Bromination of Imidazole Complexes of Pentaamminecobalt(III). Synthesis, Structure and Reactivity†

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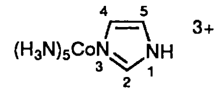
The preparations and properties (^{1}H, ^{13}C NMR spectra; pK_a data) of various bromoimidazole complexes of pentaamminecobalt(III) are reported. Improved methods are given for synthesising and isolating related methyl imidazole derivatives. Hydrolysis of $[Co(NH_3)_5(tbim)]^{2+}$ (tbim = 2,4,5-tribromoimidazolate) to give $[Co(NH_3)_5(OH_2)]^{3+}$ or $[Co(NH_3)_5(OH)]^{2+}$ and 2,4,5-Htbim follows the rate equation $k_{obs} = (k_1[H^+] + k_2K_a[OH^-])/([H^+ + K_a)$ with $k_1 = 2.07 \times 10^{-4}$ s^{-1}, $k_2 = 0.11$ dm^3 mol^{-1} s^{-1} and $K_a = 1.49 \times 10^{-2}$ mol dm^{-3} at 250 °C and $I = 1.0$ mol dm^{-3} ($NaClO_4$); k_1 corresponds to the spontaneous hydrolysis of $[Co(NH_3)_5(Htbim)]^{3+}$, and k_2 to the OH^--catalysed reaction of its conjugate base. Isomerisation of $[Co(NH_3)_5(4\text{-}Hbim)]^{3+}$ (4-Hbim = 4-bromoimidazole) to its 5-bromoimidazole congener follows the rate equation (in D_2O at 70 °C) $k_{obs} = kK_a[OD^-]/(K_w + K_a[OD^-])$ with $k = 1.67 \times 10^{-4}$ s^{-1} and pK_a = 6.86; k corresponds to the spontaneous reaction of the deprotonated $[Co(NH_3)_5(4\text{-}bim)]^{2+}$ ion and a π-bonded, or solvent-cage-trapped, transition state is suggested. A crystal structure analysis of the dimer $[(H_3N)_5Co(im)Co(NH_3)_5]Br_5{\cdot}3H_2O$ (im = imidazolate) has been carried out: space group $P2_1/n$, $a = 12.946(4)$, $b = 14.469(5)$, $c = 14.022(4)$ Å, $\beta = 107.18(2)°$, $Z = 4$, 2191 reflections, $R = 0.0576$. Less accurate structures of four other complexes have been determined for the purpose of identifying the positions of bromine substitution.

The present study was carried out in order to obtain information on the substitution pattern and stabilities of the products, or possible products, of the aqueous bromination of cobalt(III)-co-ordinated imidazoles. Such reactions are usually rapid, but addition of Br_2(aq) to the imidazole ring is not necessarily rate determining. Unstable Wheland intermediates appear to be formed, at least under acidic conditions.[1] The preparations, properties (including hydrolytic behaviour), and structures of several bromo-substituted imidazole complexes of the pentaamminecobalt(III) ion are described. Also reported is the intramolecular isomerisation of $[Co(NH_3)_5L]^{3+}$ (L = 4-bromoimidazole) to its 5-bromo isomer.‡ This reaction resembles in many ways that recently described[3] for the corresponding 4-methylimidazole complex, although some differences in interpretation are given.

The following $[Co(NH_3)_5L]^{n+}$ complexes have previously been described in the literature: $n = 3$, L = imidazole;[4] 1-,[5] 2-,[5] 4-,[3] or 5-methylimidazole;[3] 1,4-, 1,5- or 2,5-dimethylimidazole;[6] $n = 2$, L = 5-nitroimidazolate.[7] Structural information is available on the latter[7] and on $[Co(NH_3)_5L]Cl_3{\cdot}2H_2O$[8] (L = 5-methylimidazole).

Results and Discussion

Synthesis of $[Co(NH_3)_5(Him)]^{3+}$ **1** (*Him = imidazole*) *and its Methyl-substituted Derivatives.*—The syntheses of the complex $[Co(NH_3)_5(Him)]^{3+}$ **1** and many of its Me-substituted derivatives (1-, 2-, 4- and 5-Me) have been reported previously.[3–7] Our synthetic methods are similar to those reported, but the isolation procedures and the isomeric purities of the complexes have been considerably improved. We used the general preparative method given by equation (1) with the choice of cobalt(III) reactant being made by trial and error. In general a colour change from red or red-violet to orange-brown occurred slowly over 45–90 min at 80 °C in the appropriate solvent, except for the *C*-methyl complexes which turned an intense purple. Chromatography on either Dowex 50W × 2 or Sephadex SP-C25 cation-exchange resin with sodium phosphate buffer (pH 6.8)§ followed by elution with HCl was generally used for product purification and recovery.



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As has been reported previously[3] the reaction of $[Co(NH_3)_5(OH_2)]^{3+}$ with 4-methylimidazole (4-Hmim) in Me_2SO gives two isomeric products, the major one being the 'remote' isomer, **2**, equation (2). We found that the two isomers could be easily separated using Dowex resin and phosphate buffer (pH 6.8) as eluent: **2** elutes prior to the 'adjacent' isomer, **3**. Previously,[3] recovery of **3** required 'nearly 30 fractional recrystallisations' and only very small amounts of the pure complex were obtained. The corresponding reaction of the 2,5-dimethylimidazole (2,5-Hdmim) ligand gives only the remote isomer, **4**. Presumably steric interactions, already present in **3**, are accentuated with 2,5-dimethylimidazole, but electronic factors may also be important (see below). The identification of **4** proved important in reaching an understanding of the process by which co-ordinated imidazole is brominated since this

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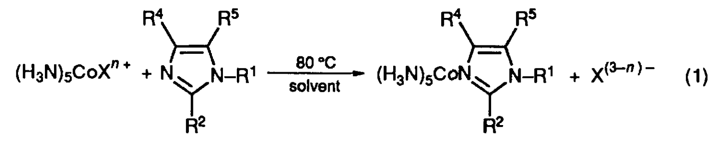
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

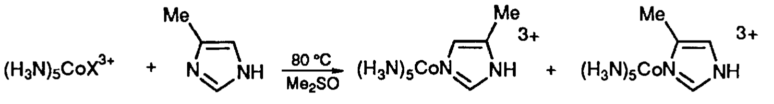
Non-SI unit employed: mmHg ≈ 133 Pa.

‡ The IUPAC numbering scheme used in this paper differs from the scheme used in refs. 1, 2 and 13. In the latter the co-ordinated pyridine-type nitrogen of imidazole is numbered as N^1 and the protonated nitrogen as N^3. The ligand abbreviations used in this paper also differ from those in refs. 1, 2 and 13. Thus, for example, $[Co(NH_3)_5(2,5\text{-}Hdmim)]^{3+}$ and $[Co(NH_3)_5(4,5,2\text{-}Hdbmim)]^{3+}$ in this paper would be written $[Co(NH_3)_5\ 2,4\text{-}Me_2ImH]^{3+}$ and $[Co(NH_3)_5\ 4,5\text{-}Br_2,\ 2\text{-}MeImH]^{3+}$ in the companion publications.

§ With this eluent impurities such as $[Co(NH_3)_6]^{3+}$ and $[Co(NH_3)_5(OH_2)]^{3+}$ elute before $[Co(NH_3)_5(Him)]^{3+}$. Thus removal of cobalt hexaammine from the desired complex is less wasteful than the method used by Harrowfield *et al.*[4]

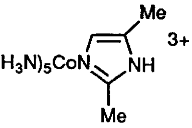

(1)

X = OH_2 or Me_2SO (n = 3) R = H or Me Solvent = Me_2SO
X = $CF_3SO_3^-$ (n = 2) R^1, R^2, R^3, R^4, = H, R^5 = Br Solvent = $(BuO)_3PO$
X = ONO_2^- (n = 2) R = H or Me Solvent = Me_2SO


(2)

X = OH_2 or Me_2SO

2 ('remote' isomer) **3** ('adjacent' isomer)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complex brominates more rapidly than any other, particularly at low pH, and it was this reaction which gave the clearest indication of formation of a Wheland addition intermediate.[1] We were not able to prepare the 2,4,5-trimethylimidazole complex using any method or starting material, presumably because of prohibitive steric factors.

Treatment of $[Co(NH_3)_5(im)][ClO_4]_2$ {prepared by deprotonation of $[Co(NH_3)_5(Him)]^{3+}$}[4] with $[Co(NH_3)_5(OSMe_2)]^{3+}$ in Me_2SO gave excellent yields of the bridged dimer **5**. The two signals at δ 7.80 (one proton) and 7.15 (two protons) in the ^1H NMR spectrum implies a symmetrical environment for the imidazolato ligand, and this was subsequently confirmed by a crystal structure (see below). Following the completion of this work this complex was reported by others.[9,10] Unlike the earlier preparation no evidence was found for formation of the trimer $[(H_3N)_5Co(im)Co(NH_3)_4(im)Co(NH_3)_5]^{7+}$.

Bromo-substituted Derivatives.—These complexes have not been described previously. Attempts to prepare a monobrominated complex by treating $[Co(NH_3)_5(Him)]^{3+}$ with Br_2 in water or dimethyl sulphoxide were unsuccessful, and only polybrominated complexes were formed (see below). These arose through the faster bromination of the monobromo complexes compared to bromination of $[Co(NH_3)_5(Him)]^{3+}$.[1] However, complex **6** was successfully prepared by using the separately synthesised 4-bromoimidazole (4-Hbim) ligand, equation (3). Proton NMR spectroscopy of the total recovered 3+ band and reversed-phase high-performance ion-pair chromatography (RP-HPIPC) demonstrated only one product for this reaction. Location of the bromo substituent was established by an X-ray study on $[Co(NH_3)_5(4\text{-Hbim})][ClO_4]_{0.5}Br_{1.5}\cdot H_2O$. We had expected the less-hindered remote isomer **7** to be formed, and the identification of the position of substitution was very important to our understanding of the bromination mechanism.[1] The adjacent stereochemistry of **6** almost certainly results from a predominance of the 4-Hbim tautomer in the ligand equilibrium (4), for which K_T = 3–152.[11]

The same reasoning would suggest that the corresponding reaction of 4(5)-methylimidazole would produce $[Co(NH_3)_5(5\text{-Hmim})]^{3+}$ since here $K_T < 1$ [estimated from the ratio of products formed in the N-methylation of 4(5)-Hmim].[12] This isomer does indeed predominate in the reaction products,[3] equation (2). Complex **6** completely isomerises to the remote isomer **7** on heating an aqueous solution, confirming that electronic factors are more important than steric factors in determining the synthetic product.* Thermal equilibration of **6** was the only method whereby we could prepare **7**, and this product has been fully characterised.

