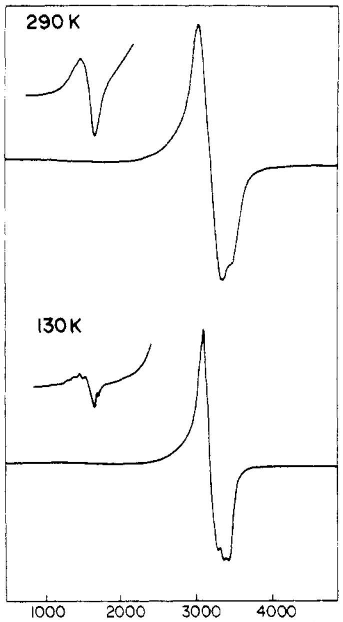

Figure 6. X-Band powder EPR spectra of complex **1** (microwave power 31 mW, microwave frequency 9.427 GHz, 10-G modulation amplitude).

The EPR spectra of complexes **2**–**4** are similar to those of **1**. The resulting EPR parameters are listed in Table VI.

Concluding Remarks

The study of four dimeric copper(II) complexes displaying large antiferromagnetic exchange interactions has been reported. The large exchange integrals arise from the important overlap of the d_{xy} magnetic orbitals which are coplanar with the oxalato or oxamido bridge.

Complex **1** is the first mepirizole compound that crystallizes with a molecule of free ligand. The structure of complex **2** is very unusual: it is built up from two crystallographically independent dimers in which the same ligands are involved with a different stereochemistry around the Cu(II) ions. On the basis of the sensible hypothesis that the antiferromagnetic interaction operating between the Cu(II) ions of unit **2B** is similar to that calculated for complex **1**, the magnitude of the antiferromagnetic interaction operating between the Cu(II) ions of unit **2A** has been evaluated.

Acknowledgment. We thank Dr. J. Galy for his constant interest in this work. We are grateful to Dr. J. V. Folgado for his friendly help. L.S. acknowledges the CNRS for permission to carry out part of this research at the Laboratoire de Chimie de Coordination, Toulouse, France, and the Generalitat Valenciana, Conselleria de Cultura, Educacio i Ciencia of Valencia, Spain, and the CAICYT (932/84) for financial assistance.

Registry No. **1**, 121886-87-1; **2**, 121865-93-8; **3**, 105236-60-0; **4**, 121865-94-9.

Supplementary Material Available: Figures 7–9, showing a side view of the $[Cu_2L_2(ox)(H_2O)_2]^{2+}$ cation of **1** (tilted by 10°), a partial representation of the crystal packing of **1** (projection onto (010)) and a side view of unit **2A** of complex **2**, respectively, Figures 10–12, showing the experimental and calculated molar magnetic susceptibility per dimer and effective magnetic moment per Cu(II) ion vs temperature for **1**, **3**, and **4**, respectively, Tables VII–IX, XI, XII, and XIV, listing crystallographic data, hydrogen atom positional parameters, final non-hydrogen atom thermal parameters, and deviations of atoms from least-squares planes for complexes **1** and **2**, respectively, and Tables XV–XVIII, listing the experimental magnetic susceptibility data for complexes **1**–**4**, respectively (23 pages); Tables X and XIII, listing the observed and calculated structure factor amplitudes for complexes **1** and **2**, respectively (35 pages). Ordering information is given on any current masthead page.

Notes

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University of Otago, P.O. Box 56, Dunedin, New Zealand

Stereochemical Change in the Hg^{2+}-, Ag^{+}-, and Cl_2-Induced and Spontaneous Reactions of Pentaamminecobalt(III)-Acido Species: A Reexamination

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Some 20 years ago we demonstrated by ^1H NMR spectroscopy the essential retention of stereochemistry when *trans*-$[Co(NH_3)_4(ND_3)X]^{2+}$ species ($X = N_3^-, NH_2CO_2^-, Cl^-, Br^-$) were treated with NO^+ or Hg^{2+} in the replacement of coordinated X^- by H_2O,[1] viz.

