A Novel Kinetic *Cis* Effect Induced by Coordinated Sulfite in Cobalt(III) Amine Complexes

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Presently the literature witnesses an increased interest in the coordination chemistry of sulfitocobalt(III) complexes [1]. Evidence has accumulated over the last decade that the coordinated sulfito ligand in cobalt(III) complexes exerts a strong kinetic as well as a structural *trans* effect. No indications of significant *cis* effects have been reported.

Proton exchange rate constants are a convenient qualitative measure for the *trans* effect in cobalt(III) amine complexes [2]. Normally in complexes $[Co(NH_3)_5X]^{n+}$ the hydrogens on the NH_3 positioned *trans* to X exchange more rapidly than the *cis* ones [2, 3]. *Trans* labilizing ligands as CN^- and NO_2^- [2, 3] and possibly SO_3^{2-} [2] decelerate the exchange of hydrogens on a *trans*-coordinated NH_3. The ligands CN^- and NO_2^- are also anomalous by the fact that for their pentaamminecobalt(III) complexes the ^1H NMR resonances of *cis* hydrogens do not appear downfield from the *trans* ones [2–5]. In view of these exceptions it would be interesting to have chemical shift and proton exchange data for the $[Co(NH_3)_5(SO_3)]^+$ ion. Unfortunately, this ion is only stable in ammoniacal aqueous solution [6], where proton exchange is too rapid to be followed and solution ^1H NMR is impossible. Therefore we studied the sulfito complex in liquid ammonia, in which solvent it is also stable and the exchange can be slowed down by adding acid (NH_4ClO_4). ^1H NMR (90 MHz) resonances (at –36.5 °C; solvent peak saturated before acquisition; δ relative to the solvent) were observed at 2.33 ppm (12 H, *cis*-NH_3) and 3.51 ppm (3 H, *trans*-NH_3). As expected the resonances follow the order of the nitro and the cyano complexes.

The rate of *trans*-NH_3 solvent exchange (k_{ex}) was obtained from the disappearance (obeying a first-order rate law) of the ^1H(*trans*-$^{15}NH_3$, $J(^{15}N–H)$ = 68 Hz) doublet of the labelled *trans*-$[Co(NH_3)_4(^{15}NH_3)(SO_3)]ClO_4$ [7]. k_{ex} (–36.5 ± 0.2 °C, I = 1.00) = (0.35 ± 0.05) × 10^{-4} s^{-1}, independent of the acid concentration, varied between 10^{-3} and 0.6 mol kg^{-1}. The H–D exchange was studied in ND_3 by observing the disappearance of the ^1H resonances under the conditions indicated for k_{ex}. The proton exchange process is clearly acid dependent, as expected for amminecobalt(III) complexes [7, 8]. As H–D exchange at *trans*-NH_3 and loss of NH_3 (solvent exchange) had similar rates, a deviation from first-order behaviour was observed. Approximate values for the rate constant of the overall process of H–D exchange range from 10^{-4} ($[NH_4ClO_4]$ = 3 × 10^{-3} mol kg^{-1}) to 2.5 × 10^{-4} (10^{-3} mol kg^{-1}) s^{-1}.

Assuming the rate law for proton exchange at trans-coordinated NH_3 to be: $k_{trans} = k^1_{trans}[NH_4ClO_4]^{-1}$ [9], k^1_{trans} is approximately 2 × 10^{-7} s^{-1} mol kg^{-1}. As the H–D exchange at *trans*-NH_3 of $[Co(NH_3)_5Cl]^{2+}$ is instantaneous, down to –74 °C and high acidity (1 mol kg^{-1}), the *trans*-positioned sulfito group strongly decelerates the proton exchange. Clearly both the kinetic *trans* effects, the labilization of the *trans*-coordinated NH_3 group and the deceleration of proton exchange at this position are present in the sulfitopentaamminecobalt(III) ion.

