Structural and Mechanistic Studies of Co-ordination Compounds. Part IX.[1] Acidity and Proton-exchange Kinetics of some Octahedral Cobalt(III) Amine Complexes

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The preparation and characterization of the cations *trans*-$[Co(cyclam)(A)OH_2]^{2+}$ (cyclam = 1,4,8,11-tetra-azacyclotetradecane; A = CN, NCS, and NO_2) and *trans*-$[Co(cyclam)(NH_3)OH]^{2+}$ are described. pK_a Values of these and other related aquo-complexes in aqueous solution have been determined by pH titration at 25·0 °C. The amine proton-exchange kinetics of the cations *trans*-$[Co(am)_4(NH_3)_2]^{3+}$ and -$[Co(am)_4(NH_3)Cl]^{2+}$ [$(am)_4$ = cyclam or two ethylenediamine (en) molecules] have been followed by n.m.r. spectroscopy at 34·5 °C. Within a given molecule, the axial ammine ligands exchange faster than the in-plane cyclam and en ligands. For a given series of analogous complexes, the proton-exchange rate constant of the axial ammine ligands decreases in the following order of $(am)_4$: cyclam > $(en)_2$ > $(NH_3)_4$. The acidity of the corresponding aquo-complexes *trans*-$[Co(am)_4(A)OH_2]^{n+}$ (A = CN, N_3, NCS, NO_2, NH_3, and OH_2) also decreases along this series. These results are in accordance with the nephelauxetic effect of the amine ligands on the central cobalt(III) ion. Solvation effects on the order of acidity of the complexes are discussed and it is concluded that these are of little importance for axial aquo- and amine ligands of analogous complexes.

In an attempt to rationalize differences in some thermodynamic and kinetic properties of octahedral cobalt(III) cyclam and corresponding $(en)_2$ complexes (cyclam and en = 1,4,8,11-tetra-azacyclotetradecane and ethylenediamine respectively) attention has been drawn,[2] among other factors, to the importance of the nephelauxetic effect of these amine ligands. It was deduced spectroscopically[2,3] that the extent of delocalization of 3*d* electrons away from the central cobalt(III) ion of analogous complexes of the type *trans*-$[Co(am)_4(A)X]^{n+}$ (A and X = two unidentate ligands) decreased in the order of $(am)_4$: cyclam > $(en)_2$ > $(NH_3)_4$. It was then proposed[2,4,5] that, for a given pair of A and X in analogous complexes, the following properties would vary systematically in the above order of $(am)_4$: (*i*) the aquation rate constant for release of X would increase; (*ii*) the base-hydrolysis rate constant for release of X would decrease; (*iii*) the relative stability of a lower- to a higher-charged complex would decrease; and (*iv*) the acidity of the complexes would decrease. The first three propositions have been substantiated experimentally.[1,3,6-10] However, there is little information concerning the acidity of these complexes. Usually, pK_a values of co-ordinated amine ligands[11] are greater than 14 and it is not possible to measure these values directly by any conventional method. It is, however, fair to assume, in the light of linear free-energy relations, that the more acidic the co-ordinated amine ligand is for these complexes the greater the rate of amine proton exchange will be, or *vice versa*.[11]

This paper describes kinetic studies of amine proton-exchange reactions of the cations *trans*-$[Co(am)_4(NH_3)_2]^{3+}$ and -$[Co(am)_4(NH_3)Cl]^{2+}$ [$(am)_4$ = cyclam and $(en)_2$] in order to determine the effect of the amine ligands on the acidity of the axial ammines. Corresponding data for tetra-ammine analogues are known.[12,13] The paper also describes the preparation of the cations *trans*-$[Co(cyclam)(A)OH_2]^{2+}$ (A = CN, NCS, and NO_2) and *trans*-$[Co(cyclam)(NH_3)OH]^{2+}$, and the p$K_a$ measurement of these and other related aquo-complexes *trans*-$[Co(am)_4(A)OH_2]^{n+}$ (A = CN, NCS, NO_2, N_3, and NH_3). Many of the pK_a values for the cations *trans*-$[Co(en)_2(A)OH_2]^{n+}$ have been previously measured under different conditions. For a better comparison, these values were redetermined under identical conditions to those for the other aquo-complexes.