$$\textit{trans}\text{-}[Co(NH_3)_4(ND_3)X]^{2+} + NO^+ \rightarrow \textit{trans}\text{-}[Co(NH_3)_4(ND_3)OH_2]^{3+} + N_2 + N_2O \quad (1)$$

$$X = N_3^-, OCONH_2^-$$

$$\textit{trans}\text{-}[Co(NH_3)_4(ND_3)X]^{2+} + Hg^{2+} \rightarrow \textit{trans}\text{-}[Co(NH_3)_4(ND_3)OH_2]^{3+} + HgX^+ \quad (2)$$

$$X = Cl^-, Br^-$$

A similar result was found for the slower spontaneous aquation reaction (at 45 °C)

$$\textit{trans}\text{-}[Co(NH_3)_4(ND_3)Br]^{2+} + H_2O \rightarrow \textit{trans}\text{-}[Co(NH_3)_4(ND_3)OH_2]^{3+} + Br^- \quad (3)$$

Although not high by today's standards (a 60-MHz instrument was used), the quality of the data sufficed to distinguish the absence of major stereochemical change, and the results were interpreted in terms of dissociative S_N1 chemistry with formation of square-pyramidal intermediates as opposed to those of the trigonal-bipyramidal variety.

Since then extensive evidence has accumulated substantiating the dissociative nature of these reactions, and the focus of attention has shifted to evaluating the lifetime of the five-coordinate intermediate or intermediates so formed.[2] This cannot be very long since they appear to capture their immediate solvent–anion surroundings, and in some cases the reactions retain a small leaving-group dependence because of this. It also appears[3] that the major part of anion incorporation (i.e. in competition experiments when another group Y^- is available for entry) arises by direct association of Y^- with the inducing agent (i.e. as NOY, HgY^+, or ClCl in Cl_2 oxidation experiments).

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(1) Buckingham, D. A.; Olsen, I. I.; Sargeson, A. M. *Aust. J. Chem.* **1967**, *20*, 597.

(2) Jackson, W. G.; McGregor, B. C.; Jurisson, S. S. *Inorg. Chem.* **1987**, *26*, 1286. This recent article lists most previous references on this topic and gives an account of the problems of mechanism that remain.

(3) Buckingham, D. A.; Clark, C. R.; Webley, W. S. *Inorg. Chem.* **1982**, *21*, 3353. This article discusses in some detail the anion dependence of the NO^+-induced reaction, but we were not the first to observe this (Haim, A.; Taube, H. *Inorg. Chem.* **1963**, *2*, 1199). Early publications also describe kinetic contributions from anions in the Hg^{2+} (Posey, F. A.; Taube, H. *J. Am. Chem. Soc.* **1957**, *79*, 255) and Ag^+ (Dolbear, G. E.; Taube, H. *Inorg. Chem.* **1967**, *6*, 60) cata Our own recent work in this area (unpublished) shows that anion contributions dominate the rate laws and products for the Hg^{2+}- and Ag^+-induced reactions, with anion-independent processes being of very minor importance.

0020-1669/89/1328-3386$01.50/0

We now believe that the many previous studies using "constant ionic strength" conditions to hold activity coefficients at the same value ($NaClO_4$ or $NaCF_3SO_3$ have often been used as supporting electrolytes in these studies) have resulted in much detail being lost for the anion-dependent processes (i.e. a process involving Y^- may be partially or totally obscured by pathways involving ClO_4^- or $CF_3SO_3^-$). Also, these pathways are much more important in the overall reaction than has generally been recognized. To examine such factors, we have carried out parallel experiments on several induced and spontaneous reactions using both unsupported media involving only one anion and media involving two "detectable" anions whose concentrations can be varied to maintain a constant total electrolyte concentration. As part of this study it has been necessary to repeat the above-mentioned stereochemical experiments to examine with greater precision the reported absence of stereochemical change. This note describes the results obtained.

Experimental Section

The *trans*-$[Co(NH_3)_4(^{15}NH_3)Br]X_2$ (X = Br^-, $CF_3SO_3^-$) complexes were prepared as described recently.[4] *trans*-$[Co(NH_3)_4(^{15}NH_3)OH_2](ClO_4)_3$ was prepared by treating 1 g of the $CF_3SO_3^-$ salt dissolved in 5 cm^3 of 0.1 M $HClO_4$ with 0.8 M $Hg(ClO_4)_2$/0.2 M $HClO_4$ until all of the bromide had precipitated as $HgBr_2$.

trans-$[Co(NH_3)_4(^{15}NH_3)OH_2](ClO_4)_3$ crystallized on adding $NaClO_4$ to the filtered and cooled solution. This was recrystallized from warm 0.1 M $HClO_4$ by adding $NaClO_4$ and cooling, and the recovered material was washed with MeOH and dried in air.