The most remarkable effect found in this study is the deceleration of H–D exchange at the ammine sites in the *cis* position. Again in ND_3, under the above conditions, we found the exchange rate to obey the rate law: $k_{cis} = k^1_{cis}[NH_4ClO_4]^{-1}$ [9], with k^1_{cis} = (7 ± 1) × 10^{-7} s^{-1} mol kg^{-1}. At the temperature used (–36.5 °C) the extrapolated value for k^1_{cis} of the chloropentaamminecobalt(III) ion is: 6 × 10^{-4} s^{-1} mol kg^{-1} [10]. Apparently there is a substantial *cis* decelerating effect exerted by the coordinated sulfito group on the exchange of ammine protons at the *cis* positions. No similar effect has been observed for ligands with otherwise comparable behaviour, as CN^- and NO_2^- [3]. Qualitative measurements on H–D exchange in D_2O at the *cis* positions of *trans*-$[Co(en)_2(SO_3)(NH_3)]^+$ and *trans*-$[Co(en)_2(SO_3)(H_2O)]^+$ indicated a similar extraordinary inertness induced by the sulfito ligand. The observation reported here is valuable for two fields of research: first, the theory of the *trans* effect, connecting lability, proton exchange and chemical shifts. Second, it offers the possibility of constructing complexes with proton sites ineffective towards deprotonation, to be used as model compounds demanded in the study of the conjugate-base mechanism.

As an example of the second class of applications we studied the ammoniation of the *trans*-$[Co(en)_2(SO_3)(DMSO)]^+$ ion. Independent of reaction conditions (temperature varied between –70 and –35 °C and acid concentration between 2 × 10^{-3} and 0.5 mol kg^{-1}) this ion instantaneously gives *trans*-$[Co(en)_2(SO_3)(NH_3)]^+$. The reaction product was identified by its ^1H NMR (250 MHz,

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-70 °C; solvent signal suppressed) spectrum: δ (relative to the solvent) = 1.6 and 1.8 ppm (8 H, H–C); 1.7 ppm (6 H, uncomplexed $(CH_3)_2SO$); 2.80 ppm (3 H, *trans*-NH_3); 3.28 and 4.90 ppm (each 4 H, N–H). Substitution of NH_3 by ND_3 as solvent gave an identical product spectrum, with only the 2.80 ppm resonance missing. Repeating the experiment with the fully N-deuterated complex in NH_3 also resulted in the spectrum of the *trans*-amminesulfito complex. However, this time the N–H resonances of ethylenediamine were completely missing and only appeared after some time, without any accompanying change in the other resonances. From the reaction sequences outlined above it follows that not a simple proton of the amine complex is exchanged during ammoniation. This makes the *trans*-$[Co(en)_2(SO_3)(DMSO)]^+$ unique, as the first cobalt(III) amine complex, for which a spontaneous (not base-catalyzed) ammoniation is demonstrated. Undoubtedly, this phenomenon is due to the combination of the kinetic *trans* effect on the coordinated DMSO and the kinetic *cis* effect on the *cis* N–H deprotonation.

Preparations

$[Co(NH_3)_5(SO_3)]ClO_4$ and its $^{15}NH_3$-labelled analogue were prepared as described earlier [11].

trans-$[Co(en)_2(SO_3)(H_2O)]ClO_4$ was synthesized according to Baldwin [12]. The compound was deuterated in D_2O at pD = 10, followed by rapid addition of $HClO_4$ to pD = 1. The per-N-deuterated complex then precipitated as the perchlorate. The procedure was repeated to get >99% isomeric purity. *trans*-$[Co(en)_2(SO_3)(DMSO)]ClO_4$ and its per-N-deuterated analogue were prepared by dissolving the respective *trans*-aquasulfito compound (1.9 g) in 40 ml dried, slightly acidified DMSO, nearly saturated with $LiClO_4$. The rapidly formed DMSO complex was precipitated with ethanol, washed with ethanol and ether and dried *in vacuo*.

The identity and the purity of the compounds used in this study were checked by ^1H NMR.

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