EXPERIMENTAL

Preparation of the Complexes.—trans-*Amminehydroxo-(1,4,8,11-tetra-azacyclotetradecane)cobalt*(III) *chloride tetrahydrate*. This complex was prepared by dropwise addition, with stirring, of a concentrated ammonia solution (2 cm^3, s.g. 0·88) to an aqueous solution of *trans*-$[Co(cyclam)(NH_3)Cl]Cl_2$[10] (1 g in 3 cm^3). The solution was set aside at room temperature for 15 min. Excesses of alcohol and ether were added successively to crystallize out the desired *product* (yield 0·4 g) (Found: C, 27·8; H, 8·10; Cl, 16·6; N, 15·8. Calc. for $C_{10}H_{36}Cl_2CoN_5O_5$: C, 27·6; H, 8·25; Cl, 16·3; N, 16·1%).

trans-*Aquonitro*(1,4,8,11-*tetra-azacyclotetradecane*)*cobalt*(III) *perchlorate*. This complex was prepared by essentially the same method as that for *trans*-$[Co(cyclam)(N_3)OH_2](ClO_4)_2$ described previously[1] by the action of perchloric acid (10 cm^3, 2M) on *trans*-$[(O_2N)Co(cyclam)O_2Co(cyclam)(NO_2)](ClO_4)_2$[14] (1 g) (yield 0·2 g) (Found: C, 23·7; H, 4·80; Cl, 13·4; N, 13·5. Calc. for $C_{10}H_{26}Cl_2CoN_5O_{11}$: C, 23·0; H, 5·00; Cl, 13·6; N, 13·4%).

trans-*Aquoisothiocyanato*(1,4,8,11-*tetra-azacyclotetra-*

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[1] Part VIII, C. K. Poon and H. W. Tong, *J.C.S. Dalton*, 1974, 1.

[2] C. K. Poon, *J. Amer. Chem. Soc.*, 1970, **92**, 4467.

[3] C. K. Poon and H. W. Tong, *J.C.S. Dalton*, 1973, 1301.

[4] C. K. Poon, *Inorg. Chim. Acta Rev.*, 1970, **4**, 123.

[5] C. K. Poon, *Co-ordination Chem. Rev.*, 1973, **10**, 1.

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[10] W. K. Lee and C. K. Poon, *Inorg. Chem.*, 1973, **12**, 2016.

[11] F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions,' 2nd edn., Wiley, New York, 1967.

[12] F. Basolo, J. W. Palmer, and R. G. Pearson, *J. Amer. Chem. Soc.*, 1960, **82**, 1073.

[13] J. W. Palmer and F. Basolo, *J. Phys. Chem.*, 1960, **64**, 778.

[14] B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, 1966, **5**, 1514.

decane)cobalt(III) *perchlorate*. This complex was similarly prepared by the action of perchloric acid (10 cm^3, 2M) on *trans*-[(SCN)Co(cyclam)O_2Co(cyclam)(NCS)]$(ClO_4)_2$ [14] (1 g) (yield 0·3 g) (Found: C, 23·7; H, 4·95; N, 12·4; S, 5·90. Calc. for $C_{11}H_{26}Cl_2CoN_5O_9S$: C, 23·9; H, 5·05; N, 12·7; S, 5·80%).

trans-*Aquocyano*(1,4,8,11-*tetra-azacyclotetradecane*)*cobalt*(III) *perchlorate*. An aqueous solution of the complex *trans*-[Co(cyclam)(CN)SO_3] [3,6] (1 g in 15 cm^3) was digested on a steam-bath for 10 min. To the cooled solution, concentrated perchloric acid (2 cm^3, 70%) was added with stirring. After effervescence of SO_2 had subsided (*ca.* 0·5 h), the solution was filtered. On setting aside at room temperature for 2 days, orange *crystals* of the complex *trans*-[Co(cyclam)(CN)OH_2]$(ClO_4)_2$ slowly separated out (yield 0·2 g) (Found: C, 26·5; H, 5·15; Cl, 14·5; N, 14·1. Calc. for $C_{11}H_{26}Cl_2CoN_5O_9$: C, 26·3; H, 5·20; Cl, 14·0; N, 14·0%).

