Absence of Common Five-co-ordinate Intermediates in the Induced Reactions of Some Cobalt(III)–Acido Complexes

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Summary The stereochemistry of the aqua and hydroxo products formed in the induced aquation (Hg^{2+}, Ag^+, NO^+) and base hydrolysis reactions of anti-p, syn-p, and s-[Co(Metren)NH_3X]$^{n+}$ ions ($n = 2$ or 3; tren = 2,2′,2″-triaminotriethylamine; X = Cl, Br, N_3, NH_3; p = primary, s = secondary) show a dependence on leaving group, type of reaction, and reactant stereochemistry, thereby eliminating the formation of common intermediates.

CONSIDERABLE evidence now exists for the formation of common 5-co-ordinate intermediates in the induced aquation and base hydrolysis of colbalt(III)–acido complexes of the type [Co(NH$_3$)$_5$X]$^{2+}$.[1] This evidence comes from two main sources; the stereochemistry of the products is independent of leaving group, and the competition ratios for nucleophiles relative to water (both anions and neutral species) are also essentially independent of leaving group. The first set of data includes the Hg^{2+} (X = Cl, Br, I),[2] NO^+ (N_3, NH_2CO_2)[2,3] and, more recently, Cl_2 induced oxidation (Me_2SO)[3,4] of trans-[(NH$_3$)$_4$(ND$_3$)CoX]$^{2+}$ or of cis- and trans-[Co(en)$_2$YX]$^{n+}$ ($n = 1$ or 2; en = ethylenediamine; X = Cl, Br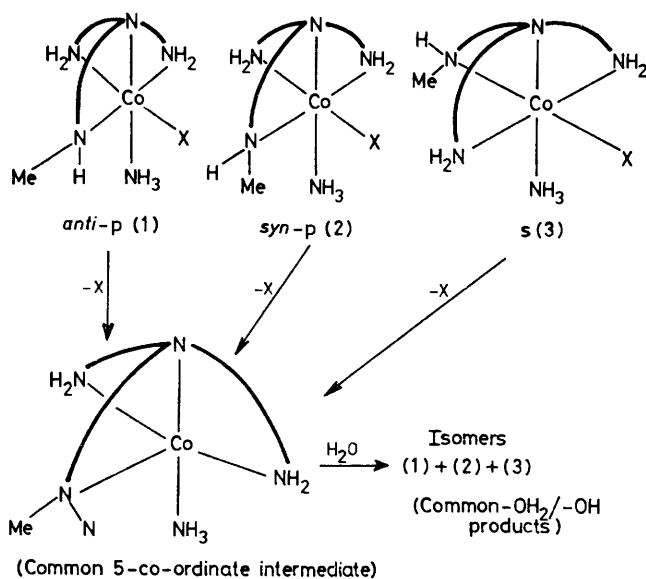, N_3, NH_3) ions,[5,6] while both properties have been observed in the various products of base hydrolysis of a previously studied cobalt(III)–acido ions.[1,7]

By choosing a rather delicately balanced ligand stereochemistry in an otherwise normal cobalt(III)–amine system we have now been able to show that the stereochemical criteria are not upheld, and that common 5-co-ordinate intermediates do not exist in either the induced aquation or base hydrolysis reactions. The choice of ligand stereochemistry also gives some appreciation of the lifetime of the 5-co-ordinate intermediate, and the direction of entry of the incoming water molecule or competing anion.

The three [Co(Metren) (NH$_3$)X]$^{n+}$ ($n = 2$ or 3; tren = 2,2′,2″-triaminotriethylamine) isomers‡ (1), (2), and (3) were chosen because the direction of entry of H_2O can easily be determined, and only a small bond rotation ($<30°$) is necessary in a limiting dissociative process (D) to make the three 5-co-ordinate intermediates equivalent. Trigonal bipyramidal intermediates of this type are clearly called for since the induced aquation and base hydrolysis of these 'red' p-[Co(Metren) (NH$_3$)X]$^{2+}$ ions‡ leads exclusively to p-products.[8] Also, structures of this stereochemistry have been demonstrated for all known cases of 5-co-ordinate metal complexes containing tren or Me_6tren.[9]