Addition of Br_2 to complex **1** in neutral or acidic aqueous solution results in the formation of both **8** and **9a**, equation (5). No monobrominated product was detected (RP-HPIPC, ^1H NMR spectroscopy), and the relative amounts of **8** and **9a** depended on the amount of Br_2 used. The maximum yield of **8** was obtained using 2 mol equivalents of Br_2. Chromatography on Dowex removed unreacted $[Co(NH_3)_5(Him)]^{3+}$ (first to elute) and complex **8** eluted before **9a** under acidic conditions, but not when aqueous NaCl was used when the latter eluted as its deprotonated 2+ ion **9**. This form has been characterised through an X-ray structure on $[Co(NH_3)_5(tbim)][ClO_4]Br$ (tbim = 2,4,5-tribromoimidazolate). Numerous attempts to grow suitable crystals of **8** failed (Br^-, ClO_4^-, PF_6^-, BF_4^- counter anions were used) but there is no doubt as to the positions of bromine substitution (^1H and ^{13}C NMR spectroscopy, see below). The 4,5-disubstitution pattern was further confirmed by electrolytic reduction of **8**, recovery of the ligand, and comparison (m.p., ^1H NMR spectrum) with authentic 4,5-dibromoimidazole. Complex **8** is stable in aqueous solution in the dark (no change after 10 h in acetate buffer), but exposure to laboratory light produced a slow colour change and eventual precipitation of CoO(OH). Reduction to Co^{2+}(aq) was not detected.

The complex $[Co(NH_3)_5(tbim)][ClO_4]Br$ **9** crystallised overnight as large red crystals following the addition of 3 mol of Br_2 to $[Co(NH_3)_5(Him)]Br_3$ in aqueous NaBr–$NaClO_4$ at pH 6.8 (phosphate). The parabanate complex **10** was also formed to some extent but this did not crystallise.† Complex **9a** is formed almost quantitatively on addition of excess of Br_2(aq) in acidic solution, but hydrolysis, with loss of the Htbim ligand, occurs rather rapidly under these conditions (see below).

Addition of limited amounts of Br_2(aq) (1 mol equivalent) to $[Co(NH_3)_5L]^{3+}$ (L = 4- or 5-Hmim) resulted in rapid (within

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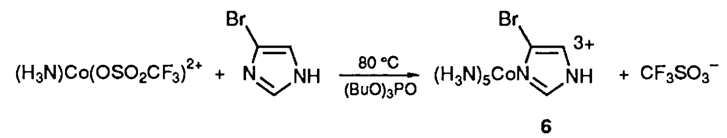
* As a result of these considerations an attempt was made to synthesise the 4-nitroimidazolate complex (the 5-NO_2 derivative is the only known isomer, *cf.* ref. 7) by treating 5-nitroimidazole with $[Co(NH_3)_5(OSO_2CF_3)][CF_3SO_3]_2$ in tributyl phosphate as solvent (K_T = 320–500, ref. 12, p. 365). However no imidazole complex resulted, perhaps because 5-nitroimidazole is such a poor base (pK_a = 0.05, ref. 11, p. 385).

† Oxidation products accompany bromination under neutral or alkaline conditions (buffer catalysed). These reactions are dealt with in a separate publication.[13]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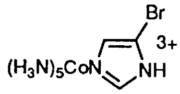
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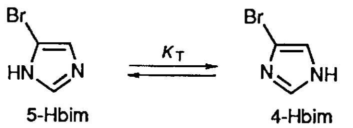
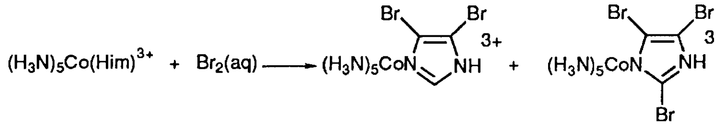
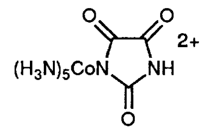

5-Hbim 4-Hbim

(4)


1 **8** **9a**

(5)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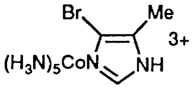
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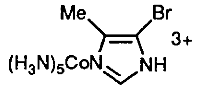
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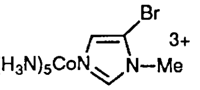
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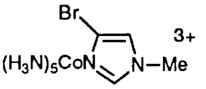
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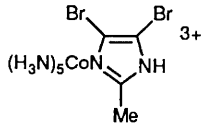
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1 and 5 min respectively) formation of the monobrominated species **11** and **12**. No attempt was made to prepare the dibromo derivatives (with further substitution at C^2), but undoubtedly these could be made by using excess of Br_2(aq) and longer reaction times.

Addition of 1.5 mol equivalents of Br_2(aq) to $[Co(NH_3)_5(mim)]^{3+}$ (mim = 1-methylimidazole) results in the slow formation of complex **13**. Overnight standing was required to form large amounts, and the slowness of the reaction (compared to the other brominations) has implications for the bromination mechanism.[1] No evidence was found for the isomer **14** (RP-HPIPC), ^{1}H NMR spectroscopy), and the position of substitution was confirmed by a crystal structure determination on $[Co(5\text{-bmim})]Br_3{\cdot}2H_2O$ (5-bmim = 5-bromo-1-methylimidazole).

Addition of Br_2(aq) (2 mol equivalents) to $[Co(NH_3)_5(2\text{-Hmim})]^{3+}$ results in the rapid formation of complex **15**. No evidence was found for a monobrominated species even when 1 mol equivalent of Br_2(aq) and shorter reaction times were used. Complex **15** is not very stable since ion-exchange chromatography using acidic eluents (3 mol dm^{-3} HCl) resulted in complete conversion into $[Co(NH_3)_5(OH_2)]^{3+}$. This aquation behaviour is analogous to that found for $[Co(NH_3)_5(Htbim)]^{3+}$ (see below).

Treatment of the imidazolato dimer **5** with aqueous Br_2 (1 mol equivalent) for 30 min resulted in a moderate yield of the monobrominated species **16**, equation (6). Proton and ^{13}C NMR data (Tables 1 and 2) are consistent with substitution at the 4(5) position rather than at C^2. No attempt was made to prepare the μ-4,5-dibromoimidazolate species.

Proton and ^{13}C *NMR Spectra*.—Proton and ^{13}C NMR data were usually sufficient to characterise the position of substitution in the brominated complexes. However, the unambiguous identification of **13** was given by nuclear Overhauser effect (nOe) experiments. Irradiation of the methyl signal at δ 3.85 resulted in H^2 enhancement only, consistent with bromination at C^5. This assignment was subsequently confirmed by a crystal structure.

(*a*) ^{1}H. Storm *et al.*[15] have previously given assignments for most of the methyl-substituted complexes using NOE and deuterium substitution effect on relaxation times (DESERT) experiments. We agree with their assignments, and resonances for the new complexes were similarly assigned. Unresolved ^{1}H–^{59}Co coupling between the cobalt nucleus ($I = \frac{7}{2}$) and the adjacent H^2 and H^4 protons usually manifested itself as a slight broadening of these signals relative to H^5.[16] No ^{1}H–^{1}H coupling was observed for any complex. The data in Table 1 show that replacement of a proton by a Me or Br substituent has little effect on the chemical shifts of the other ring protons. Introduction of a methyl group gives a small (0–0.5 ppm) upfield shift, but introduction of a bromine atom has essentially no effect. It is interesting that $[(H_3N)_5Co(im)Co(NH_3)_5]^{5+}$ has a ^{1}H NMR spectrum almost identical to that of free imidazole (for which the NH proton is in fast tautomeric equilibrium).

(*b*) ^{13}C. Following Henderson *et al.*[14] heteronuclear correlation (HETCOR) spectroscopy allowed unambiguous C assignments based on known ^{1}H assignments. These are given in Table 2. Carbon atom C^2 was found to resonate at lowest field for every complex. As expected, substitution causes large chemical shifts in the resonances of the substituted carbons. Methyl substitution gives a 10–15 ppm downfield shift while Br substitution gives a 10–20 ppm upfield shift. These shifts are consistent with those generally observed for aromatic systems[17] but are opposite in sense to those expected on simple electronic grounds. Electronic effects are apparently rendered insignificant by other 'heavy-atom effects', and these are not fully understood.[18] However, Br or Me substitution has little effect on the chemical shift of the unsubstituted ring atoms. For example, comparison of $[Co(NH_3)_5(4,5\text{-Hdbim})]^{3+}$ (4,5-Hdbim = 4,5-dibromoimidazole) with $[Co(NH_3)_5(Him)]^{3+}$ shows H^2 to be shifted upfield by only 0.12 ppm, and C^2 downfield by only 2.9 ppm, whereas the acidities of these two complexes differ by 5.41 pK_a units.

Acidity Constants.—These are listed in Table 3, and included are values obtained by other investigators; K_a measures the

Table 1 Proton NMR data for pentaamminecobalt(III) imidazole complexes in D_2O [see equation (1) for labelling]

Substituent	R^1	R^2	R^4	R^5
H		8.11	7.12	7.45
2-Methyl		2.46	6.79	7.32
1-Methyl	3.77	8.12	7.12	7.46
5-Methyl		7.93	6.77	2.32
4-Methyl		7.89	2.21	7.11
2,5-Dimethyl		2.27	6.58	2.09
5-Bromo		8.10	7.10	
4-Bromo		8.01		7.47
4,5-Dibromo		7.99		
1-Methyl-5-bromo	3.85	8.19	7.17	
5-Methyl-4-bromo		8.00		2.36
1-$Co(NH_3)_5{}^{3+}$		7.80	7.15	7.15
4-Methyl-5-bromo		7.94	2.18	
2,5-Dimethyl-4-bromo		2.47		2.20
2-Methyl-4,5-dibromo		2.47		
4(5)-Br,1-$Co(NH_3)_5{}^{3+}$		7.82	7.06	
1,2-dimethyl*	3.66	2.31	6.85	7.45
1,5-Dimethyl*	3.66	8.51	7.19	2.23
1,4-Dimethyl*	3.67	8.39	2.08	7.11
Imidazole (ligand)		7.77	7.14	7.14
1-Methylimidazole (ligand)		7.57	7.07	7.00

* Ref. 14. Spectra in this paper were recorded in $(CD_3)_2SO$ relative to $SiMe_4$.