Other *trans*-complexes [Co(cyclam)$(NH_3)_2$]Cl_3,[15] [Co(cyclam)(NH_3)Cl]Cl_2,[10] [Co(cyclam)(N_3)OH_2]$(ClO_4)_2$,[3] [Co(en)$_2(NH_3)_2$]Cl_3,[16] [Co(en)$_2$(NH_3)Cl]Cl_2,[16] [Co(en)$_2$(CN)OH_2]$(NO_3)_2$,[17] [Co(en)$_2$(N_3)OH_2]$(ClO_4)_2$,[18] [Co(en)$_2$(NCS)OH_2]$(NO_3)_2$,H_2O,[16] [Co(en)$_2$(NH_3)OH_2]$(NO_3)_3$,[16] [Co(en)$_2$(NO_2)OH_2](SO_4),[16] [Co$(NH_3)_4$(CN)OH_2]$(NO_3)_2$,[19] and [Co$(NH_3)_4$(NO_2)OH_2]$(NO_3)_2$,[7] and the complex [Co$(NH_3)_5OH_2$]$(ClO_4)_3$ [20] were prepared by methods described in the literature.

pK_a *Determinations*.—The pK_a of the cation *trans*-[Co(cyclam)(NH_3)OH_2]$^{3+}$ was determined by pH titration of *trans*-[Co(cyclam)(NH_3)OH]$^{2+}$ against standard nitric acid in a thermostatted titration vessel maintained at 25·0 °C. pK_a Values of other complexes of the type *trans*-[Co(am)$_4$(A)OH_2]$^{n+}$ were determined under identical conditions by pH titration of these aquo-complexes against standard sodium hydroxide.

Kinetics.—Amine proton-exchange reactions were studied in either DCl or $MeCO_2^-$–$MeCO_2D$ in D_2O buffer solutions by n.m.r. spectroscopy ($MeCO_2D$ was prepared by heating a known quantity of acetic anhydride in D_2O in a sealed tube for 2 days). Reactions were initiated by adding the appropriate solvent, previously brought to the probe temperature of the spectrometer (34·5 °C), to the samples in n.m.r. tubes, maintained at the same temperature at the preheater of the spectrometer. The n.m.r. tube was then rapidly inserted into the spectrometer and full-range ^{1}H n.m.r. spectra and integrals were scanned at known time intervals. The pD of the solution at the end of the reaction was obtained either by measuring the pH of the solution in a thermostatted vessel, maintained at 34·5 °C, in a conventional manner as if it were a protic solution and then using the established relation [21] of $pD = pH + 0{\cdot}40$, or by directly reading the pD value on a pH meter which, together with the microelectrodes, had previously been calibrated against a standard D_2O solution of sodium dihydrogencitrate.[22] pD Values determined by these two methods agreed to within ±0·05 pD unit and the latter procedure was adopted for all pD determinations. The ionic product of D_2O at 34·5 °C was found, by extrapolating published data at other temperatures,[23] to be 14·545 from which the OD^- ion concentration for each kinetic run could be determined.

I.r. spectra of Nujol mulls between KBr windows were measured with a Perkin-Elmer 337 spectrophotometer. ^{1}H N.m.r. spectra were measured with a 60 MHz Perkin-Elmer R-20 spectrometer. The pH of buffer solutions was measured with a Radiometer pH meter type PHM26 using a set of microelectrodes of types K4112 (calomel electrode) and G222C (glass electrode). These electrodes were suitable for small-volume (0·5 cm^3) pH measurement.

RESULTS

pH Titration of all the aquo-complexes against standard hydroxide gave typical curves for weak acids and strong bases from which the pK_a values of these complexes could be deduced fairly accurately. These data are collected in Table 1.

