactions of pyrazole, 1,2,4-triazole and imidazole with *trans*-[$(CH_3)Co((DO)(DOH)pn)H_2O]^+$ and *trans*-[$(CH_3)Co(Hdmg)_2H_2O$] (in brackets) were found to be +3.7 ± 0.1 (+4.5 ± 0.4), +3.4 ± 0.1 (+4.0 ± 0.1) and +2.7 ± 0.1 (+3.1 ± 0.2) $cm^3\ mol^{-1}$, respectively. Although not large, these differences suggest that an enhanced dissociative character of the process operates in the cobaloximes with respect to the imino-oxime complexes. The activation volumes for the reaction of *trans*-[(R)Co(Hdmg)$_2H_2O$] (R = CH_2Cl, CH_2Br and CH_2I) with pyridine and thiourea clearly support the operation of a dissociative interchange (I_d) mechanism.

The DFT calculated bond lengths in Table 3 and the available structural data are in reasonable agreement for *trans*-[$(CH_3)Co(Hdmg)_2H_2O$] and *trans*-[$(CH_3)Co(Hdmg)_2Py$], *viz.* Co–OH_2 = 2.15 and 2.058[52] Å, respectively, and Co-N(Py) = 2.13 and 2.068[54] Å, respectively. More recent structural data for closely related complexes[55] report Co–OH_2 and Co–N(Py) bond lengths that are in almost perfect agreement with the calculated bond lengths reported in Table 3. The calculated bond lengths for

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Co–O in *trans*-[(R)Co(Hdmg)$_2$H$_2$O], where R = CH_2Cl, CH_2Br and CH_2I, have very similar values which account for the similarity in the second order rate constants. Therefore, the lability of coordinated water in these complexes is the same, which further supports the dissociative character of the reaction mechanism. Apparently, the difference in the electronegativity and σ-donor property of CH_2X (X = Cl, Br and I) is not large enough to affect the rate of the ligand substitution reactions of these complexes.

For the substitution of water by imidazole in *trans*-[(CH_3)Co(en)$_2$H$_2$O]$^{2+}$, the following kinetic parameters were reported:[24] k = 198 ± 13 M^{-1} s^{-1} at 25 °C, $\Delta H^{\ddagger}$ = 53 ± 2 kJ mol^{-1}, $\Delta S^{\ddagger}$ = −22 ± 7 J K^{-1} mol^{-1} and $\Delta V^{\ddagger}$ = +4.7 ± 0.1 cm^3 mol^{-1}. The bond length of Co–OH_2 in *trans*-[(CH_3)Co(en)$_2$H$_2$O]$^{2+}$ is longer than that in *trans*-[(CH_3)Co((DO)(DOH)pn)H$_2$O]$^+$ and *trans*-[(CH_3)Co(Hdmg)$_2$H$_2$O]. The stoichiometric mechanism that is more complicated in the substitution reaction of *trans*-[(CH_3)Co(en)$_2$H$_2$O]$^{2+}$ with respect to the other two complexes, makes it difficult to compare the kinetic parameters for these complexes. Nevertheless, there is little doubt that the same I_d mechanism is operative in all the examined cases. On the basis of the available, it can be concluded that the *cis* effect exerted by the three equatorial systems is of comparable entity and that the main factor governing the axial substitution reactions is the *trans* effect of the strong electron donating methyl group.

Another aspect of the chemistry of imino-oxime complexes that has been considered, concerns the reaction of *trans*-[$(CH_3)_2$Co((DO)(DOH)pn)] with protons. It is well known that mono-alkylated complexes such as *trans*-[(R)Co((DO)(DOH)pn)H$_2$O]$^+$ and *trans*-[(R)Co(Hdmg)$_2$H$_2$O] do not undergo dealkylation in acidic media. However, dialkyl imino-oxime complex in dilute acid generates the mono alkylaqua complex and methane according to eqn (10) and (11). The products of the reaction suggest that a heterolytic cleavage of the cobalt–carbon bond takes place. In order to elucidate the reaction mechanism, we studied the reaction as function of the acid concentration, temperature and pressure. The reaction was studied under nitrogen atmosphere and in absence of light, since it is well known that cobalt-alkyl complexes are light sensitive.

The kinetic data reported for the protonation reaction sequence, (eqn (10) and (11)), presented in Fig. 5 exhibits some curvature from which K = 0.56 ± 0.06 M^{-1} and k = 120 ± 12 s^{-1} were estimated. The overall second-order rate constant, kK, for protonation and release of methane in *trans*-[$(CH_3)_2$Co((DO)(DOH)pn)] is 68 M^{-1} s^{-1} (see Table 2), in satisfactory agreement with the previously reported value of 40 M^{-1} s^{-1} at 25 °C and 0.10 M ($LiClO_4$) ionic strength.[31] The curvature in Fig. 5 is too small to allow a detailed study of the temperature and pressure dependence of both K and k. We, therefore, selected a low [H^+] (≤ 0.025 M) where eqn (9) reduces to $k_{obs} = kK[H^+]$, to study the temperature and pressure dependence of the overall second-order rate constant (see Table 2). The low value of $\Delta H^{\ddagger}$ (37 ± 1 kJ mol^{-1}) suggests that little energy is required for the proton-assisted elongation of the cobalt–carbon bond on going from the ground state to the transition state. This is expected on the basis of the strong *trans* effect exerted by the non-labile methyl group on the outgoing methyl group. However, the reaction is slowed down because of the unfavourable (negative) value of $\Delta S^{\ddagger}$ (−86 ± 3 J mol^{-1} K^{-1}). The negative values of both $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$ (−18.9 ± 0.7 cm^3 mol^{-1}) are consistent with a polar transition state, where electrostriction effects play an important role. This is coherent with a bimolecular process, where the transition state may be seen as a mono-cationic species since it forms through the interaction of the neutral complex with a proton.

A question that arises from the fact that Co((DO)(DOH)pn) complexes are capable to generate dialkyl complexes, but not so in the case of the corresponding cobaloximes. This is rather surprising since the data reported in the first part of the paper concerning axial ligand substitution clearly indicate that the transmission of electronic and steric effects exerted by the methyl group in the *trans* position occur to about the same extent in the two types of complexes. In order to justify this apparent incongruence, an attractive hypothesis can be made on the basis of kinetic arguments. It can be imagined that cobaloximes are also capable to generate (short-lived) dialkyl derivatives. The reaction of these mono-anionic species with protons could involve neutral transition states. Such a process must to be characterized by positive activation entropies, which are associated with fast reactions rendering the detection of the dimethyl-cobalt complex to be problematic. Similarly to that observed for cobaloximes, there is no evidence for the occurrence of dialkyl corrinoids.[56–58] However, it has been observed that the reaction of the Co(I) form B_{12s} with methyl iodide produces in addition to methyl-cobalamin (the so called methylcobalamin β) a small amount of methylcobalamin α, a distereoisomer in which the methyl group replaces the 3,5-dimethyl benzimidazole in the "lower" position and water occupies the "upper" axial position. Later,[59,60] several other alkylcobalamins with more complicated alkyl groups have been characterized both in the α and β form, and facile α/β diastereomerism has been demonstrated to occur in several cases. Although, evidence for dialkyl cobalamines has not been reported, it is reasonable to hypothesize the existence of these complexes as unstable intermediates.

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