^1H NMR spectra were recorded on a Varian VXR 300 spectrometer using a thermostated (25 °C) 5 mm probe. Samples were dissolved in 0.1 M DCl (deuterated-TSP standard) or DMSO-d_6 (DMSO, 2.600 ppm), and a 2.00-s delay was introduced between transients (cf. Figure 1 for further details). Ion-exchange chromatography used Dowex 50W-X2 or Sephadex SP-C25 resins with 1–3 M HCl or 0.2 and 0.5 M CF_3CO_2H eluents, respectively.

The following induced aquation experiments were carried out with *trans*-$[Co(NH_3)_4(^{15}NH_3)Br](CF_3SO_3)_2$ as reactant. (a) A 300-μL amount of 0.4 M $Hg(CF_3SO_3)_2$/0.1 or 0.2 M CF_3SO_3H was added to 50 mg of complex dissolved in 3 cm^3 of 1 M $NaCF_3SO_3$ at 25 °C. After 2 min the solution was diluted with water and sorbed on Sephadex resin and $CoOH_2^{3+}$ was eluted with 0.5 M CF_3CO_2H. This was reduced to dryness at room temperature by rotary evaporation. (b) An identical experiment was carried out in a ClO_4^- medium. (c) A 50-mg amount of complex in water (2.5 cm^3) was added to 2.5 cm^3 of a 0.1 M Hg^{2+}/0.02 M H^+/2.0 M NO_3^- solution at 25 °C. After 2 min the solution was diluted with water and sorbed on Sephadex, the column was eluted with CF_3CO_2H (0.2 M, $CoONO_2^{2+}$; 0.5 M, $CoOH_2^{3+}$), and the bands were reduced to dryness. (d) A 50-mg amount of complex dissolved in water (2.5 cm^3) was added to 2.5 cm^3 of 2 M Ag^+/0.1 M H^+/2.0 M ClO_4^- solution at 25 °C. After 20 min HCl (3.9 cm^3, 1 M) was added and precipitated AgCl removed. The $CoOH_2^{3+}$ product was recovered as previously described. (e) A 20-mg amount of complex dissolved in water (10 cm^3) was added to 10 cm^3 of 1.8 M Ag^+/0.2 M H^+/2.0 M NO_3^- solution. After 5 min HCl (20 cm^3, 1 M) was added, precipitated AgCl removed, and the filtrate diluted with water and sorbed on Dowex 50W-X2 resin. The $CoONO_2^{2+}$ and $CoOH_2^{3+}$ products were eluted with 1.5 and 3 M HCl, respectively, and reduced to dryness. They were then separately readsorbed on Sephadex resin and eluted with CF_3CO_2H as described above (the chloride salts are not particularly soluble in DMSO-d_6). (f) A 20-mg amount of complex dissolved in DMSO (1 cm^3) was added to 1 cm^3 of 2.0 M $AgClO_4$ in DMSO. After 30 min the solution was diluted with water, treated with HCl (25 cm^3, 1 M), and worked up as in (e) above. (g) $Cl_2(g)$ (free of HCl) was bubbled into a solution of 50 mg of complex dissolved in $HClO_4$ (3 cm^3, 0.05 M). The color change from purple to red was complete in about 5 s. Concentrated HCl was added after 2 min, whence the chloride salt of the product crystallized (ice bath). This solid was recovered.

Spontaneous Aquation. A 20-mg amount of *trans*-$[Co(NH_3)_4(^{15}NH_3)Br](CF_3SO_3)_2$ was dissolved in 2 cm^3 of 0.1 M $HClO_4$ and kept at 25 °C for 6 days. The resulting $CoOH_2^{3+}$ product was recovered from Dowex 50W-X2 cation-exchange resin as described above.