Table 2 Carbon-13 NMR data for pentaamminecobalt(III) imidazole complexes

Substituent	C^2	C^4	C^5	R^1	R^2	R^4	R^5
H	139.9	128.4	121.8				
2-Methyl	150.1	128.6	121.0		14.1		
1-Methyl	141.8	129.1	126.1	36.2			
5-Methyl	139.0	124.9	132.4				10.4
4-Methyl	140.0	138.8	119.3			13.2	
2,5-Dimethyl	149.2	125.1	131.4		14.3		10.3
5-Bromo	141.9	128.5	104.7				
4-Bromo	141.5	115.1	122.9				
4,5-Dibromo	142.8	116.8	107.8				
2,4,5-Tribromo[a]	127.8	117.9	112.3				
1-Methyl-5-bromo	143.1	129.3	109.3	35.6			
5-Methyl-4-bromo	139.8	112.9	131.4				10.6
2,5-Dimethyl-4-bromo	149.6	111.7	130.9				10.8
1-$Co(NH_3)_5{}^{3+}$	147.0	130.6	130.6				
4-Methyl-5-bromo	140.9	136.9	103.1			12.5	
2-Methyl-4,5-dibromo	152.8	115.8	107.0				
4(5)-Br,1-$Co(NH_3)_5{}^{3+}$	149.2	131.1	115.3		16.3		
1,2-Dimethyl[b]	149.0	126.3	124.8				
1,5-Dimethyl[b]	139.9	124.4	133.2				
1,4-Dimethyl[b]	140.6	138.4	122.2				
Imidazole (ligand)	137.3	123.0	123.0				
1-Methylimidazole (ligand)	139.7	122.5	128.7	34.1			

[a] Recorded in acetate buffer. Signals are therefore those of the deprotonated (imidazolate) complex. [b] Ref. 14. Spectra in this paper were recorded in 50% water–50% D_2O.

equilibrium (7). The $Co(NH_3)_5{}^{3+}$ moiety has a moderate Lewis-acid effect on the pyrrole proton (pK_a 10.1 *vs.* 14.9 for the free ligand), and this has been commented on previously.[4,7]

Table 3 pK_a Data for pentaamminecobalt(III) imidazole complexes

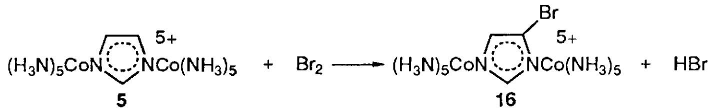
Substituent	pK_a	Conditions (I/mol dm^{-3}, T/°C)	Ref.
H	10.10 ± 0.04	1.0 ($NaClO_4$), 25.0	*a*
H	10.00 ± 0.03	1.0 (NaBr), 25.0	*a*
H	9.99 ± 0.08	0.1, 25.0	6
H	10.02 ± 0.04	1.0 ($NaClO_4$), 25.0	4
H	10.00 ± 0.1	Not specified	19
H	9.92 ± 0.03	1.0 ($NaClO_4$), 30.0	*a*
H	9.82 ± 0.02	1.0 ($NaClO_4$), 35.0	*a*
H	9.62 ± 0.03	1.0 ($NaClO_4$), 40.0	*a*
2,4,5-Trideuterio	10.04 ± 0.01	1.0 (NaBr), 25.0	*a*
5-Bromo	6.38 ± 0.03	1.0 ($NaClO_4$), 25.0	*a*
4-Bromo	8.06 ± 0.03	1.0 ($NaClO_4$), 25.0	*a*
4,5-Dibromo	4.69 ± 0.03	1.0 ($NaClO_4$), 25.0	*a*
2,4,5-Tribromo	1.83	1.0 ($NaClO_4$), 25.0	*b*
2-Methyl	10.67 ± 0.08	0.1, 25.0	5
5-Methyl	10.70 ± 0.08	0.1, 25.0	5
4-Methyl	10.46 ± 0.08	0.1, 25.0	5
4,5-Dimethyl	11.04 ± 0.08	0.1, 25.0	5
Imidazole (ligand)	14.90		11
1-Methylimidazole (ligand)	7.30		11

[a] This work. [b] An accurate value could not be obtained due to concomitant acid hydrolysis. The value given is derived from the hydrolysis rate data (see text).

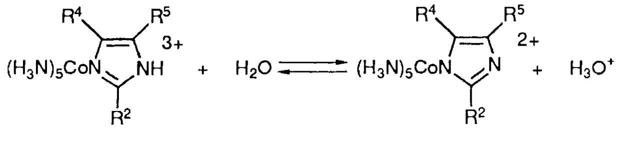
Methyl substitution generally causes an acid-weakening effect.[6] Bromine substitution on the other hand results in a substantial acid-strengthening effect (as expected), and when fully substituted, as in $[Co(NH_3)_5(Htbim)]^{3+}$, the imidazole ligand is reasonably acidic, pK_a = 1.83. The enhanced acidity of $[Co(NH_3)_5(5\text{-Hbim})]^{3+}$ (pK_a = 6.38) compared to $[Co(NH_3)_5(4\text{-Hbim})]^{3+}$ (pK_a = 8.06) is also to be expected from the location of the substituent adjacent to the pyrrole proton. This effect has been noted previously in C^4 and C^5 chloro- and nitro-substituted *N*-methylimidazoles.[11] However, deuterium substitution as in the 2,4,5-trideuterioimidazole derivative has no measurable acid-weakening effect. This again is to be expected.[20] Hoq and Shepherd[6] have previously reported ΔH for deprotonation of $[Co(NH_3)_5(Him)]^{3+}$ as 58 ± 2 kJ mol^{-1}. We have remeasured this under conditions appropriate to our mechanistic requirements.[1] The pK_a data included in Table 3 give $\Delta H = 55 \pm 3$ kJ mol^{-1} (I = 1.0 mol dm^{-3}), in excellent agreement with the value found by Hoq and Shepherd.

Hydrolysis of $[Co(NH_3)_5(Htbim)]^{3+}$.—This complex undergoes both H^+- and OH^--catalysed hydrolysis. After 30 min in 0.1 mol dm^{-3} acid RP-HPIPC analysis indicated both $[Co(NH_3)_5(OH_2)]^{3+}$ and free 2,4,5-tribromoimidazole in addition to unreacted $[Co(NH_3)_5(Htbim)]^{3+}$. However, the complex is stable under neutral conditions and crystallises without change from phosphate buffer (pH 6.8). Solutions of complex **9** decompose on exposure to laboratory light irrespective of solution pH.

Rate data for the hydrolysis are given in Table 4. For pH > 9.75 kinetics first order in $[OH^-]$ are observed, while



(6)



(7)

Table 4 Rate data for the hydrolysis of $[Co(NH_3)_5(tbim)]^{2+}$ **9***

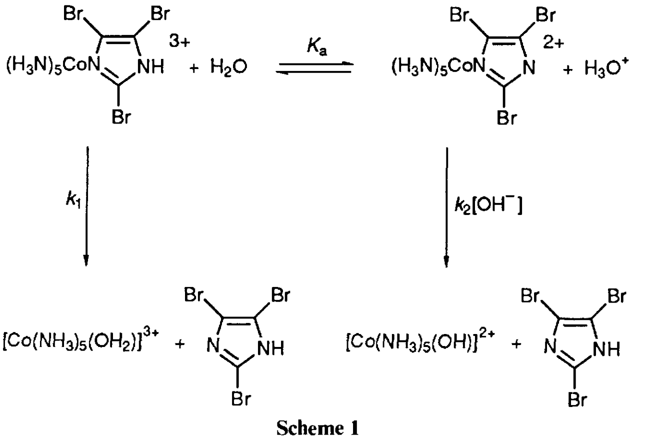
pH	k_{obs}/s^{-1}
0.11	1.93×10^{-4}
1.11	1.75×10^{-4}
2.11	1.09×10^{-4}
2.75	2.26×10^{-5}
3.37	7.31×10^{-6}
4.09	1.55×10^{-6}
9.75	1.52×10^{-5}
10.41	3.54×10^{-5}
10.96	1.36×10^{-4}
11.66	6.14×10^{-4}
12.66	7.22×10^{-3}
13.66	3.61×10^{-2}

* λ = 490, 340 nm; 25.0 °C, $[Co]_T = 1.00 \times 10^{-3}$ mol dm^{-3}, I = 1.0 mol dm^{-3} ($NaClO_4$).

Table 5 Rate data for the isomerisation of $[Co(NH_3)_5(4\text{-}Hbim)]^{3+}$ **6** in D_2O, 70.0 °C, I variable

pH*[a]	pD[b]	$[OD^-]^c$/mol dm^{-3}	k_{obs}/s^{-1}
7.86[d]	6.56	8.71×10^{-8}	6.05×10^{-5}
8.36[d]	7.06	2.75×10^{-7}	9.63×10^{-5}
9.24[d]	7.94	2.09×10^{-6}	1.46×10^{-4}
11.07[e]	9.77	1.41×10^{-4}	1.74×10^{-4}

[a] Meter reading at 25.0 °C. [b] Values at 70.0 °C calculated using pD = pH* − 1.3.[3] [c] Values at 70.0 °C calculated using $pK_w(D_2O)$ (70.0 °C) = 13.62. [d] $[hepes]_T$ = 0.20 mol dm^{-3}. [e] $[caps]_T$ = 0.2 mol dm^{-3}.