TABLE 1

pK_a Values for complexes of the type *trans*-[Co(am)$_4$(A)OH_2]$^{n+}$ at 25·0 °C

A	cyclam	(en)$_2$	(en)$_2$ [a]	$(NH_3)_4$
CN	6·40	7·40	7·45 [b]	7·60
N_3	5·53	6·00		
NO_2	5·15	6·55	6·44 [c]	7·10
NH_3	4·58	5·58	5·8 [d,e]	6·08
NCS	3·58	5·30	6·3 [e]	
H_2O	2·82 [f]	4·45 [g]	4·45 [g]	5·79 [h]

[a] Data from the literature. [b] At 16 °C; S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 1963, 966. [c] Temperature not specified; F. Basolo, B. D. Stone, J. G. Bergmann, and R. G. Pearson, *J. Amer. Chem. Soc.*, 1954, **76**, 3079. [d] At 20 °C; D. F. Martin and M. L. Tobe, *J. Chem. Soc.*, 1962, 1388. [e] At 20 °C; M. L. Tobe, *Science Progress*, 1960, **48**, 483. [f] C. K. Poon and M. L. Tobe, *Inorg. Chem.*, 1968, **7**, 2398. [g] J. Bjerrum and S. E. Rasmussen, *Acta Chem. Scand.*, 1952, **6**, 1275. [h] Gross acid dissociation for the *cis*–*trans*-equilibrium. The equilibrium *cis*–*trans* ratio is 0·17 : 1; R. G. Pearson, R. E. Meeker, and F. Basolo, *J. Amer. Chem. Soc.*, 1956, **78**, 709; R. G. Yalman and T. Kuwana, *J. Phys. Chem.*, 1955, **59**, 298.

The general characteristic of the ^{1}H n.m.r. spectra of these complexes is that the signal of the co-ordinated ammonia ligand coincides with the rather broad methylene signal of the in-plane amines. Thus the spectrum of the cation *trans*-[Co(en)$_2(NH_3)_2$]$^{3+}$ in DCl, first characterized by Buckingham *et al.*,[24] showed two distinct peaks at τ 4·6 and 6·5 with Me_4Si (τ 10) as external standard. These were assigned to the eight amine protons of the two en molecules and to the combined methylene and ammonia protons respectively. The spectrum of the cation *trans*-[Co(cyclam)$(NH_3)_2$]$^{3+}$ in [$^2H_6$]dimethyl sulphoxide showed three groups of peaks centred around τ 3·15, 6·8, and 7·45 with Me_4Si as internal standard. With reference to the known spectrum of the cation *trans*-[Co(cyclam)$(OH_2)_2$]$^{3+}$,[25] the absorption peak at τ 3·15 was assigned to the four cyclam amine protons. This was supported by the correct integration ratio of 2 : 13 for this peak to the remaining absorptions. Like the cation *trans*-[Co(en)$_2(NH_3)_2$]$^{3+}$, the NH_3 signal was hidden under the broad band at τ 6·8 which

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[15] B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, 1965, **4**, 1102.

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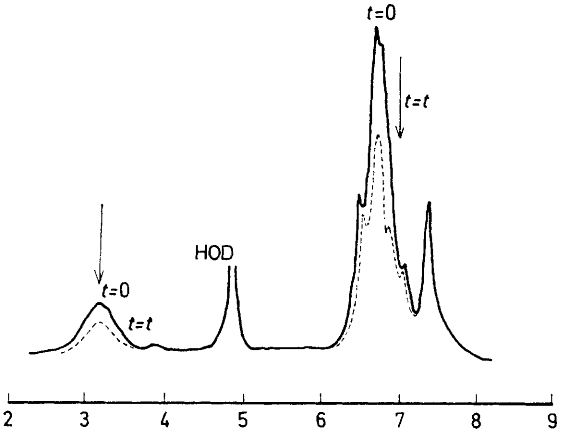
[25] C. K. Poon and M. L. Tobe, *J. Chem. Soc.* (*A*), 1968, 1549.

could be assigned to the 16 cyclam α-methylene protons. A relatively sharp band at τ 7·45 was tentatively assigned to the four cyclam β-methylene protons. These β protons are most remote from the cobalt metal ion and from the electronegative nitrogen atoms. Consequently, they were expected to occur at a field higher than the α-methylene protons. In DCl solution, the spectrum of this complex was virtually the same as that described above, except that here an external Me_4Si reference was used. Sodium 2,2-dimethyl-2-silapentane-5-sulphonate was not suitable as the internal reference because it precipitated the metal complex from the fairly concentrated solution.