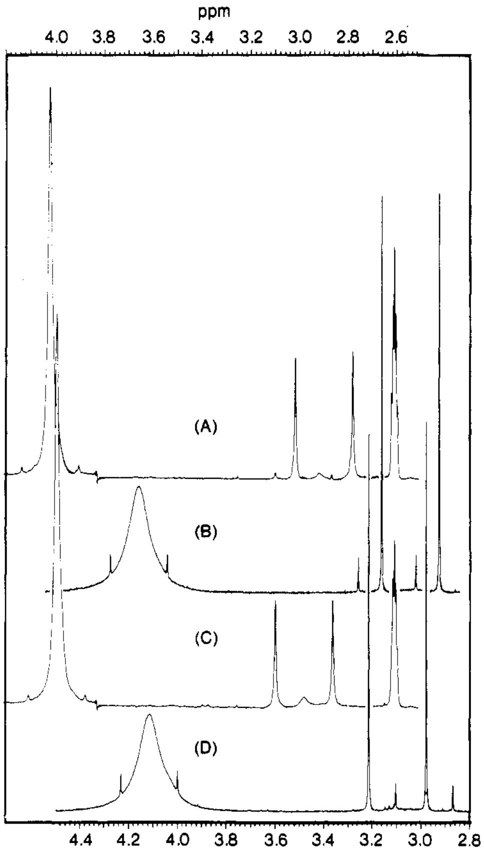

Figure 1. Representative ^1H NMR spectra (300 MHz) of the products from the reactions of *trans*-$[Co(NH_3)_4(^{15}NH_3)Br](CF_3SO_3)_2$. Spectra for the reaction with 0.05 M Hg^{2+} in 0.075 M H^+, 1.0 M NO_3^- (experiment 9, Table I): (A) $CoONO_2^{2+}$ product, in acidified DMSO-d_6 (288 transients); (B) $CoONO_2^{2+}$ product, in 0.1 M DCl (64 transients); (C) $CoOH_2^{3+}$ product, in acidified DMSO-d_6 (1024 transients); (D) $CoOH_2^{3+}$ product, in 0.1 M DCl (64 transients). The low-field (3.9–4.2 ppm) signals (small ^{15}NH proton doublet centered about large ^{14}NH proton signal) represent the trans ammine, while the high-field (2.8–3.1 ppm) signals (large ^{15}NH proton doublet centered about small ^{14}NH proton singlet) represent the cis ammine groups. The top scale is given for spectra A and C and the bottom scale for B and D. Other parameters: spectral band width 2608.9 Hz; Acquisition time 1.006 s; pulse width 5.4 μs; delay 2.000 s.

Water Exchange and Stereochemical Change. A 0.1-g amount of *trans*-$[Co(NH_3)_4(^{15}NH_3)OH_2](ClO_4)_3$ was dissolved in 2.0 cm^3 of 0.1 M $HClO_4$ and kept at 25 °C. Periodically samples (0.3 cm^3) were removed and treated as for the spontaneous aquation experiment.

Water Exchange and Anation. A 0.5-g amount of *trans*-$[Co(NH_3)_4(^{15}NH_3)OH_2](ClO_4)_3$ dissolved in water (10 cm^3) was converted to the chloride salt by passing through Dowex 1-X4 anion (Cl^-) exchange resin (tested with Ph_4AsCl to ensure complete removal of ClO_4^-), and the solution volume was reduced by rotary evaporation to 5 cm^3. Half of this solution was mixed with 2.5 cm^3 of 2 M HCl and the other half mixed with 2.5 cm^3 of 4 M HCl. Both solutions were kept at 25 °C, and crystallized $[Co(NH_3)_4(^{15}NH_3)Cl]Cl_2$ was removed at various times. At these times a sample of the solution was loaded onto Dowex 50W-X2 resin and $CoOH_2^{3+}$ recovered as previously described.

Solid-State Anation. A sample of *trans*-$[Co(NH_3)_4(^{15}NH_3)OH_2](ClO_4)_3$ prepared as in reaction b above was converted to the chloride salt (by elution from Dowex 50W-X2 resin with 3 M HCl and reduction to dryness by rotary evaporation below room temperature) and half the solid heated at 90 °C under vacuum for 90 min to produce the purple chloro complex. The remaining solid was retained for stereochemical analysis.