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‡ The nomenclature employed here is a logical extension of that used for the [Co(tren)(NH$_3$)X]$^{2+}$ ions (ref. 8) viz., p-, s-, and t- denote primary, secondary, and tertiary N centres, respectively, trans to the electronegative group X, and anti- and syn- denote the relationship of the methyl substituent to X.

anti-p (1)   syn-p (2)   s (3)

(Common 5-co-ordinate intermediate)

The various p-[Co(Metren) $(NH_3)X]^{n+}$ complexes ($n = 2$ or 3; X = Cl, Br, N_3, NH_3) were prepared, and their configurational isomers separated by methods to be given in detail elsewhere.[10] The stereochemistries of the chloro complexes have been defined by X-ray studies on two of the isomers, and the stereochemistries of the bromo, azido, ammino, and aqua ions have been related to these by the rates and products of the various induced reactions (Hg^{2+}, NO^+, OH^-), and by [1]H n.m.r. spectra.[10] The configuration of one of the [Co(Metren)$(NH_3)_2](ClO_4)_3$ isomers remains uncertain at present since, under the conditions of base hydrolysis, two of the hydroxo products, the syn-p- and anti-p-forms, mutarotate rapidly.

The stereochemistries of the products (Table) were determined using 9% and (subsequently) 30% [13]CH_3-enriched

complexes. The [1]H n.m.r. spectra (Varian HA-100 or FX-60) of the aqua products clearly distinguished the s- from the syn-p + anti-p ions, while [13]C n.m.r. spectra (FX-60) distinguished the anti-p from the syn-p + s products. 150—200 mg of the complex in ca. 2 ml of D_2O was used and, following the reaction, data collection took ca. 2 min for each nuclei. In this way slow isomerization and mutarotation processes were avoided.[10] Reproducibility within each experiment was excellent (1—2%), and the experiments were normally at least duplicated. For base hydrolysis the products were quenched to pH 1 or ca. 4 ($DClO_4$, CF_3CO_2D) before measurement, and other experiments showed that no significant isomerization occurred in the hydroxo ions under the hydrolysis conditions.

The products (Table, expts. 5—7) show a dependence on reaction type (Hg^{2+}, Ag^+, NO^+, base hydrolysis), nature of the acido group [X = Cl or Br (Hg^{2+}, Ag^+), X = Cl, Br, or NH_3 (base hydrolysis)], and stereochemistry of the reactant [isomers (1), (2), and (3)]. Thus for all three isomers the Hg^{2+} (expts. 1—6) and Ag^+ (expts. 7—11) induced removal of Cl and Br do not agree, and a similar result obtains for the NO^+ catalysed removal of N_3 (expts. 12—14). A common intermediate, or set of intermediates, is therefore not possible for these processes. A similar leaving group dependence obtains for base hydrolysis. Larger amounts of 3-OH are formed from 1-Cl (expt. 15) than from 1-NH_3 (expt. 17), and a more obvious difference is shown in the 3-OH formed from 3-Cl, 3-Br, and 3-NH_3 (expts. 20—23). Under the latter conditions, 1-OH and 2-OH mutarotate rapidly so that a common ratio obtains (ca. 10:1) for these species independent of reactant. The differing amounts of 3-OH however rules out a common 5-co-ordinate intermediate for the different leaving groups of the same isomer, and for the same leaving group with the three isomers.

This new evidence can be accommodated by either a purely dissociative process in which each 5-co-ordinate intermediate reacts with its own pre-conditioned immediate environment before this has had time to equilibrate with the

TABLE. Products of the Hg^{2+}, Ag^+, and NO^+ induced aquation and base hydrolysis reactions of the three [Co(Metren) $(NH_3)X]^{n+}$ isomers ($n = 2$ or 3; X = Cl, Br, N_3, NH_3) at 25 °C with [Co] = 0·15—0·3 mol dm^{-3}.