Scheme 1

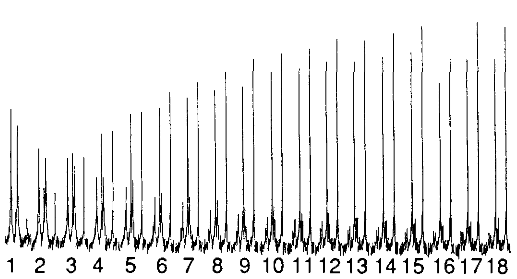
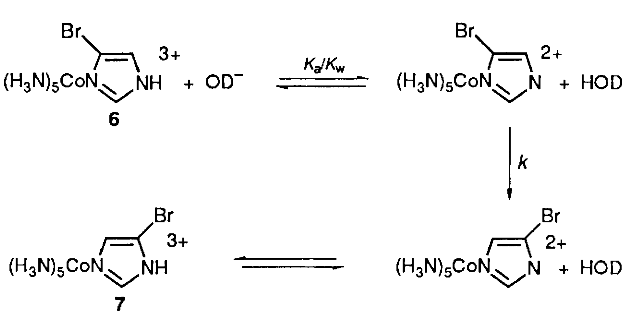


Fig. 1 Proton NMR spectra (300 MHz) for the decay of $[Co(NH_3)_5(4\text{-}Hbim)]^{3+}$ (δ 7.55, H^2; 7.25, H^5) to its 5-Hbim tautomer (δ 7.33, H^2; 6.83, H^4) at 70.0 °C in D_2O (pD 7.06). Spectra **1**–**18** were spaced at 30 min intervals with a 1.29 ppm spectra window



Scheme 2

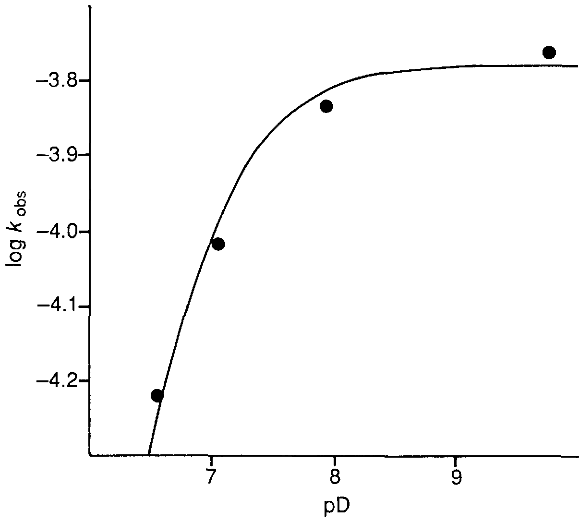


Fig. 2 Observed (●) and calculated [——, equation (9)] data for the isomerisation of $[Co(NH_3)_5(4\text{-}Hbim)]^{3+}$ to $[Co(NH_3)_5(5\text{-}Hbim)]^{3+}$ (70 °C in D_2O); *cf.* Table 5

under acidic conditions first-order behaviour in $[H^+]$ occurs to pH ≈ 2. At even lower pH an acid-independent rate is found. The data are consistent with the rate equation (8), with k_1

$$k_{obs} = (k_1[H^+] + k_2K_a[OH^-])/([H^+] + K_a) \quad (8)$$

corresponding to the acid-independent hydrolysis of the protonated reactant, $[Co(NH_3)_5(Htbim)]^{3+}$, and k_2 to the OH^- catalysed hydrolysis of its conjugate base. Analysis gives $k_1 = 2.07 \times 10^{-4}$ s^{-1} and $k_2 = 1.11 \times 10^{-1}$ dm^3 mol^{-1} s^{-1} using $K_a = 1.49 \times 10^{-2}$ mol dm^{-3}, Scheme 1; K_a represents the acidity constant for the protonated 3+ complex (pK_a = 1.83). The OH^- dependence may be attributed to the usual $S_N1(CB)$ mechanism for hydrolysis of cobalt(III) acido complexes, in which ammine deprotonation occurs prior to the rate-determining loss of ligand.[21]

Isomerisation of $[Co(NH_3)_5(4\text{-}Hbim)]^{3+}$.—Isomerisation of sterically hindered metal-bound heterocyclic ligands is well known. Examples include the isomerisations of cobalt(III) complexes containing 4-methylimidazole,[3] 5-phenyltetrazole[22] and 5-methyltetrazole[22] to their less sterically demanding remote isomers, and the adjacent-to-remote isomerisation of histidine co-ordinated to $[Fe(CN)_5]^{3-}$.[23]

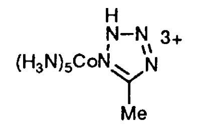
Rate data for isomerisation of complex **6** to **7**, Table 5, were collected using ^1H NMR spectroscopy at 70 °C by integration of the ligand peaks at regular time intervals. Representative spectra are given in Fig. 1. Fig. 1 shows the decay of the adjacent isomer **6** (7.55 and 7.25 ppm signals), and appearance of the remote isomer **7** (absorptions at δ 7.33 and 6.83). The final few spectra show the appearance of another set of peaks due to the free ligand, but the intensity of these suggests that the isomerisation process involves little decomposition. It is likely that slow hydrolysis of the product occurs. The rate increases with increasing pD, approaching a limiting value at about pD 9. The variation in the observed pseudo-first-order rate constant is given by equation (9) where $k = 1.67 \times 10^{-4}$ s^{-1} and $K_a = 1.37 \times 10^{-7}$ dm^3 mol^{-1} [pK_w (D_2O, 70 °C)

$$k_{obs} = kK_a[OD^-]/(K_w + K_a[OD^-]) \quad (9)$$

Table 6 Crystal data, data collection and refinement of compounds **1**, **5**, **6**, **9** and **13**

	$[Co(NH_3)_5(Him)]Br_3$ **1**	$[(H_3N)_5CoimCo(NH_3)_5]Br_5{\cdot}3H_2O$ **5**	$[Co(NH_3)_5(4\text{-}Hbim)][ClO_4]_{0.5}Br_{2.5}{\cdot}H_2O$ **6**	$[Co(NH_3)_5(tbim)][ClO_4]Br$ **9**	$[Co(NH_3)_5(5\text{-}bmim)]Br_3{\cdot}2H_2O$ **13**
Empirical formula	$C_3H_{19}Br_3CoN_7$	$C_3H_{39}Br_5Co_2N_{12}O_3$	$C_3H_{20}Br_{3.5}Cl_{0.5}CoN_7O_3$	$C_3H_{15}Br_4ClCoN_7O_4$	$C_4H_{24}Br_4CoN_7O_2$
M	451.88	808.81	558.58	627.20	580.84
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group[a]	$P2_12_12_1$ (no. 19)	$P2_1/n$ (no. 14)[b]	$P2_1/m$ (no. 11)	$P2_1/n$ (no. 14)[b]	$Pmcn$ (no. 62)[c]
a/Å	7.382(2)	12.946(4)	10.543(4)	8.886(2)	6.957(3)
b/Å	14.781(5)	14.469(5)	7.207(2)	16.209(5)	10.570(4)
c/Å	26.124(8)	14.022(4)	11.788(5)	11.049(2)	23.430(9)
α/°	90	90	90	90	90
β/°	90	107.18(2)	92.40(4)	101.69(2)	90
γ/°	90	90	90	90	90
U/Å^3	2851(2)	2509(1)	894.9(6)	1558.5(6)	1733(1)
$D_c(D_m)$/g cm^{-3}	2.11 (2.10)	2.14	1.78	2.67	1.93
Z	4	4	2	4	4
Crystal size/mm	0.20 × 0.15 × 0.11	0.32 × 0.18 × 0.10	0.72 × 0.12 × 0.2	0.31 × 0.13 × 0.06	0.32 × 0.13 × 0.13
μ(Mo-Kα)/cm^{-1}	101.48	98.42	69.95	122.09	84.15
F(000)	1744	1576	468	1192	980
T/K	295 ± 5	133 ± 5	163 ± 5	163 ± 5	138 ± 5
Scan speed/° min^{-1}	5.86	6.10	7.32	15.36	7.32
Data limits/°	$4 < 2\theta < 45$	$4 < 2\theta < 45$	$4 < 2\theta < 45$	$4 < 2\theta < 45$	$5 < 2\theta < 55$
Reflections measured	h,k,l	$h,k,\pm l$	$h,k,\pm l$	$h,k,\pm l$	h,k,l
Crystal decay[d] (%)	< 1	< 1	< 2	< 1	< 2
Transmission (max., min.)	0.863, 0.642	0.926, 0.371	0.853, 0.640	0.923, 0.705	0.851, 0.644
Total reflections[e]	2224	3297	1353	2274	2070
Unique data ($I > 2\sigma I$)	1197	2191	885	1547	1170
Number of variables	155[f]	192	90	171	84
$R = \Sigma\Delta F/\Sigma\lvert F_o\rvert$	0.0788	0.0576	0.0813	0.0774	0.0816
$R' = \Sigma w^{\frac{1}{2}}(\Delta F)/\Sigma w^{\frac{1}{2}}F_o$	0.0787	0.0532	0.0855	0.0817	0.0834
Weight (w)	$[1.4015/(\sigma^2F + 0.003\,064F^2)]$	$[1.3764/(\sigma^2F + 0.000\,74F^2)]$	$[1.4186/\sigma^2F + 0.028\,97F^2)]$	$[1.0000/(\sigma^2F + 0.0117\,39F^2)]$	$[1.8117/(\sigma^2F + 0.001\,839F^2)]$
Residual density/e Å^{-3}	1.16, −1.04	1.28, −1.08	2.36, −1.62	2.33, −1.36	1.40, −2.08

Details in common: Mo-Kα radiation (λ = 0.710 69 Å); scan type ω–2θ; empirical absorption correction; [a] Ref. 25. [b] A non-standard setting $P2_1/c$ (no. 14). [c] A non-standard setting of *Pnma*. [d] Standard reflections (6 0 0) (0 8 0) (0 0 10) for complex **1**; (0 −3 −2) (−1 −4 −2) (−1 −4 −5) for **5**; (0 4 0) (3 0 3) (−2 2 −2) for **6**; (8 0 0) (0 6 0) (0 0 6) for **9**; (2 0 0) (0 4 0) (0 0 6) for **13** measured after every 100 reflections. [e] Lorentz and polarisation corrections and empirical corrections were applied using the SHELXTL system.[26] [f] Two unique molecules in the asymmetric unit.



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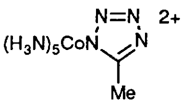

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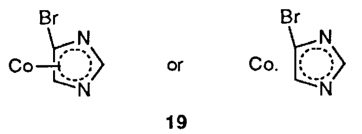

19

$= 13.62]^3$, Scheme 2. The solid line in Fig. 2 is calculated using these constants. The pK_a value in D_2O (6.86, 70 °C, I variable) is to be compared with the measured value in water of 8.06 [Table 3, 25.0 °C, I = 1.0 mol dm^{-3} ($NaClO_4$)]. The conjugate base form of the complex, $[Co(NH_3)_5(4\text{-}bim)]^{2+}$, is the only important reactant in the pD range 6.5–9.8.

The OH^- dependence is inconsistent with an $S_N1(CB)$ mechanism involving deprotonation of an ammine ligand since this would not show the rate-limiting behaviour found above pD ≈ 7. Scheme 2 differs from that proposed by Ellis and Purcell[22] for the isomerisation of the 5-methyltetrazole complex where **17** was shown to be the reactive species at low pH, and **18** the reactant above pH ≈ 3 (by spontaneous, and OH^--catalysed paths). Likewise Hoq *et al.*[3] found $[Co(NH_3)_5(4\text{-}Hmim)]^{3+}$ **3** to be reactive as well as its conjugate base, whereas **6** appears to be quite stable towards isomerisation in acid solution.