Results

Hereafter the *trans*-$[Co(NH_3)_4(^{15}NH_3)X]^{2+/3+}$ reactant is abbreviated as $CoBr^{2+}$ or $CoOH_2^{3+}$, and the various products are designated as $CoOH_2^{3+}$, $CoONO_2^{2+}$, $CoCl^{2+}$, etc.

Two requirements were essential to this reinvestigation: first, the need for a stereochemically defined starting material whose relationship to (possible) rearranged products is clear-cut and,

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(4) Brasch, N. E.; Buckingham, D. A.; Clark, C. R.; Finnie, K. S. Submitted for publication in *Inorg. Chem.*

(5) Buckingham, D. A.; Olsen, I. I.; Sargeson, A. M. *J. Am. Chem. Soc.* **1968**, *90*, 5129, 6539.

(6) Balt, S.; Gamelkoorn, H. J.; Renkema, W. E. *J. Chem. Soc., Dalton Trans.* **1983**, 2415. Gamelkoorn, H. J. *J. Chem. Soc., Dalton Trans.* **1985**, 659.

Table I. Stereochemical Results for Induced Reactions of $CoBr^{2+}$ (25 °C)

expt. no.	concn, mol dm^{-3}		% cis impurity reactant (±0.2%)	product	% cis (±0.2%)	% cis change	
	reagent	medium					
1	0.04 (Hg^{2+}) 0.01 (H^+)	1.0 ($CF_3SO_3^-$)	1.6	$CoOH_2^{3+}$	4.4	2.8	
2	0.01 (H^+)	1.0 ($CF_3SO_3^-$)	1.6	$CoOH_2^{3+}$	4.7	3.1	
3	0.08 (Hg^{2+}) 0.02 (H^+)	1.0 ($CF_3SO_3^-$)	1.6	$CoOH_2^{3+}$	4.3	2.7	
4	0.04 (Hg^{2+}) 0.02 (H^+)	1.0 ($CF_3SO_3^-$)	3.5	$CoOH_2^{3+}$	6.1	2.6	
						2.8 ± 0.4 (av)	
5	0.05 (Hg^{2+}) 0.025 (H^+)	1.0 (ClO_4^-)	3.5	$CoOH_2^{3+}$	6.9	*3.4 ± 0.4*	
6	0.05 (Hg^{2+})	1.0 (NO_3^-)	1.6	$CoOH_2^{3+}$	3.6	2.0	
	0.01 (H^+)			$CoONO_2^{2+}$	2.4		0.8
7	0.01 (H^+)	1.0 (NO_3^-)	1.6	$CoOH_2^{3+}$	4.0	2.4	
				$CoONO_2^{2+}$	1.9		0.3
8	0.05 (Hg^{2+})	1.0 (NO_3^-)	3.5	$CoOH_2^{3+}$	5.7	2.2	
	0.025 (H^+)			$CoONO_2^{2+}$	4.2		0.7
9	0.05 (Hg^{2+})		3.5	$CoOH_2^{3+}$	5.6	2.1	
	0.075 (H^+)			$CoONO_2^{2+}$	4.0		0.5
				$CoOH_2^{3+}$		*2.2 ± 0.4* (av)	
				$CoONO_2^{2+}$			*0.6 ± 0.4* (av)
10	1.0 (Ag^+)	1.0 (ClO_4^-)	1.6	$CoOH_2^{3+}$	3.4	2.8	
11	1.0 (Ag^+) 0.025 (H^+)	1.0 (ClO_4^-)	3.5	$CoOH_2^{3+}$	5.8	2.3	
							2.6 ± 0.4 (av)
12	0.9 (Ag^+)	1.0 (NO_3^-)	1.6	$CoOH_2^{3+}$	4.7	3.1	
	0.1 (H^+)			$CoONO_2^{2+}$	1.8		0.2
13	1.0 (Ag^+)	1.0 (NO_3^-)	3.5	$CoOH_2^{3+}$	6.6	3.1	
	0.1 (H^+)			$CoONO_2^{2+}$	3.6		0.1
				$CoOH_2^{3+}$		*3.1 ± 0.4* (av)	
				$CoONO_2^{2+}$			*0.15 ± 0.4* (av)
14	1.0 (Ag^+)	1.0 (ClO_4^-) DMSO	1.6	$Co(DMSO)^{3+}$	3.6 ± 0.4	*2.0 ± 0.6*	
15	Cl_2(g)	0.05 ($HClO_4$)	1.6	$CoCl^{2+}$	1.2	*−0.4 ± 0.4*	
16	none	0.1 ($HClO_4$) (6 days)	1.6	$CoOH_2^{3+}$	4.4	*2.8 ± 0.4*	

