Structures of intermediates produced in acid and base hydrolysis of complexes of cobalt(III); a molecular-orbital and molecular-mechanics study

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A molecular-orbital study is used to generate spin-paired square-pyramidal $[Co(NH_3)_5]^{3+}$ (mean Co–N 1.97 Å), as well as an $S = 1$ trigonal-bipyramidal intermediate (mean Co–N 2.05 Å), which are proposed intermediates in substitution reactions of cobalt(III) complexes, and a molecular-mechanics model of these five-coordinate species is used to explore steric aspects of the kinetics of substitution on complexes of cobalt(III).

Many years of extensive experimentation have demonstrated[1–5] that in ligand-substitution reactions of Co^{III}, a square-pyramidal (*SPY*) transition state is formed by rate-determining loss of one unidentate ligand. If this *SPY* species is sufficiently long lived, it rearranges to a trigonal-bipyramidal (*TBPY*) intermediate, with loss of configuration. Compared to other nucleophiles, ligand replacement by OH^- is some 10^6 times faster, where the intermediate is stabilised by deprotonation of an N–H group on the complex, and π bonding between R_2N^- and Co^{III}. The electronic and molecular structure of these five-coordinate species is unknown.

There seems to be[5] a steric contribution from non-exchanging ligands to rates of ligand substitution. For example, as ethylenediamine (en) ligands on complexes such as $[Co(en)_2Cl_2]^+$ have progressively more C-methyl groups added, the rate of acid hydrolysis to lose chloride increases rapidly. Generation of *SPY* and *TBPY* intermediates by molecular-orbital (MO) calculations, and parameters for modelling these intermediates by molecular mechanics (MM), are presented. The program ZINDO[6,7] has been incorporated in the CAChe

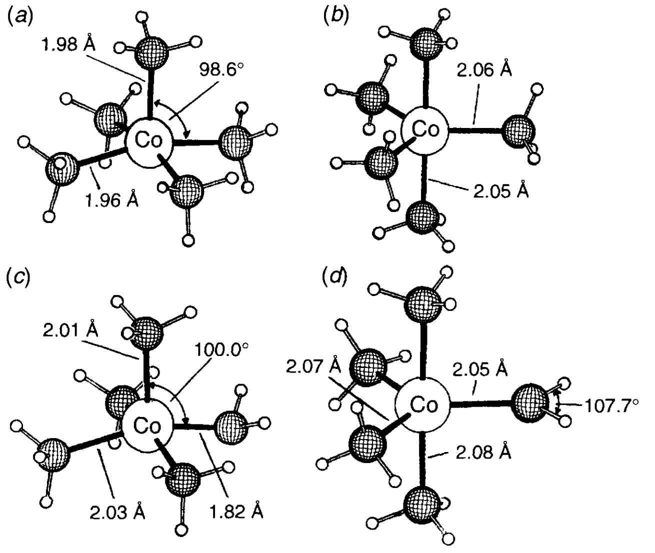

Fig. 1 Structures of five-coordinate intermediates produced in substitution reactions of $[Co(NH_3)_5Cl]^{2+}$. Structures (*a*) and (*b*) are respectively the ($S = 0$) square-pyramidal and ($S = 1$) trigonal-bipyramidal $[Co(NH_3)_5]^{3+}$ intermediates, produced during acid hydrolysis; (*c*) and (*d*) are respectively the corresponding structures for the $[Co(NH_3)_4(NH_2)]^{2+}$ intermediates produced during base hydrolysis. Cross-hatched atoms are nitrogen and small open circles are hydrogen. The structures were generated with the program ZINDO.[6,7]

