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Rate of Proton Exchange at Cobalt(III) Amine Complexes in Liquid Ammonia

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A way towards a more detailed understanding of the conjugate-base mechanism [1] for the hydrolysis of inert amine complexes of cobalt(III) and rhodium(III) has been opened by the realization that liquid ammonia as solvent, enables a separation of parameters for pre-equilibrium (K^{CB}) and rate-determining step [2, 3]. In working out this separation a disturbing factor soon becomes apparent. A single polyamine complex generally contains more than one potentially acidic proton, while each proton is characterized by its own acidity constant K^{CB}. This leads to a double problem: which of the protons in the complex is the most acidic one and which deprotonation leads to the most reactive conjugate base [4, 5]. For aqueous solutions this problem has been attacked by measuring ^{2}H–^{1}H exchange at cobalt(III) complexes [6], taking the rate of exchange as a criterion for the acidity [4]. However, this procedure has been criticized on the grounds that the inherent assumption of a constant (diffusion controlled) rate of proton capture could be proved to be invalid in at least one case [5].

As a start to the treatment of the problem of different acidity of geometrically different H-atoms in cobalt(III) amines in liquid ammonia we present here preliminary ^{2}H–^{1}H exchange rate measurements on the fully N-deuterated forms of the compounds $Co(NH_3)_6(ClO_4)_3$, $Co(NH_3)_5Cl(ClO_4)_2$, $Co(NH_3)_5F(ClO_4)_2$, and *trans*-Co{(RS)-2,3,2-tet}Cl_2ClO_4 [(RS)-2,3,2-tet = (RS)-1.9-diamino-3,7-diazanonane].

Experimental

The cobalt(III) complexes were prepared and deuterated by conventional methods; the other chemicals used were of analytical grade and were dried before use. Liquid ammonia solutions of the ammine complexes (0.30 m; m = mol kg^{-1}) of varying acidity (realized by adding ammonium perchlorate) and constant ionic medium (added potassium perchlorate, I = 1.5 m for the hexaammine and I = 1.0 m for the pentaammines) in a 10 mm diameter NMR tube were prepared at a temperature at least 10 °C lower than the measuring temperature. The tubes were then transferred to the sample compartment of a Bruker WH-180 WB Fourier NMR spectrometer (operating at 4.3 Tesla; ^{2}H at 27.64 MHz) and quickly brought to temperature with the help of a specially constructed thermostat using cold nitrogen gas to give a temperature constancy inside the NMR tube of ±0.5 °C. The ^{2}H–^{1}H exchange rate was then calculated from the decrease in time of the ^{2}H NMR peak area relative to the total ^{2}H area. ^{2}H NMR was used instead of ^{1}H NMR because of the advantage of using NH_3 over N^2H_3 as solvent. For each kinetic run *circa* 20 data points were collected up to 4 half flives of the exchange. A first-order rate-law was strictly adhered to (correlation coefficient >0.995), showing the absence of a secondary kinetic isotope effect.

TABLE I. Rates of ^{2}H–^{1}H Exchange at Cobalt(III) Ammines in Liquid Ammonia.

Temp. °C	$(NH_4ClO_4)^{-1}$ m^{-1}	10^4 k$_{obsd}$^{a} s^{-1}
	$Co(N_2H_3)_6(ClO_4)_3$	
−61.5	5	8.8
−61.5	10	9.4
−61.5	20	10.8
−67.5	5	1.4
−67.5	10	1.5
−67.5	47	2.6
−74.5	25	0.3
	$Co(N_2H_3)_5Cl(ClO_4)_2$	
−56.5	5	2.1^c
−56.5	10	3.1^c
−56.5	20	4.0^c
−56.5	47	10.9^c
−71.0	0.3	35^t
−79.0	0.3	5.6t
	$Co(N_2H_3)_5F(ClO_4)_2$	
−52.5	5	4.3^c 6.9^t
−52.5	10	4.7^c 7.1^t
−52.5	20	5.2^c 7.7^t

^{a}*c* = *cis* position; t = *trans* position.

Results and Discussion

For all compounds studied the exchange rates were found to be dependent on the acidity of the

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TABLE II. Rate Parameters for $^2H–^1H$ Exchange.

Compound	Temp. °C	$10^4\ k_0^a$ s^{-1}	$10^5\ k_1^a$ ms^{-1}
$Co(N_2H_3)_6(ClO_4)_3$	–67.5	1.2	0.3
	–61.5	8.1	1.3
	–56.5	36^b	4.1^b
	–52.5	106^b	9.4^b
$Co(N^2H_3)_5Cl(ClO_4)_2$	–56.5	0.7^c	2.1^c
$Co(N^2H_3)_5F(ClO_4)_2$	–52.5	4.1^c	0.6^c
	–52.5	6.6^t	0.5^t

[a] c = *cis* position; t = *trans* position. [b] Extrapolated values.

solution and followed the relation: $k_{obsd} = k_0 + k_1 (NH_4ClO_4)^{-1}$. The exchange results are collected in Table I. The values of the rate parameters k_0 and k_1 are summarized in Table II. In general geometrically different ^1H atoms give different chemical shifts [7], thus allowing separate monitoring of *cis* and *trans* protons in pentaammines [4]. This advantage is partially lost for ^2H chemical shifts. Only $Co(N^2H_3)_5F^{2+}$ gave separate *cis* and *trans* ^2H shifts. For $Co(N^2H_3)_5Cl^{2+}$ the exchange of 20% of the deuterons was immeasurably fast at the temperature (–56.5 °C) used for the study of the exchange of the remaining 80% deuterons. Obviously the *trans* deuterons exchange much faster than the *cis* ones. Only at –71 °C and an ammonium concentration of 3 m was a measurable rate for the first 20% exchange (*trans* deuterons) attained.