second, a method for determining with precision and accuracy small amounts of rearrangement. These requirements are met respectively by the *trans*-$[Co(NH_3)_4(^{15}NH_3)X]^{2+}$ complexes and a 300-MHz ^1H NMR spectrometer. The ^{15}N nucleus gives sharp and well-separated trans- and cis-ammine ^1H doublets that define the position of entry of the entering group with respect to the leaving group: retention from the same face or inversion from an opposite face. This complex has been used previously for examining stereochemical change in the base hydrolysis reaction,[5,6] and it is ideal for such a purpose, being independent of any N–H exchange of the ammine protons.

Since the amount of stereochemical change is small, some comment is needed as to the method of assessment. Spectra were recorded in 0.1 M DCl, DMSO-d_6 acidified with D_2SO_4, or both. Figure 1 gives spectra in both solvents for the $CoOH_2^{3+}$ and $CoONO_2^{2+}$ products following treatment of $CoBr^{2+}$ with Hg^{2+} in a 1.0 NO_3^- medium (experiment 9, Table I). The spectra in aqueous DCl give sharper ^{15}N doublets than in DMSO (Figure 1A,C) (0.9 Hz at half-height for the trans doublets in DCl vs 1.8 Hz in DMSO), but the cis-$^{15}NH_3$ doublets lie on the sloping background of a large and broad $^{14}NH_3$ signal. Conversely, the spectra in DMSO show sharper $^{14}NH_3$ signals with the small cis-$^{15}NH_3$ doublets now lying on a flatter background, but the doublet itself is broader than in aqueous DCl. These contrasting bandwidths for the $^{15}NH_3$ and $^{14}NH_3$ signals in the two solvents meant that the sloping background was virtually the same when scale expansions were carried out. Figure 2 shows how this was done. Vertical and horizontal expansions of the cis-$^{15}NH_3$ signals (top) gave areas comparable to that on horizontal expansion of the larger trans-$^{15}NH_3$ signals (bottom). These were cut out along the indicated base lines, the mass of paper was weighed (both parts of the doublet), and the relative areas were determined. Ex-

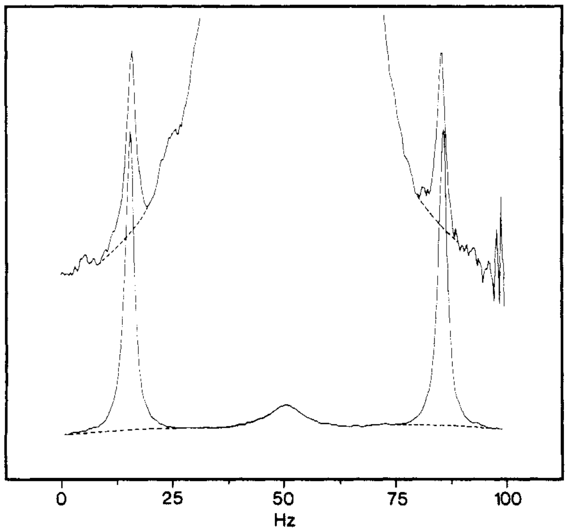

Figure 2. Representative expansion of the ^1H NMR spectrum of $CoOH_2^{3+}$ from the Hg^{2+}-induced reaction of *trans*-$CoBr^{2+}$ (experiment 9, Table I) in acidified DMSO-d_6 as solvent used to evaluate the percent cis product: (Top) 10x vertical expansion of cis-ammine region; (bottom) trans-ammine region. The complete spectrum is given in Figure 1C. Peak areas indicated by the dotted lines were cut out, and the paper was weighed on a microbalance.