We support a π-bonded or 'trapped' solvent-cage transition state **19** for the isomerisation of $[Co(NH_3)_5(4\text{-}bim)]^{2+}$, rather than a C^2-bound ylide species. Although this form is known in ruthenium(II)[24] chemistry our observation of no ^1H exchange at C^2 during the isomerisation process (the NMR experiment was carried out in D_2O) argues against an ylide intermediate.

X-Ray Crystal Structures.—(*a*) *Monomeric complexes.* Structures of the monomeric imidazole complexes $[Co(NH_3)_5(4\text{-}Hbim)][ClO_4]_{0.5}Br_{2.5}{\cdot}H_2O$ **6**, $[Co(NH_3)_5(tbim)][ClO_4]Br$ **9**, and $[Co(NH_3)_5(5\text{-}bmim)]Br_3{\cdot}2H_2O$ **13** were determined largely to identify unequivocally the position of bromine substitution; this was of particular importance for **6** since its remote isomer **7** was anticipated. The structure of the parent complex $[Co(NH_3)_5(Him)]Br_3$ **1** was also determined; it has not been reported previously. Crystal data are given in Table 6. Since the structures are not of high quality, and are otherwise of little interest, no additional information is given in this paper, but is available from the authors on request.

(*b*) *Imidazolatodicobalt dimer.* The structure of $[(H_3N)_5Co(im)Co(NH_3)_5]Br_5{\cdot}3H_2O$ **5** was more accurately defined. Selected bond lengths and angles are given in Table 7, atomic

Table 7 Bond lengths (Å) and angles (°) for $[(H_3N)_5Co(im)Co(NH_3)_5]Br_3{\cdot}3H_2O$

Co(1)–N(11)	1.96(1)	N(3)–C(4)	1.39(2)
Co(1)–N(12)	1.98(1)	N(3)–Co(2)	1.90(2)
Co(1)–N(13)	1.97(1)	C(4)–C(5)	1.37(2)
Co(1)–N(14)	1.98(1)	Co(2)–N(21)	1.95(1)
Co(1)–N(15)	1.95(1)	Co(2)–N(22)	1.96(1)
Co(1)–N(1)	1.92(1)	Co(2)–N(23)	1.97(1)
N(1)–C(2)	1.34(2)	Co(2)–N(24)	1.97(1)
N(1)–C(5)	1.39(2)	Co(2)–N(25)	1.97(1)
C(2)–N(3)	1.39(2)		
N(11)–Co(1)–N(1)	179.1(5)	C(2)–N(3)–Co(2)	124(1)
N(12)–Co(1)–N(1)	90.3(5)	C(4)–N(3)–Co(2)	131(1)
N(13)–Co(1)–N(1)	90.0(5)	N(3)–C(4)–C(5)	110(1)
N(14)–Co(1)–N(1)	90.9(5)	N(3)–Co(2)–N(21)	90.1(5)
N(15)–Co(1)–N(1)	89.4(5)	N(3)–Co(2)–N(22)	89.5(5)
Co(1)–N(1)–C(2)	123(1)	N(3)–Co(2)–N(23)	91.0(5)
Co(1)–N(1)–C(5)	130(1)	N(3)–Co(2)–N(24)	90.0(5)
C(2)–N(1)–C(5)	104(1)	N(3)–Co(2)–N(25)	178.1(5)
N(1)–C(2)–N(3)	114(1)	N(1)–C(5)–C(4)	106(1)
C(2)–N(3)–C(4)	103(1)		

Table 8 Final parameters with estimated standared deviations in parentheses for complex **5**

Atom	*X/a*	*Y/b*	*Z/c*
Co(1)	0.7197(1)	0.2474(2)	0.6803(2)
N(11)	0.7193(9)	0.2404(9)	0.8200(9)
N(12)	0.5682(9)	0.2044(9)	0.638(1)
N(13)	0.6636(8)	0.3745(8)	0.6732(9)
N(14)	0.8711(8)	0.2908(9)	0.725(1)
N(15)	0.7754(9)	0.1214(9)	0.6857(9)
N(1)	0.7180(8)	0.2553(9)	0.5429(8)
C(2)	0.749(1)	0.330(1)	0.503(1)
N(3)	0.7295(8)	0.3260(8)	0.4045(8)
C(4)	0.682(1)	0.241(1)	0.380(1)
C(5)	0.674(1)	0.197(1)	0.463(1)
Co(2)	0.7449(1)	0.4274(1)	0.3235(1)
N(21)	0.8012(9)	0.3444(9)	0.2410(9)
N(22)	0.5966(8)	0.4075(9)	0.2388(8)
N(23)	0.6845(9)	0.5127(9)	0.4026(9)
N(24)	0.8925(8)	0.4488(9)	0.4118(9)
N(25)	0.7636(9)	0.5346(9)	0.2437(9)
Br(1)	0.8663(1)	0.4318(1)	0.9185(1)
Br(2)	0.8694(1)	0.5289(1)	0.6498(1)
Br(3)	0.4765(1)	0.3497(1)	0.8082(1)
Br(4)	0.5750(1)	0.1981(1)	0.0938(1)
Br(5)	0.9597(1)	0.1206(1)	0.9251(1)
O(1)	0.4241(8)	0.0227(9)	0.6504(9)
O(2)	0.9155(8)	0.097(1)	0.5492(8)
O(3)	0.1706(8)	0.0746(9)	0.5340(8)

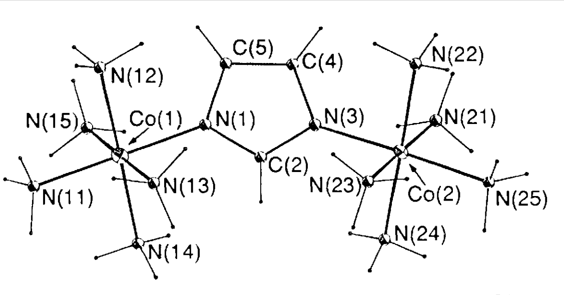

Fig. 3 Perspective view of the $[(H_3N)_5Co(im)Co(NH_3)_5]^{5+}$ cation **5** showing the atom numbering schemes. The ORTEP plot has thermal ellipsoids enclosing 50% probability levels for the anisotropic atoms

coordinates in Table 8 and an ORTEP[27] representation of the complex cation is given in Fig. 3 (which also gives the atom numbering scheme). The structure consists of two pentaamminecobalt(III) units bridged by co-ordination to the pyridine and deprotonated pyrrole nitrogens of an unsubstituted imidazolate moiety. The similarity of bond distances within the imidazolate ring suggests a delocalised electronic structure for the heterocyclic anion. The Co(1)–N(1) [1.92(1) Å] and Co(2)–N(3) [1.90(2) Å] bond lengths are significantly shorter than the corresponding linkages in the other molecules reported here; the Co–N (ammine) distances are unremarkable, [average 1.97(1) Å] and there is no evidence for a significant *trans* influence of the imidazolate ligand. In common with the monometallic complexes the imidazole ring approximately bisects the N(12)–Co(1)–N(15), N(13)–Co(1)–N(14), N(21)–Co(2)–N(22) and N(23)–Co(2)–N(24) angles. In this minimum-energy conformation the ammine ligands in the equatorial planes of the two cobalt co-ordination spheres are eclipsed when viewed down the Co(1) • • • Co(2) vector. Inspection of the plots based on the co-ordinates of the related trinuclear ion $[(H_3N)_5Co(im)Co(NH_3)_4(im)Co(NH_3)_5]^{7+}$ (ref. 9) shows that this arrangement of the imidazole ligand with respect to the equatorial ammines extends to the trinuclear system. Thus the imidazole ring plane adopts a bisecting configuration with respect to the ammine ligands in both the tetra- and pentaamine moieties.

Experimental

General.—All reagents were LR or AR grade. Dimethyl sulphoxide was purified by drying over calcium hydride followed by vacuum distillation (34 °C, 0.15 mmHg). Tributyl phosphate and sulpholane (tetrahydrothiophene 1,1-dioxide) were used as received. Both were stored over molecular sieves (4 Å). Residual Br_2 was removed from AR HBr (48%) by distillation (Rotavap). Solutions of aqueous bromine were standardised by addition to aqueous sodium iodide and titration of liberated iodine with standard sodium thiosulphate solution (Volucon). Proton and ^{13}C NMR spectra were recorded on a Varian VXR 300 spectrometer in D_2O at 25.0 °C. Chemical shifts (δ) are relative to 3-(trimethylsilyl)-2,2,3,3-tetradeuteriopropionic acid, sodium salt (^1H, δ 0.00) or 1,4-dioxane (^{13}C, δ 67.8) as internal reference standards. Visible spectra were recorded at 25.0 °C on a Cary 219 spectrophotometer using quartz cells (1 cm). Absorption coefficients (ε) are reported in units of $dm^3\ mol^{-1}\ cm^{-1}$. Microanalyses were performed by the Campbell Microanalytical Laboratory, University of Otago. Reported elemental percentages (C, H, N, Cl, Br, I, S) are accurate to ±0.3%. pH Measurements were made at 25.0 °C using a Radiometer PHM 62 pH meter fitted with G2040B glass and K4040 calomel electrodes. Measurements were carried out using a salt bridge ($NaNO_3$ 0.20 mol dm^{-3}, NH_4NO_3 1.60 mol dm^{-3}) to separate the solution from the saturated calomel electrode (SCE).

pK_a Values for the pentaamminecobalt(III) imidazole complexes were measured by potentiometric titration. A solution of complex [0.01 or 0.02 mol dm^{-3}, I = 1.0 mol dm^{-3} ($NaClO_4$ or NaBr)] in a thermostatted glass vessel (25.0 °C) flushed with N_2 was titrated with NaOH (0.1 or 0.2 mol dm^{-3}) in 0.1 mol equivalent aliquots. The pH was measured after the addition of each aliquot and the complete titration required 1.0 mol equivalent. The pH data were treated by the method of Albert and Serjeant,[28] and corrections were made for volume changes occurring during the titration, and for $[OH^-]$ for pH readings above 9.0.

Variable temperature data (25.0, 30.0, 35.0, 40.0 °C) for the acid–base equilibrium (7) ($R^2 = R^4 = R^5$ = H) were obtained by potentiometric titration of a solution of the complex [0.02 mol dm^{-3}, 30 cm^3, I = 1.0 mol dm^{-3} ($NaClO_4$)] in a thermostatted glass vessel with NaOH (0.2 mol dm^{-3}, 3.00 cm^3) under nitrogen. The pK_a values of $[Co(NH_3)_5L]Br_3$ (L = 2,4,5-trideuterioimidazole or imidazole) were determined similarly by potentiometric titration at 25.0 °C (I = 1.0 mol dm^{-3}, NaBr).