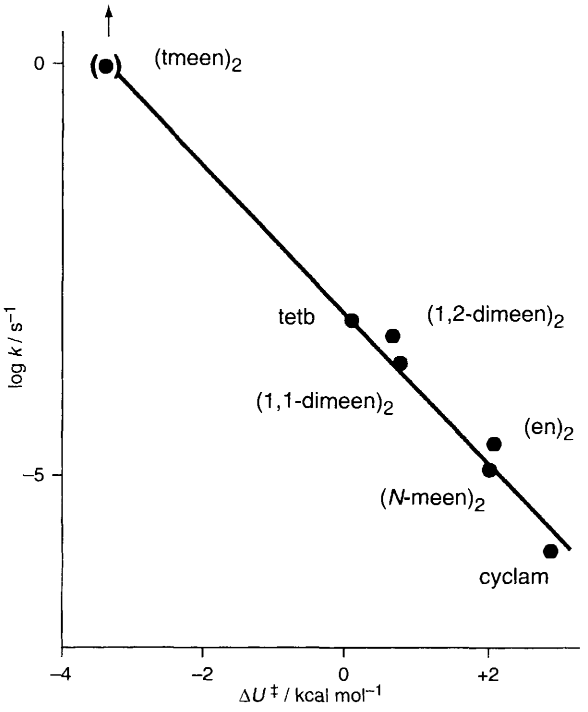

Fig. 2 Correlation between the logarithms of the rate constants (log *k*) for acid hydrolysis[5] of *trans*-$[Co(L–L)_2Cl_2]^+$ complexes to give $[Co(L–L)_2Cl(H_2O)]^{2+}$, and $\Delta U^‡$, the steric energy of activation, which is the difference in steric energy between the ground-state *trans*-$[Co(L–L)_2Cl_2]^+$ complex, and transition-state $S = 0$ square-pyramidal $[Co(L–L)_2Cl]^{2+}$ species. The non-leaving ligands (L–L) are en, 1,1,2,2-tetramethyl-1,2-diaminoethane (tmeen), 1,1,-dimethyl-1,2-diaminoethane (1,1-dimeen), *rac*-1,2-dimethyl-1,2-diaminoethane (1,2-dimeen), *N*-methylethylenediamine (*N*-meen); or $(L–L)_2$, 1,4,8,11-tetraazacyclotetradecane (cyclam), or *rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (tetb).

Acid hydrolysis:

$[Co(NH_3)_6]^{3+} - NH_3 \longrightarrow [Co(NH_3)_5]^{3+}\ (SPY,\ S = 0) \longrightarrow [Co(NH_3)_5]^{3+}\ (TBPY,\ S = 1)$

Base hydrolysis:

$[Co(NH_3)_5(NH_2)]^{2+} - NH_3 \longrightarrow [Co(NH_3)_4(NH_2)]^{2+}\ (SPY,\ S = 0) \longrightarrow [Co(NH_3)_4(NH_2)]^{2+}\ (TBPY,\ S = 1)$

Scheme 1

program,[8] and can be used[6,7] for modelling complexes of transition-metal ions. *SPY* and *TBPY* structures were generated of both $[Co(NH_3)_5]^{3+}$ and $[Co(NH_3)_4(NH_2)]^{2+}$, the respective intermediates in acid and base hydrolysis of a complex such as $[Co(NH_3)_5Cl]^{2+}$. These were then energy-minimized using ZINDO. A low-energy spin-paired ($S = 0$) *SPY* complex was found for $[Co(NH_3)_5]^{3+}$ (Fig. 1). The *TBPY* $S = 0$ form is 30 kcal mol^{-1} (cal = 4.184 J) higher in energy, and should not be important in reactions of Co^{III}. With two unpaired electrons ($S = 1$) the *TBPY* complex becomes the more stable (Fig. 1). The calculations performed here refer to the gas phase, and ignore solvation effects. They suggest, however, that the *SPY* and *TBPY* intermediates formed in the base-hydrolysis sequence shown in Scheme 1 are of considerably lower energy than those formed in the acid-hydrolysis sequence, accounting for the greater rapidity, and loss of configuration, of base-hydrolysis reactions.

Table 1 Force-field parameters required, in addition to those present[9] in MM2, for modelling the transition-state complexes of the type $[Co(L\text{–}L)_2Cl]^{2+}$, where Co^{III} is low spin with square-pyramidal coordination geometry, and L–L is a saturated polyamine[a]

Co^{III} (*SPY*, $S = 0$)		
Bond length deformation[b]		
	K_B/mdyn A^{-1}	r^0/Å
Co–N	2.5	1.93
Co–Cl	1.4	2.20
Bond angle deformation[c]		
	K_θ/mdyn Å rad^{-2}	θ^0/rad
N–Co–N	0.43	1.571
Co–N–C	0.63	1.911
Co–N–H	0.36	1.911
N–Co–Cl	0.45	1.571

[a] All torsional constants involving the metal ion are set to zero. [b] K_B is the bond length deformation constant, and r^0 is the ideal bond length. 1 mdyn = 10^{-8} N. [c] K_θ is the bond angle deformation constant, and θ^0 is the ideal bond angle.

Table 1 gives additional parameters to those present[10] in MM2, for modelling $S = 0$ *SPY* transition-state complexes of Co^{III}. Steric energies of the ground-state complex, *trans*-$[Co(L\text{–}L)_2Cl_2]^+$, and of the transition state *SPY* ($S = 0$) $[Co(L\text{–}L)Cl]^{2+}$, were calculated using MM2, where L–L is a variety of polyamines (Fig. 2). The energy difference between the ground- and transition-state complexes is then $\Delta U^{\ddagger}$, the steric component of the activation energy. Fig. 2 shows a good inverse relationship between $\Delta U^{\ddagger}$ and the logarithm of the rate constant for acid hydrolysis[5] of *trans*-$[Co(L\text{–}L)Cl_2]^+$ complexes. These results suggest that MO and MM calculations will be useful in analysing steric aspects of substitution reactions of transition-metal complexes.

The author thanks the Foundation for Research Development, and the University of the Witwatersrand, for generous support for this work.

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Received, 8th January 1996; Com. 6/00141F