Table II. Rate Data for Stereochemical Change in $CoOH_2^{3+}$ [a] in 0.1 M $HClO_4$ (25 °C)

time, days	% trans[b]	time, days	% trans[b]
0	95.7	54	72.7
6	92.7	102	56.2
46	77		

[a] The initial reactant *trans*-$[Co(NH_3)_4(^{15}NH_3)(OH_2)](ClO_4)_2$ contained a 4.3% impurity of the cis isomer. [b] ^1H NMR comparisons of cis- and trans-$^{15}NH_3$ doublets (in 0.1 M DCl).

Table III. Stereochemical Change in $CoOH_2^{3+}$ and Its Anation Product $CoCl^{2+}$ as a Function of Time (25.0 °C)

reacn medium	time, h	product	% cis
1 M HCl	0	$CoOH_2^{3+}$	4.3
	44	$CoOH_2^{3+}$	6.3
		$CoCl^{2+}$	5.5
	116	$CoOH_2^{3+}$	7.5
		$CoCl^{2+}$	6.8
	186	$CoOH_2^{3+}$	10.1
		$CoCl^{2+}$	8.1
	450	$CoOH_2^{3+}$	12.1
		$CoCl^{2+}$	8.9
2 M HCl	0	$CoOH_2^{3+}$	4.3
	44	$CoOH_2^{3+}$	5.7
		$CoCl^{2+}$	5.5
	116	$CoOH_2^{3+}$	6.3
		$CoCl^{2+}$	6.4
	186	$CoOH_2^{3+}$	7.6
		$CoCl^{2+}$	7.6

periments showed that variations in the time delay between acquisitions (1.0–5.0 s) did not alter the result so that both cis and trans signals are fully relaxed. This means that areas can be related to concentrations. Both NMR solvents gave comparable results (±0.2%, Table I). It was also possible in a number of cases to compare the areas of the small trans-$^{14}NH_3$ signals with that of the large cis-$^{14}NH_3$ signal (by instrument integration) when DMSO was used as solvent (Figure 1A,C). The results were the same as those obtained from the ^{15}N ^1H doublets.

Results for the Hg^{2+}-, Ag^+-, and Cl_2-induced reactions of $CoBr^{2+}$ are given in Table I. The estimated error of ±0.4% arises from experiments (and duplicates) carried out as described above. It was shown that no subsequent stereochemical change accompanies chromatography and workup, so that observed changes result from the reaction. Two independent workers using separately prepared samples of *trans*-$[Co(NH_3)_4(^{15}NH_3)Br](CF_3SO_3)_2$ and obtaining their results 1 year apart determined the values given. Their agreement was excellent.

Table II gives the results of stereochemical change in *trans*-$[Co(NH_3)_4(^{15}NH_3)OH_2](ClO_4)_3$ dissolved in 0.1 M $HClO_4$ at 25 °C as a function of time. The data fit the expression $\ln [(\% \text{ trans}_t) - 20] = -kt + \text{constant}$, giving $k = 7.3 \times 10^{-3}$ day^{-1}.

Table III gives results for stereochemical change when a solution of *trans*-$[Co(NH_3)_4(^{15}NH_3)OH_2]Cl_3$ in HCl (1.0 and 2.0 mol dm^{-3}) was kept at 25 °C. As time progressed and $CoCl^{2+}$ was formed, it crystallized from solution as the chloride salt, leaving largely unreacted $CoOH_2^{3+}$ behind. These crystals were periodically removed and analyzed, and at the same time a sample of $CoOH_2^{3+}$ was recovered from the aqueous phase and analyzed. The table lists stereochemical change in both $CoCl^{2+}$ and $CoOH_2^{3+}$. In another experiment a sample of $CoOH_2^{3+}$ containing a rather large cis-$^{15}NH_3$ impurity (39 ± 3%) was treated overnight in 50% aqueous concentrated HBr (warmed to keep the complex solution) and $[Co(NH_3)_4(^{15}NH_3)Br]Br_2$ recovered. Analysis showed no significant stereochemical change (41 ± 3% cis). In another experiment a solid sample of *trans*-$[Co(NH_3)_4(^{15}NH_3)OH_2]Cl_3$ (4.4 ± 0.2% cis impurity) was heated at 90 °C for 1.5 h. The recovered $CoCl^{2+}$ product in this case showed significant stereochemical change (12 ± 1% cis).