Preparations—(*a*) *Reagents and ligands*. Phosphate buffer (0.85 mol dm^{-3} total phosphate) was prepared by addition of

85% phosphoric acid (290 cm^3) to a solution of NaOH (100 g) and KOH (280 g) in water, and dilution with water to 5 dm^3. Pyridinium acetate was prepared by mixing pyridine with an equimolar amount of acetic acid and dilution to the appropriate concentration with water. Sodium trimethylacetate was prepared by the method of Puntambeker and Zoellner.[29] Hydroxypropanone was prepared by the method of Lipshutz and Morey,[30] b.p. 65–72 °C (13 mmHg). NMR (D$_2$O): ^{1}H, δ 4.82 (s, 2 H), 2.17 (s, 3 H) and 2.14 (s, 3 H); ^{13}C δ 205.8, 172.0, 65.7, 24.5 and 19.0. 1,3-Dimethylimidazolium iodide was prepared by the method of Benac *et al.*[31] The very hygroscopic product was recrystallised from butan-1-ol and stored in a vacuum desiccator (Found: C, 27.05; H, 4.35; I, 56.75; N, 12.05. Calc. for C$_5$H$_9$IN$_2$: C, 26.80; H, 4.05; I, 56.65; N, 12.50%). Conversion into the bromide salt was accomplished by shaking an aqueous solution of the iodide salt with excess of solid AgBr. The bromide salt could not, however, be isolated as a crystalline solid. 2,5-Dimethylimidazole was prepared by the method of Lipshutz and Morey.[30] The product was distilled *in vacuo* (120 °C, 0.04 mmHg) as a pale yellow oil which solidified on standing. NMR (D$_2$O): ^{1}H, δ 6.61 (s, 1 H), 2.25 (s, 3 H), 2.08 (s, 3 H); ^{13}C, δ 146.3, 133.4, 117.4, 13.6 and 11.8. 2,4,5-Trimethylimidazole was prepared by the method of Cowgill and Clark.[32] Isolation of the crude free base followed by sublimation *in vacuo* (80 °C, 0.02 mmHg) afforded a white solid, m.p. 132 °C (lit.,[33] 131 °C) (Found: C, 65.00; H, 9.05; N, 25.40. Calc. for C$_6$H$_{10}$N$_2$: C, 65.40; H, 9.15; N, 25.45%). 2,4,5-Tribromoimidazole was prepared by the method of Balaban and Pyman[34] (Found: C, 11.65; H, 0.30; Br, 78.45; N, 8.95. Calc. for C$_3$HBr$_3$N$_2$: C, 11.80; H, 0.35; Br, 78.65; N, 9.20%). 4-Bromoimidazole was prepared by the method of Balaban and Pyman,[34] m.p. 132 °C (lit.,[34] 134 °C) (Found: C, 24.50; H, 2.10; Br, 54.20; N, 19.60. Calc. for C$_3$H$_3$BrN$_2$: C, 24.50; H, 2.05; Br, 54.35; N, 19.05%). 4-Nitroimidazole was prepared by the method of Chang.[35]

(*b*) *Complexes.* All complexes were washed with absolute ethanol and diethyl ether, and air dried prior to elemental analysis. **CAUTION:** All perchlorate salts are potentially explosive. Those for use in syntheses involving heating in solution were thoroughly washed with absolute ethanol to remove any trace of acid, and air dried.

The complex [Co(NH$_3$)$_5$(OH$_2$)][ClO$_4$]$_3$ was prepared by the method of Diehl *et al.*[36] Crystallisation from hot water afforded the bromide-free product. The complex [Co(NH$_3$)$_5$(OH$_2$)][CF$_3$SO$_3$]$_3$ was prepared by the method of Kupferschmidt and Jordan,[37] [Co(NH$_3$)$_5$(OSMe$_2$)][ClO$_4$]$_3$ by the method of Buckingham *et al.*[38] and [Co(NH$_3$)$_5$(OSO$_2$CF$_3$][CF$_3$SO$_3$]$_2$ by the method of Kupferschmidt and Jordan[37] by dehydrating [Co(NH$_3$)$_5$(OH$_2$)][CF$_3$SO$_3$]$_3$ at 100 °C *in vacuo*. The latter preparation also affords [Co(NH$_3$)$_6$][CF$_3$SO$_3$]$_3$ in small quantities but this appeared to be an impurity in the [Co(NH$_3$)$_5$(OH$_2$)][CF$_3$SO$_3$]$_3$.

[Co(NH$_3$)$_5$(Him)]Br$_3$ **1**. A solution of [Co(NH$_3$)$_5$(OSMe$_2$)][ClO$_4$]$_3$ (10 g) and imidazole (5 g) in dry dimethyl sulphoxide (50 cm^3) was heated at 80 °C for 0.75 h. Following dilution with water to 1 dm^3, the solution was loaded onto Dowex 50W × 2 cation-exchange resin (H$^+$ form), washed with water, and impurities removed by elution with 1–3 mol dm^{-3} HCl. The orange-yellow product was then eluted with 3 mol dm^{-3} HCl. The eluate was taken to dryness by rotary evaporation and the solid twice crystallised from hot water by adding LiBr and cooling (Found: C, 8.25; H, 4.45; Br, 53.00; N, 21.65. Calc. for C$_3$H$_{19}$Br$_3$CoN$_7$: C, 7.95; H, 4.25; Br, 53.05; N, 21.70%). Electronic spectrum [ε(λ$_{max}$/nm); 0.01 mol dm^{-3} HClO$_4$]: 60.0 (473) and 68.3 (336).

The salt [Co(NH$_3$)$_5$(Him)][ClO$_4$]$_3$ was prepared by adding excess of NaClO$_4$ to a solution of the chloride salt of the complex and removing any remaining chloride from the recovered solid by treatment with aqueous AgClO$_4$. The precipitated AgCl was removed, the solution reduced to dryness by rotary evaporation, and the solid crystallised from hot water by addition of NaClO$_4$. The salt [Co(NH$_3$)$_5$(im)][ClO$_4$]$_2$ was prepared by dissolving [Co(NH$_3$)$_5$(Him)][ClO$_4$]$_3$ in excess of NaOH and precipitating the product by adding NaClO$_4$. This material was crystallised from hot water containing a few drops of NaOH by adding NaClO$_4$ and cooling in ice.

[Co(NH$_3$)$_5$(mim)]Br$_3$·2H$_2$O. A solution containing [Co(NH$_3$)$_5$(OH$_2$)][ClO$_4$]$_3$ (10 g) and 1-methylimidazole (3.6 g) dissolved in dimethyl sulphoxide (50 cm^3) was heated at 80 °C for 1.5 h. The solution was then cooled, diluted to 1.5 dm^3 with water, and loaded onto Dowex 50W × 2 cation-exchange resin (H$^+$ form). Elution with 3 mol dm^{-3} HCl, rotary evaporation to dryness, and addition of LiBr to an aqueous solution afforded the bromide salt as orange microcrystals on cooling (4.6 g, 42%) (Found: C, 9.35; H, 4.90; Br, 47.65; N, 19.30. Calc. for C$_4$H$_{21}$Br$_3$CoN$_7$·2H$_2$O: C, 9.55; H, 5.05; Br, 47.75; N, 19.55%). Electronic spectrum [ε(λ$_{max}$/nm) 0.01 mol dm^{-3} HClO$_4$]: 62.4 (474) and 71.2 (336).

[Co(NH$_3$)$_5$(2-Hmim)][ClO$_4$]$_3$. A solution of [Co(NH$_3$)$_5$(OSMe$_2$)][ClO$_4$]$_3$ (10 g) and 2-methylimidazole (5 g) in dimethyl sulphoxide (50 cm^3) was heated at 80 °C for 1.5 h. Dilution with water and removal of a solid purple impurity by filtration through Celite gave an orange solution. This was sorbed onto Dowex 50W × 2 cation-exchange resin (H$^+$ form) and eluted with 3 mol dm^{-3} HCl. Following rotary evaporation to dryness, addition of NaClO$_4$ to a hot, concentrated, aqueous solution and slow cooling gave the desired complex as orange microcrystals (Found: C, 9.15; H, 4.25; Cl, 20.35; N, 18.80. Calc. for C$_4$H$_{21}$Cl$_3$CoN$_7$O$_{12}$: C, 9.15; H, 4.05; Cl, 20.25; N, 18.70%). Electronic spectrum [ε(λ$_{max}$/nm), 0.01 mol dm^{-3} HClO$_4$]: 60.8 (481) and 78.7 (334). Isolation of the complex cation as the bromide salt (using LiBr) gave orange crystals which turned purple on drying in air.

[Co(NH$_3$)$_5$(5-Hmim)]Br$_3$·2H$_2$O **2** *and* [Co(NH$_3$)$_5$(4-Hmim)]Br$_3$·0.5H$_2$O **3**. These complexes were prepared as described by Hoq *et al.*[3] but an improved method for their separation was devised. The salt [Co(NH$_3$)$_5$(OH$_2$)][ClO$_4$]$_3$ (20 g) and 5-methylimidazole (7.1 g) in dimethyl sulphoxide (100 cm^3) were heated at 70 °C for 1.5 h. The solution was diluted to 1 dm^3 with water and a solid purple impurity removed by filtration. The resulting orange solution was loaded onto Dowex 50W × 2 cation-exchange resin (Na$^+$ form) and the sorbed complexes eluted with phosphate buffer (0.85 mol dm^{-3} total phosphate) at pH ≈7. A purple impurity eluted rapidly {presumably [Co(NH$_3$)$_5$(OH)]$^{2+}$} and the broad orange 3+ band separated into two components. Orange [Co(NH$_3$)$_5$(5-Hmim)]$^{3+}$ eluted first (≈75%), followed by orange-yellow [Co(NH$_3$)$_5$(4-Hmim)]$^{3+}$ (≈ 25%). The separated bands were collected and desalted on Dowex 50W × 2 resin by elution with 3 mol dm^{-3} HCl following initial washing with 1 mol dm^{-3} HCl. The complex bromide salts crystallised from water on adding LiBr to a concentrated aqueous solution. They were once recrystallised. Physical data for the two isomers are as follows: [Co(NH$_3$)$_5$(5-Hmim)]Br$_3$·2H$_2$O (6.5 g, 32%) (Found: C, 9.30; H, 5.35; Br, 47.50; N, 19.55. Calc. for C$_4$H$_{21}$Br$_3$CoN$_7$·2H$_2$O: C, 9.55; H, 5.00; Br, 47.75; N, 19.55%). Electronic spectrum [ε(λ$_{max}$/nm), 0.01 mol dm^{-3} HClO$_4$]: 66.7 (475); [Co(NH$_3$)$_5$(4-Hmim)]Br$_3$·0.5H$_2$O (0.77 g, 4%) (Found: C, 10.10; H, 4.65; Br, 50.75; N, 20.15. Calc. for C$_4$H$_{21}$Br$_3$CoN$_7$·0.5H$_2$O: C, 10.10; H, 4.65; Br, 50.45; N, 20.65%). Electronic spectrum [ε(λ$_{max}$/nm), 0.01 mol dm^{-3} HClO$_4$]: 63.5 (481).