In DCl solution, even at a pD close to unity, the intensity of the peak at τ 3·15 of the complex *trans*-$[Co(cyclam)(NH_3)_2]^{3+}$ gradually decreased and finally disappeared (Figure). The intensity of the broad band for the combined absorptions at τ 6·8 and 7·45 also decreased at an even faster rate and finally dropped to *ca.* 3/4 of its initial value. This latter observation is fully consistent with complete exchange of the six ammine protons with the 20 methylene protons (α and β) remaining to give rise to the final spectrum. The two absorptions at τ 6·8 and 7·45 in the final spectrum became distinctly separated and their integrations were accurately determined and had the expected ratio of 4 : 1 respectively.



^1H N.m.r. spectral change of the cation *trans*-$[Co(cyclam)(NH_3)_2]^{3+}$ in DCl solution at pD 1; solid line at $t = 0$ and dashed line at $t = t$

The kinetics of proton exchange of the cation *trans*-$[Co(cyclam)(NH_3)_2]^{3+}$ were studied in DCl solution with sodium chloride added to maintain a constant ionic strength of 0·5M; this included the complex concentration of *ca.* 0·1—0·2M. Integrals for particular types of amine proton at a given time t (expressed as the percentage integral, A_t, of the total number of protons present in solution, in order to eliminate any possible fluctuation of signal intensity with time) were evaluated. Pseudo-first-order exchange rate constants, k_{obs}, were obtained from gradients of standard semilogarithmic plots of $\log(A_t - A_\infty)$ against time, where A_∞ represents the percentage integral after 10 exchange half-lives. For the cyclam amine proton peak at τ 3·15 A_∞ was zero, whereas A_∞ was found to be about 3/4 of the initial value for the remaining broad band (combined absorptions at τ 6·8 and 7·45). The OD^- ion concentration in each of the runs was obtained by measuring the pD of the reaction solution at the reaction temperature. The linear plot obtained of k_{obs} against $[OD^-]$ satisfied the equation $k_{obs} = k_1 + k_2[OD^-]$, from the intercept and gradient of which first- and second-order exchange rate constants, k_1 and k_2 respectively, could be determined. The exchange reaction of the cation *trans*-$[Co(en)_2(NH_3)_2]^{3+}$ was similarly studied in $MeCO_2^-$–$MeCO_2D$ buffer solutions, also maintained at an ionic strength of 0·5M with sodium chloride.

The corresponding chloroammine complexes gave very similar ^1H n.m.r. spectra to those of the diammine analogues, except that initial integrations gave a different ratio and the reactions proceeded at much slower rates. The kinetics of these reactions were also studied in $MeCO_2^-$–$MeCO_2D$ buffer solutions at an ionic strength of 0·5M. Attempts were made to study amine proton-exchange reactions of complexes of the type *trans*-$[Co(am)_4(NH_3)OH_2]^{3+}$, but these were unsuccessful because of acetate anation of the aquo-complexes. All exchange-rate data are summarized in Table 2.

TABLE 2

Pseudo-first-order rate constants for the amine proton-exchange reactions of complexes of the type *trans*-$[Co(am)_4(NH_3)X]^{n+}$ at 34·5 °C and at I = 0·5M