Expt.	Reactant isomer	X		Conditions[a]	$-OH_2/-OH$ Product composition[b]		
					(1)	(2)	(3)
1	(1)	Cl	1·0 M Hg^{2+}–0·1 M $DClO_4$	(6)	65·5	3·5	31
2	(1)	Br	"	(3)	60	4	36
3	(2)	Cl	"	(4)	7	79	14
4	(2)	Br	"	(2)	13	61	26
5	(3)	Cl	"	(3)	20	0	80
6	(3)	Br	"	(2)	26	<2	72
7	(1)	Cl	1·0 M Ag^+–0·1 M $DClO_4$	(2)	59	4	37
8	(1)	Br	"	(1)	55	5	40
9	(2)	Cl	"	(2)	12	64	24
10	(2)	Br	"	(1)	20	50	30
11	(3)	Cl	"	(1)	23	2	75
12	(1)	N_3	$NaNO_2$–0·25 M $DClO_4$	(2)	50	7	43
13	(2)	N_3	"	(2)	12	62	26
14	(3)	N_3	"	(1)	28	2	70
15	(1)	Cl	2 M NaOD; pH 6·9; 2 min	(4)	87	7	6
16	(1)	Br	"	(2)	87	8	5
17	(1)	NH_3	2 M NaOD; pH 9·5, 8 min	(6)	89	9	2
18	(2)	Cl	2 M NaOD; pH 8, 20 min	(4)	83	7	10
19	(2)	Br	2 M NaOD; pH 7·6, 20 min	(2)	82	7	11
20	(3)	Cl	2 M NaOD; pH 8·2, 6 min	(2)	48	5	47
21	(3)	Br	2 M NaOD; pH 8, 6 min	(2)	55	6	39
22	(3)	NH_3	2 M NaOD	(2)	21	7	72
23	(3)	NH_3	pH 11·2, 8 min	(3)	40	4	56

[a] Number of separate experiments is given in parentheses. [b] Obtained from n.m.r. integration (^{1}H), or pulsed (^{13}C, 100 pulses, 2·2 s per pulse; ^{1}H, 15—20 pulses, 4·2 s per pulse) storage data.

bulk solution phase (D_{int} mechanism;[11] $k_{assoc} > 10^{10}$ s^{-1}), or by an I_d process where some small degree of bond-making accompanies loss of the acido group. Certainly increasing bulk of the leaving group, Cl$^-$ (for base hydrolysis) <HgCl$^+$ <AgCl <HgBr$^+$ <AgBr <NNNNO, results in less incorporation of an adjacent water molecule (retention), but this may merely reflect an increased structure-breaking effect on this side of the molecule.

The large degree of stereochemical retention in each isomer also requires that the 5-co-ordinate species do not relax towards a common trigonal structure (C_{3v} or D_{3h}). This process could well be faster ($k_{relax} = ca.\ 10^{12}$—10^{14} s^{-1}) than either solvent diffusion or bond formation since only

a small change in bond angle(s) is required. Both the X-ray data[9] and strain energy minimization calculations[10] indicate that this is a very desirable structural change. We therefore favour immediate capture of H$_2$O, with some degree of bond-making prior to complete severance of the Co–X bond (*i.e.*, an I_d process). A clear experimental distinction between a D_{int} and an I_d process may well prove difficult to devise, but it appears that the induced aquation reactions of these Co^{III}–acido species do not involve 5-co-ordinate intermediates of any chemically significant lifetime.

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[8] A similar result obtains with the tren complexes: D. A. Buckingham, P. J. Cresswell, and A. M. Sargeson, *Inorg. Chem.*, 1975, **14**, 1485.

[9] These are approximately of C_{3v} symmetry: P. C. Jain and E. C. Lingafelter, *J. Amer. Chem. Soc.*, 1967, **89**, 724; M. Di Vaira and P. L. Orioli, *Acta Cryst.*, 1968, **B24**, 595 (Cu^{II}, Ni^{II}); *Inorg. Chem.*, 1967, **6**, 490 (Co^{II}).

[10] D. A. Buckingham, J. D. Edwards, T. Lewis, and G. M. McLaughlin, unpublished results.

[11] This mechanism is tantamount to reaction within Winstein's R$^+$X$^-$ intimate ion pair: *cf.* S. Winstein, P. E. Klinedinst, Jr., and G. C. Robinson, *J. Amer. Chem. Soc.*, 1961, **83**, 885; for a recent compilation, see C. D. Ritchie 'Solute–Solvent Interactions,' eds. J. F. Coetzee and C. D. Ritchie, Marcel Dekker, New York, 1969, Ch. 4; see also C. D. Ritchie *Accounts Chem. Res.*, 1972, **5**, 348.