[Co(NH$_3$)$_5$(2,5-Hdmim)]Br$_3$·2H$_2$O **4**. The salt [Co(NH$_3$)$_5$(OH$_2$)][ClO$_4$]$_3$ (10 g) and 2,4-dimethylimidazole (4 g) in dimethyl sulphoxide (50 cm^3) were heated at 80 °C for 1 h. Dilution with water and removal of a solid purple impurity by filtration yielded an orange solution. This was sorbed onto Dowex 50W × 2 cation-exchange resin. Washing with phosphate buffer removed low-charged impurities and the product was eluted with 4 mol dm^{-3} HCl after washing with 1 mol dm^{-3} HCl. The orange solid recovered by rotary evaporation was dissolved in the minimum volume of water and LiBr added. The precipitated orange product was collected and crystallised from warm water by adding LiBr and cooling (Found: C, 11.70; H, 5.00; Br, 46.50; N, 18.90. Calc. for $C_5H_{23}Br_3CoN_7{\cdot}2H_2O$: C, 11.65; H, 5.30; Br, 46.45; N, 19.00%). Electronic spectrum [$\varepsilon(\lambda_{max}/nm)$, 0.01 mol dm^{-3} $HClO_4$]: 63.0 (482) and 103 (340).

$[(H_3N)_5Co(im)Co(NH_3)_5]Br_5$ **5**. The salts $[Co(NH_3)_5(im)][ClO_4]_2$ (2.05 g) and $[Co(NH_3)_5(OSMe_2)][ClO_4]_3$ (2.60 g) in dimethyl sulphoxide (20 cm^3) were heated at 80 °C for 1 h. The solution was diluted to 500 cm^3 with water and loaded onto Sephadex SP C-25 cation-exchange resin. Elution with aqueous NaCl (0.7 mol dm^{-3}) removed low-charged impurities and the desired 5+ complex was then removed using 1 mol dm^{-3} pyridinium acetate. Rotary evaporation to dryness and crystallisation from warm water by addition of LiBr afforded the bromide salt as orange microcrystals (1.5 g, 40%) (Found: C, 4.60; H, 4.60; Br, 52.65; N, 22.20. Calc. for $C_3H_{33}Br_5Co_2N_{12}$: C, 4.75; H, 4.40; Br, 52.95; N, 22.25%). Electronic spectrum [$\varepsilon(\lambda_{max}/nm)$, 0.01 mol dm^{-3} $HClO_4$]: 128 (476) and 198 (336).

$[Co(NH_3)_5(4\text{-Hbim})]Br_3{\cdot}2H_2O$ **6**. A solution of $[Co(NH_3)_5(OSO_2CF_3)][CF_3SO_3]_2$ (10 g) and 4-bromoimidazole (5 g) in dry tributyl phosphate (50 cm^3) was heated at 80 °C for 1.25 h. The solution was then cooled and added dropwise to dry ether (1.5 dm^3) with stirring. The resulting orange precipitate was collected, dissolved in the minimum volume of water, and the remaining tributyl phosphate extracted by shaking with ether. Concentrated HBr (10 cm^3) was then added to the hot (60 °C) aqueous solution and the orange crystals which deposited on cooling were collected and recrystallised from the minimum volume of hot water (4.8 g, 53%) (Found: C, 6.20; H, 4.15; Br, 56.45; N, 17.20. Calc. for $C_3H_{18}Br_4CoN_7{\cdot}2H_2O$: C, 6.35; H, 3.90; Br, 56.40; N, 17.30%). Electronic spectrum [$\varepsilon(\lambda_{max}/nm)$, 0.01 mol dm^{-3} $HClO_4$]: 60.9 (478) and 92.5 (330).

$[Co(NH_3)_5(5\text{-Hbim})]Br_3{\cdot}2H_2O$ **7**. The salt $[Co(NH_3)_5(4\text{-Hbim})]Cl_3$ (6.4 g) in water (100 cm^3) was heated under reflux for 30 min during which time the mixture turned black and ammonia was evolved. Filtration gave an orange solution. This was sorbed onto Dowex 50W × 2 cation-exchange resin (H^+ form) and washed with water. Initial attempts to elute with 3 mol dm^{-3} HCl caused some product to bind irreversibly to the resin. The 3+ orange band was eluted with 3 mol dm^{-3} pyridinium acetate and the eluate rotary evaporated to dryness. The resulting orange solid was crystallised from hot water by adding LiBr (1 g, 12%) (Found: C, 6.30; H, 4.10; Br, 56.30; N, 17.55. Calc. for $C_3H_{18}Br_4CoN_7{\cdot}2H_2O$: C, 6.35; H, 3.90; Br, 56.40; N, 17.30%). Electronic spectrum [$\varepsilon(\lambda_{max}/nm)$, 0.01 mol dm^{-3} $HClO_4$]: 63.7 (474).

$[Co(NH_3)_5(4,5\text{-Hdbim})]Br_3{\cdot}2H_2O$ **8**. To $[Co(NH_3)_5(Him)]Br_3$ (2 g) dissolved in HBr (2 mol dm^{-3}, 100 cm^3) was added aqueous Br_2 (0.23 mol dm^{-3}, 2 mol equivalents) over 10 min with stirring. The product began to crystallise at the end of the addition. Stirring was continued for 10 min, then concentrated HBr (20 cm^3) was added and the mixture cooled in ice. The orange crystals were filtered off, washed with ethanol and ether and air dried (1.4 g). Purification was effected by chromatography on Dowex 50W × 2 cation-exchange resin (H^+ form). Elution with HCl (2 mol dm^{-3}) removed a minor orange band $\{[Co(NH_3)_5(Him)]^{3+}\}$ and the required product was removed slowly with 5 mol dm^{-3} HCl (chromatography was carried out in diffuse light as this complex undergoes photoaquation). The eluate was reduced to dryness (Rotavap) and the resulting orange solid was crystallised from water by adding LiBr and cooling in ice (Found: C, 5.90; H, 3.10; Br, 61.60; N, 15.10. Calc. for $C_3H_{17}Br_5CoN_7{\cdot}2H_2O$: C, 5.60; H, 3.30; Br, 61.60; N, 15.20%). Electronic spectrum [$\varepsilon(\lambda_{max}/nm)$ 0.01 mol dm^{-3} $HClO_4$]: 63.3 (480) and 127 (330).

The 4,5-dibromoimidazole ligand was characterised as follows. A solution (80 cm^3) of the complex (0.25 g) in water containing a small amount of $NaNO_3$ (pH 2) was electrolysed at −1.0 V (*vs.* SCE) in a locally constructed cell (platinum anode, mercury-pool cathode). The resulting solution was passed down a column of Sephadex SP-C25 cation-exchange resin and the column washed with water (100 cm^3). The combined eluates were concentrated (Rotavap) to about 5 cm^3 whereupon 4,5-dibromoimidazole crystallised. This was collected, washed with water, air dried and purified by vacuum sublimation (0.25 mmHg, 185 °C), m.p. 223 °C (lit.,[34] 225 °C), ^1H NMR (CF_3CO_2H) δ 8.77 (8.79).[39]

$[Co(NH_3)_5(tbim)][ClO_4]Br$ **9**. To a solution of $[Co(NH_3)_5(Him)]Br_3$ (8 cm^3, 0.04 mol dm^{-3}) 0.2 mol dm^{-3} in NaBr and 0.56 mol dm^{-3} in $NaClO_4$ was added a solution of phosphate buffer (8 cm^3, 0.4 mol dm^{-3} in Na_2HPO_4 and 0.2 mol dm^{-3} in $HClO_4$). To this was added aqueous bromine (24 cm^3, 0.04 mol dm^{-3}) 0.2 mol dm^{-3} in NaBr and 0.8 mol dm^{-3} in $NaClO_4$. The red crystals which formed on storing this mixture overnight in the dark were filtered off, washed with EtOH and ether, and dried in air (0.1 g, 51%) (Found: C, 5.95; H, 2.65; Br, 51.45; Cl, 5.75; N, 15.55. Calc. for $C_3H_{15}Br_4ClCoN_7O_4$: C, 5.75; H, 2.40; Br, 50.95; Cl, 5.65 N, 15.65%). Electronic spectrum [$\varepsilon(\lambda/nm)$ 0.01 mol dm^{-3} $HClO_4$]: 74.0 (488) and 116 (353).

$[Co(NH_3)_5(4,5\text{-Hbmim})]Br_3{\cdot}2H_2O$ **11** (4,5-Hbmim = 4-*bromo*-5-*methylimidazole*). The salt $[Co(NH_3)_5(5\text{-Hmim})]Br_3{\cdot}2H_2O$ (200 mg) in water (5 cm^3) was treated with aqueous bromine (0.1 mol dm^{-3}, 4 cm^3, 1 mol equivalent). Testing with starch-iodide paper showed that all the Br_2 had been consumed within 1 min of addition. The solution was then loaded onto Dowex 50W × 2 cation-exchange resin and the orange-yellow band eluted with 4 mol dm^{-3} HCl. The eluate was reduced to dryness (Rotavap) and the orange solid crystallised from water by slow cooling following the addition of LiBr (143 mg, 60%) (Found: C, 8.70; H, 4.75; Br, 55.25; N, 16.80. Calc. for $C_4H_{20}Br_4CoN_7{\cdot}2H_2O$; C, 8.25; H, 4.15; Br, 55.00; N, 16.90%). Electronic spectrum [$\varepsilon(\lambda_{max}/nm)$, 0.01 mol dm^{-3} $HClO_4$]: 66.4 (482) and 123 (337).