pD	$(am)_4$	X	$k_a{}^a/s^{-1}$	$k_b{}^a/s^{-1}$
2·42	cyclam	NH_3	$7·5 \times 10^{-4}$	$5·0 \times 10^{-4}$
2·32	cyclam	NH_3	$6·0 \times 10^{-4}$	$4·2 \times 10^{-4}$
2·19	cyclam	NH_3	$4·2 \times 10^{-4}$	$3·1 \times 10^{-4}$
2·04	cyclam	NH_3	$3·3 \times 10^{-4}$	$2·5 \times 10^{-4}$
1·18	cyclam	NH_3	$2·1 \times 10^{-5}$	$6·2 \times 10^{-5}$
3·88	cyclam	Cl	$1·9 \times 10^{-3}$	$4·8 \times 10^{-4}$
3·73	cyclam	Cl	$1·3 \times 10^{-3}$	$3·7 \times 10^{-4}$
3·58	cyclam	Cl	$1·0 \times 10^{-3}$	$2·5 \times 10^{-4}$
3·26	cyclam	Cl	$4·4 \times 10^{-4}$	$1·3 \times 10^{-4}$
4·52	$(en)_2$	NH_3	$4·4 \times 10^{-3}$	$2·3 \times 10^{-4}$
4·43	$(en)_2$	NH_3	$3·4 \times 10^{-3}$	$2·0 \times 10^{-4}$
4·26	$(en)_2$	NH_3	$2·3 \times 10^{-3}$	$1·4 \times 10^{-4}$
3·85	$(en)_2$	NH_3	$9·1 \times 10^{-4}$	$7·8 \times 10^{-5}$
4·84	$(en)_2$	Cl	$4·3 \times 10^{-4}$	$1·8 \times 10^{-5}$
4·79	$(en)_2$	Cl	$3·9 \times 10^{-4}$	$1·5 \times 10^{-5}$
4·62	$(en)_2$	Cl	$2·7 \times 10^{-4}$	$1·1 \times 10^{-5}$
3·55	$(en)_2$	Cl	$6·1 \times 10^{-5}$	$2·0 \times 10^{-6}$

[a] The quantities k_a and k_b represent pseudo-first-order exchange rate constants of the axial ammonia and in-plane amine ligands respectively.

DISCUSSION

The geometrical configuration of the newly prepared cyclam complexes was assigned on the basis of i.r. spectroscopy. The presence of two bands near 900 cm^{-1} and one band near 810 cm^{-1} in the 800—910 cm^{-1} region of the i.r. spectra of these complexes was taken to indicate a *trans*-configuration [26] [898, 889, and 815 cm^{-1} ($A = NO_2$); 903, 891, and 820 cm^{-1} (NCS); 905, 895, and 821 cm^{-1} (CN); and 904, 892, and 820 cm^{-1} (NH_3)].

It is clear from Table 1 that the pK_a values of the cations *trans*-$[Co(en)_2(A)OH_2]^{n+}$ determined here are, in general, with the exception of A = NCS, in reasonable agreement with published data. In view of the high acidity of the cation *trans*-$[Co(cyclam)(NCS)OH_2]^{2+}$ we tend to believe our value of 5·30 for the pK_a of *trans*-$[Co(en)_2(NCS)OH_2]^{2+}$. The variation of acidity of analogous aquo-complexes of the type *trans*-$[Co(am)_4$-

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[26] C. K. Poon, *Inorg. Chim. Acta*, 1971, **5**, 322.

(A)$OH_2]^{n+}$, over an extensive series of orienting ligand A of different electronic-displacement property, with the nature of $(am)_4$ is in the right direction as predicted by the nephelauxetic effect.

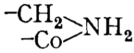
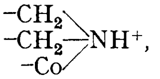
The amine proton-exchange reactions of these complexes demonstrate both spontaneous and base-catalysed paths. The quality of the n.m.r. data, however, did not give an accurate determination of the spontaneous rates which are slow and roughly of the order of 10^{-5} s^{-1}. On the other hand, second-order base-catalysed rates could fairly reliably be determined. It is clear, as shown in Table 3, that the effect of the ligands $(am)_4$ on the acidity of the axial ammines, as reflected by variation of second-order ammine proton-exchange rate constants, is also in the right direction as predicted.