As the NMR method used limited the range of magnitude of the rate constants to be measured, no direct comparison of experimental rate data for different complexes at one temperature is possible. Therefore the results on the hexaammine were extrapolated to other temperatures using the Eyring formula (Table II).

In spite of the limited number of data several interesting conclusions issue from an inspection of the Tables:

1) Proton (deuteron) abstraction follows two pathways, an acid dependent (k_1) and an acid independent (k_0) one, evidently corresponding to a reaction with NH_2^- and NH_3 respectively. The relative importance of each route changes with the complex. The general absence of the k_0 term for proton exchange in acidified aqueous solutions [1] may reflect the higher value of the autoprotolysis constant of water over liquid ammonia and/or the lower nucleophilicity of H_2O compared to NH_3.

2) The exchange rates show a pronounced temperature dependence, which must be nearly equal to that of the reverse reaction, as the acidity constants are nearly temperature independent [2, 8, 9].

3) The acidity of the various cobalt(III) amine complexes has been shown to be comparable in magnitude by both kinetic [2, 9] and potentiometric [8, 9] methods. The exchange rates, however, are markedly different. This point emphasizes Tobe's warning [5] against taking exchange rates as a measure of acidity.

4) A distinct difference exists between exchange rates of protons (deuterons) on NH_3 groups coordinated *cis* or *trans* to the group X in compounds $Co(NH_3)_5X(ClO_4)_2$. This difference is clearly dependent on the nature of the group X. Similar effects have been found for aqueous solutions [10].

5) For the labile (as to chloride ammoniation) complex $Co(NH_3)_5Cl(ClO_4)_2$ the assumption of a rapid acid to conjugate base pre-equilibrium preceding the rate-determining step is vindicated: at –56.5 °C the rate of ammoniation obeys the relation $k_{obsd} = 10^{-9} (NH_4ClO_4)^{-1}$ (extrapolated from reference 2), which is several orders of magnitude smaller than the rate of proton exchange.

Finally it seemed of interest to look at one of the few compounds for which proton abstraction is rate limiting in base-hydrolysis. For this we choose the *trans*-Co{(RS)-2,3,2-tet}Cl_2ClO_4 [11]. This complex has two rapidly exchanging secondary and four much slower exchanging primary protons. In aqueous solution the ^1H chemical shift of the two kinds are clearly separated [11]. In liquid ammonia the fully N-deuterated complex only showed one ^2H band. The disappearance of the first 33% of this band is several orders of magnitude larger than that of the remaining 67%. In this way secondary (33%) and primary (67%) deuterons may still be distinguished.

In liquid ammonia both secondary $^2H–^1H$ exchange ammoniation of this complex appeared to be so rapid that only at –80 °C and an ammoium perchlorate concentration of 3 m (both the reactions are strongly acid dependent) reasonably accurate half lives of the reactions could be established. To attain these conditions it was necessary to dissolve the complex rapidly in the appropriate medium, already brought to the temperature of the NMR probe. The half life $t_{1/2}$ for the $^2H–^1H$ exchange was 50 ± 20 s. Under the same circumstances a photometric determination of the rate of ammoniation of the deuterated complex to the *trans*-chloroammine complex gave a $t_{1/2}$ of 60 ± 5 s. Under these conditions the primary deuterons exchange with $t_{1/2}$ = 2 h. Clearly also in liquid ammonia for this complex the abstraction of a secondary proton, of necessity leading to the reactive conjugate base, is comparable in rate to the solvolysis. A further elaboration of this conclusion awaits the determination of the relative importance of the spontaneous ammoniation route which seems to be of exceptional importance for the *trans*-dichlorocobalt(III) structure [9].

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References

1 M. L. Tobe, *Accounts of Chem. Research, 3,* 377 (1970).
2 S. Balt and G. F. Pothoff, *J. Coord. Chem., 4,* 167 (1975).
3 S. Balt, *Inorg. Chem., 18,* 333 (1979).
4 D. A. Buckingham, B. M. Foxman and A. M. Sargeson, *Inorg. Chem., 9,* 1790 (1970).
5 E. Ahmed and M. L. Tobe, *Inorg. Chem., 15,* 2635 (1976).
6 Of course this is only one of the methods reported in the literature. Additional information has for instance been obtained by considering series of polydentate amine complexes (See R.A. Henderson and M. L. Tobe, *Inorg. Chem., 16,* 2576 (1977)) or cleverly designed compounds (See D. A. Buckingham, P. J. Cresswell and A. M. Sargeson, *Inorg. Chem., 14,* 1485 (1975)).
7 H. Yoneda and Y. Nakashima, *Bull. Chem. Soc. Japan, 47,* 669 (1974).
8 S. Balt and W. de Kieviet, *J. Solution Chem., 7,* 915 (1978).
9 S. Balt, J. Breman and W. de Kieviet, *J. Inorg. Nucl. Chem., 41,* 331 (1979).
10 T. Taura, U. Sakaguchi and H. Yoneda, *Bull. Chem. Soc. Japan, 49,* 1867 (1976) and references therein.
11 G. Marangoni, M. Panayotou and M. L. Tobe, *J. Chem. Soc. Dalton,* 1989 (1973).