$[Co(NH_3)_5(5,4\text{-Hbmim})]Br_3{\cdot}H_2O$ **12** (5,4-Hbmim = 5-*bromo*-4-*methylimidazole*). To $[Co(NH_3)_5(4\text{-Hmim})]Br_3{\cdot}2H_2O$ (500 mg, 1×10^{-3} mol) in water (10 cm^3) was added aqueous bromine (14.8 cm^3, 0.07 mol dm^{-3}, 1×10^{-3} mol). When starch-iodide paper gave no further positive test for bromine (≈ 5 min), the solution was rotary evaporated to dryness. The resulting solid was dissolved in the minimum volume of hot water, filtered, and the product allowed to crystallise by slow cooling following addition of LiBr(320 mg, 55%) (Found: C, 8.25; H, 4.05; Br, 56.65; N, 17.20. Calc. for $C_4H_{20}Br_4CoN_7{\cdot}H_2O$: C, 8.55; H, 3.95; Br, 56.80; N, 17.40%). Electronic spectrum [$\varepsilon(\lambda_{max}/nm)$]: 64.3 (480) and 120 (338).

$[Co(NH_3)_5(5\text{-bmin})]Br_3{\cdot}2H_2O$ **13**. The complex $[Co(NH_3)_5(mim)]Br_3{\cdot}2H_2O$ (5 g) dissolved in water (150 cm^3) was treated with bromine (0.77 cm^3, 1.5 mol equivalents). The orange-red complex which immediately precipitated was recovered and the filtrate left in a stoppered flask overnight. The precipitate was then dissolved in water, added to the filtrate, and the resulting solution extracted with chloroform to remove unreacted bromine. The aqueous phase was loaded onto Dowex 50W × 2 cation-exchange resin. Elution with 3 mol dm^{-3} HCl resulted in the separation of two orange compounds present in approximately equal amounts. The first corresponded to the starting complex and the second to the product. The latter was recovered, rotary evaporated to dryness, and crystallised from water by adding LiBr and cooling in ice (Found: C, 8.10; H, 4.40; Br, 55.00; N, 17.10. Calc. for $C_4H_{20}Br_4CoN_7{\cdot}2H_2O$: C, 8.25; H, 4.15; Br, 55.05; N, 16.90%). Electronic spectrum [$\varepsilon(\lambda_{max}/nm)$, 0.01 mol dm^{-3} $HClO_4$]: 64.0 (474).

$[Co(NH_3)_5(4,5,2\text{-Hdbmim})][ClO_4]_2Br$ **15** (4,5,2-Hdbmim = 4,5-*dibromo*-2-*methylimidazole*). To a solution of $[Co(NH_3)_5(2\text{-Hmim})][ClO_4]_3$ (500 mg, 9.5×10^{-4} mol) in warm water (20 cm^3) was added aqueous bromine (9.5 cm^3, 0.2 mol dm^{-3}, 1.9×10^{-3} mol). The solution was stored in the dark for 20 min and then rotary evaporated to dryness. The resulting orange solid was crystallised rapidly from the minimum volume of cold water by adding saturated aqueous LiBr and cooling in ice (260 mg, 41%) (Found: C, 7.30; H, 3.00; Br, 36.00; Cl, 10.75; N, 14.75. Calc. for $C_4H_{19}Br_3Cl_2CoN_7O_8$: C, 7.25; H, 2.90; Br, 36.15; Cl, 10.70; N, 14.80%). Electronic spectrum [$\varepsilon(\lambda_{max}/nm)$, 0.01 mol dm^{-3} $HClO_4$]: 66.7 (491) and 132 (341).

$[(H_3N)_5Co\{4(5)\text{-bim}\}Co(NH_3)_5]Br_5 \cdot 2H_2O$ **16**. To a solution of $[(H_3N)_5Co(im)Co(NH_3)_5]Br_5$ (110 mg) in water (10 cm^3) was added aqueous bromine (1.0 cm^3, 0.15 mol dm^{-3}, 1 mol equivalent). When starch-iodide paper gave no further positive test for bromine (30 min), the solution was reduced to dryness (Rotavap) and the solid precipitated from warm water by adding LiBr. Fractional crystallisation from warm water by adding LiBr and cooling in ice gave the pure product as orange microcrystals (50 mg, 39%) (Found: C, 4.10; H, 3.90; Br, 54.90; N, 19.25. Calc. for $C_3H_{32}Br_6Co_2N_{12} \cdot 2H_2O$: C, 4.15; H, 4.15; Br, 55.10; N, 19.35%). Electronic spectrum [$\varepsilon(\lambda_{max}/nm)$, 0.01 mol dm^{-3} $HClO_4$]: 136 (478) and 257 (337).

Attempted preparation of $[Co(NH_3)_5(Htmim)]X_3$ (Htmim = 2,4,5-*trimethylimidazole*). Numerous attempts to prepare this complex failed. Methods used included heating a 2 mol excess of ligand with the labile precursor $[Co(NH_3)_5(OSMe_2)][ClO_4]_3$ in a non-co-ordinating solvent (tributyl phosphate, dimethyl sulphoxide or sulpholane) at 80 °C for 1.5 h, heating a mixture of 2,4,5-trimethylimidazole and 2,4,5-trimethylimidazolium hydrochloride (1:1, 1:3) with $[Co(NH_3)_5(OSO_2CF_3)][CF_3SO_3]_2$ in tributyl phosphate at 80 °C for 1.5 h, and grinding a mixture of solid 2,4,5-trimethylimidazole and $[Co(NH_3)_5(OSO_2CF_3)][CF_3SO_3]_2$ with gentle heating. In each case, ^1H NMR specta of the orange 3+ product obtained following column chromatography (Dowex 50W × 2) of the diluted reaction mixtures showed no peaks in the methyl region.

Attempted preparation of $[Co(NH_3)_5(4\text{-nim})]X_2$ (4-nim = 4-*nitroimidazolate*). A solution of $[Co(NH_3)_5(OSO_2CF_3)][CF_3SO_3]_2$ (5 g) and 4-nitroimidazole (1.9 g) in tributyl phosphate (50 cm^3) was heated at 80 °C for 6 h. Chromatography on Sephadex SP-C25 cation-exchange resin gave one orange band which was identified as $[Co(NH_3)_6]^{3+}$ by the absence of imidazole proton signals in the ^1H NMR spectrum.

Rate Data.—Rate data for the isomerisation of $[Co(NH_3)_5(4\text{-Hbim})]^{3+}$ to $[Co(NH_3)_5(5\text{-Hbim})]^{3+}$ were collected on a Varian VXR 300 NMR spectrometer at 70.0 °C. A sample of the complex (≈0.05 mol dm^{-3}) in 0.02 mol dm^{-3} buffer [*N*-(2-hydroxyethyl)piperazine-*N*′-ethane-2-sulphonic acid (hepes) or cyclohexylaminopropane sulphonic acid (caps)] was made up in D_2O, and a maximum of 18 ^1H NMR spectra (64 transients) were recorded automatically after preacqusition delays ranging from 15 (pH* = 11.07) to 45 min (pH* = 7.86). The proton peaks corresponding to either the decay of the adjacent isomer or appearance of the remote isomer were machine integrated and these values used in plots of $\log(I_t - I_\infty)$ or $\log(I_\infty - I_t)$ *versus* time to determine k. These plots were found to be linear over at least two half-lives. The pH* values of the solutions were measured at 25.0 °C and converted into pD and $[OD^-]$ values as described in ref. 2, using $pK_w = 13.62$ (D_2O, 70.0 °C).

Spectrophotometric rate data for the hydrolysis of $[Co(NH_3)_5(tbim)]^{2+}$ were collected at both 490 and 340 nm at 25.0 °C. A solution of $[Co(NH_3)_5(tbim)][ClO_4]Br$ (2.00 cm^3, 2.00×10^{-3} mol dm^{-3}) was rapidly hand-mixed with an equal volume of aqueous $HClO_4$ or NaOH [0.0200, 2.00 mol dm^{-3}, $I = 2.00$ mol dm^{-3} ($NaClO_4$)] or with an appropriately neutralised solution of caps or hepes buffer [0.0500 mol dm^{-3}, $I = 2.00$ mol dm^{-3} ($NaClO_4$)] and the optical change (decrease) followed. The pH values of the latter solutions were measured at the completion of the reaction. Plots of $\log(A_t - A_\infty)$ *versus* time were linear over at least two half-lives. Treatment of the data collected at the two wavelengths gave identical first-order rate constants.

X-Ray Structure Determinations.—Data were collected on a Nicolet R3M four-circle diffractometer with graphite-monochromated Mo-Kα radiation. For the structures reported, cell parameters were obtained using 25 automatically centred reflections and crystal and instrument stability was monitored using three standards collected every 100 reflections. Space groups were deduced from systematic absences in the diffraction data. With the exception of complex **5**, the crystals obtained were small and weakly diffracting. However the X-ray data proved sufficient to solve the structures, although the crystal quality, together with disorder problems encountered in the structures of **6**, **9** and **13**, led to poor residuals and standard deviations.

The structures were solved by direct methods using SHELXTL[26] or SHELXS 86.[40] Any atoms not found in the initial E maps were found in subsequent least-squares refinement Fourier difference cycles using SHELX 76.[41] Full-matrix, least-squares refinement minimised $\Sigma w(|F_o| - |F_c|)$.[42] The cobalt, bromine and perchlorate anions were refined anisotropically in all structures, but limitations in the data precluded anisotropic refinement of other non-hydrogen atoms in some cases. Atomic scattering factors used were from SHELX 76 except for those of cobalt which were taken from the usual compilation.[42] Hydrogen atoms were input in idealised positions with fixed, isotropic thermal parameters. For complexes **6** and **13** the cobalt atoms, the imidazole ring atoms and their substituents, and the ammine ligand *trans* to the co-ordinated imidazole nitrogens lie on mirror planes and their coordinates and anisotropic thermal parameters were constrained appropriately.[43]

Refinement of the structure of complex **6** revealed two bromide anions, with the third anion site shared by a bromide and a perchlorate anion. Refinement of the occupancy factors for the Br, Cl and O atoms revealed each anion to be present in approximately equivalent proportions. The occupancy factors of these atoms were fixed at 0.5 for the final refinement cycles. This model for the structure resulted in a significant improvement in the residuals, although the high thermal parameters of the perchlorate oxygen atoms together with the observation of high peaks in the final difference maps in the vicinity of these anions suggested additional positional disorder. Partial occupancy was also observed for one of the bromide anions in **13**. The optimum final model has the bromide ion partitioned between a site on the mirror plane and one on a general position, again with 50% occupancy of the discrete locations. The final Fourier difference maps for **6**, **9** and **13** showed high peaks in the vicinity of the anions or solvate molecules but the possibility of additional disorder was not investigated further.

Additional material for complex **5** available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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