TABLE 3

Second-order rate constants for the amine proton-exchange reaction of complexes of the type *trans*-$[Co(am)_4(NH_3)X]^{n+}$ in buffered D_2O solution at 34·5 °C

$(am)_4$	X	k_a [a]/l mol^{-1} s^{-1}	k_b [a]/l mol^{-1} s^{-1}
cyclam	NH_3	$(9{\cdot}8 \pm 0{\cdot}6) \times 10^8$	$(6{\cdot}0 \pm 0{\cdot}4) \times 10^8$
$(en)_2$	NH_3	$(4{\cdot}5 \pm 0{\cdot}3) \times 10^7$	$(2{\cdot}2 \pm 0{\cdot}1) \times 10^6$
$(NH_3)_4$	NH_3	$3{\cdot}3 \times 10^6$ [b]	$3{\cdot}3 \times 10^6$ [b]
cyclam	Cl	$(8{\cdot}5 \pm 0{\cdot}5) \times 10^7$	$(2{\cdot}3 \pm 0{\cdot}1) \times 10^7$
$(en)_2$	Cl	$(2{\cdot}0 \pm 0{\cdot}1) \times 10^6$	$(8{\cdot}5 \pm 0{\cdot}6) \times 10^4$
$(NH_3)_4$	Cl	$3{\cdot}3 \times 10^5$ [b,c]	$3{\cdot}3 \times 10^5$ [b,c]

[a] The quantities k_a and k_b represent second-order exchange rate constants of the axial ammonia and in-plane amine ligands respectively. [b] Evaluated from published activation energy and rate constant at 25 °C; J. W. Palmer and F. Basolo, *J. Phys. Chem.*, 1960, **64**, 778. [c] Although the in-plane and axial ammonia molecules are not equivalent with respect to their environment, it has been suggested that they all exchange at the same rate; F. Basolo, J. W. Palmer, and R. G. Pearson, *J. Amer. Chem. Soc.*, 1960, **82**, 1073.

The variation of acidity of the in-plane amine ligands, however, is less straightforward. Here, the nature of these amine ligands is different. It is well known that, for example, the pK_a values of conjugate acids of members of the methylamine series decrease in the order $(Me)_2NH_2^+ > MeNH_3^+ > (Me)_3NH^+$.[27] In general, conjugate acids of secondary amines are weakest and those of tertiary amines strongest.[27] In terms of the number of acidic protons present, co-ordinated NH_3,1/2(en), and 1/4(cyclam), *i.e.* $-Co-NH_3^+$,  $\begin{matrix}-CH_2\\-Co\end{matrix}\!\!>\!NH_2^+$, and  $\begin{matrix}-CH_2\\-CH_2\\-Co\end{matrix}\!\!>\!NH^+$, could be regarded as conjugate acids of primary, secondary, and tertiary amines respectively. Thus, the observed variation in amine proton-exchange rate constants (Table 3), with en slowest and cyclam fastest, is in full agreement with the general trend of the variation of acidity of most amines. This order of acidity has been satisfactorily explained in terms of solvation effects.[27] Such effects on the order of acidity of the axial ammines of these complexes, however, could not be of dominant importance. The difference in the extent of alkyl substitution and chelation of the in-plane $(am)_4$ ligands is so remote from the axial ammine site that the variation in solvation energy among analogous *trans*-$[Co(am)_4(NH_3)X]^{n+}$ cations would be very nearly the same as that among their analogous conjugate bases formed by reaction (1). Therefore,

$$\textit{trans-}[Co(am)_4(NH_3)X]^{n+} + OH^- \rightleftharpoons \textit{trans-}[Co(am)_4(NH_2)X]^{(n-1)+} + H_2O \quad (1)$$

solvation effects would not contribute significantly to variation of the acidity of the axial ammine and aquo-ligands. This argument is supported by the observed similarity in acidity of a series of primary amines of different size and kind of alkyl substitution and hence of different gross solvation energy [*e.g.* the first pK_a values of $MeNH_3^+$, $Me(CH_2)_3NH_3^+$, $Me(CH_2)_6NH_3^+$, $(MeCH_2)_2CHNH_3^+$, $(Me)_3CNH_3^+$, and $H_2NCH_2CH_2NH_3^+$ are 10·66, 10·77, 10·66, 10·59, 10·83, and 10·71 respectively [28]].

Finally, the observation that the diammine complexes exchange faster than their chloroammine analogues could be satisfactorily accounted for in terms of charge effect.[13]

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[27] R. G. Pearson and D. C. Vogelsong, *J. Amer. Chem. Soc.*, 1958, **80**, 1038.

[28] Ref. 23, p. D-87.