Discussion

The averaged results for stereochemical change in the $CoOH_2^{3+}$ products from the Hg^{2+}-induced reactions of *trans*-$CoBr^{2+}$ are as follows: (Table I): in a 1.0 mol dm^{-3} $CF_3SO_3^-$ medium, 2.8 ± 0.4% cis; in 1.0 mol dm^{-3} ClO_4^-, 3.4 ± 0.4% cis; in 1.0 mol dm^{-3} NO_3^-, 2.2 ± 0.4 cis. Similar results occur for the Ag^+-catalyzed reactions: 2.6 ± 0.4% in 1.0 mol dm^{-3} ClO_4^-, 3.1 ± 0.4% in 1.0 mol dm^{-3} NO_3^-. Stereochemical change is thus small and, within the accuracy of the measurements, is the same for the two reactions. It is however possible that the Hg^{2+}-catalyzed reaction gives less stereochemical change in a NO_3^- medium than in $CF_3SO_3^-$ or ClO_4^-, since this result is consistently found. However, no significant stereochemical change occurs in the $CoONO_2^{2+}$ product formed in 1.0 mol dm^{-3} NO_3^- (0.6 ± 0.4% cis for the Hg^{2+} reaction; 0.15 ± 0.4% cis for the Ag^+ reaction), but it must be noted that in every experiment a small positive result was obtained. These results can be compared to those from the Cl_2 oxidation experiment, where full retention clearly occurs (−0.4 ± 0.4% *cis*-$CoCl^{2+}$).

These results modify the previous view of complete stereochemical retention for the induced reactions.[1] We now believe that the absence of stereochemical change in $CoONO_2^{2+}$ arises from direct insertion of nitrate from $HgONO_2^+$. In a recent unpublished study[7] we have obtained extensive rate and product data for the similar reaction of Hg^{2+} with *t*-$[Co(tren)(NH_3)X]^{2+}$ (X = Br^-, Cl^-), which shows that contributions from HgY^+ species (Y = NO_3^-, ClO_4^-, $CF_3SO_3^-$) dominate the rate under most conditions and that these processes give rise to reasonably large amounts of *t*-$[Co(tren)(NH_3)Y]^{2+}$ products. It is easy to visualize the direct insertion of Y^- from HgY^+,[7] resulting in stereochemical retention. Likewise, the major part of the $CoOH_2^{3+}$ product could arise from abstraction of water from the hydration shell of Hg_{aq}^{2+} (or Ag_{aq}^+), or from its immediate surroundings, in a manner similar to that suggested by Posey and Taube many years ago for the Tl^{3+} reaction.[8]

The rate of stereochemical change in $CoOH_2^{3+}$ in 0.1 mol dm^{-3} $HClO_4$ of 8.4×10^{-8} s^{-1} (25 °C) is to be compared with that for water exchange, $k_{ex} = 5.9 \times 10^{-6}$ s^{-1}, as measured by Hunt and Taube under similar conditions.[9] Each act of stereochemical change therefore requires some 70 acts of water exchange, or 1.4% of all water exchanges occur with stereochemical inversion at the octahedral Co(III) center. This value is not very different from those obtained above for the induced reactions, and for the water-exchange process no additional reagent is required at the reaction site. Thus, disruption of the solvent shell at the reaction site by an added reagent is not a prerequisite for stereochemical change; it seems to be a general property of the substitution process.

The rate of stereochemical change in $CoOH_2^{3+}$ in 1.0 mol dm^{-3} HCl (10.1% cis in 450 h, Table III) agrees with the above rate in 0.1 mol dm^{-3} $HClO_4$, and this demonstrates that the ability to undergo stereochemical change is unaffected by the anation process that is occurring at the same time (see below). Rutenberg and Taube have previously shown that the water-exchange rate is little affected by ionic strength.[10]

The anation results (Table III) show in general less stereochemical change in $CoCl^{2+}$ compared to $CoOH_2^{3+}$ recovered at the same time. This result is most obvious in 1.0 mol dm^{-3} HCl. However, when it is recognized that $CoCl^{2+}$ crystallized from solution as $[Co(NH_3)_2(^{15}NH_3)Cl]Cl_2$ as the reaction progressed while $CoOH_2^{3+}$ remained in solution, it is clear that the former represent time averages whereas the latter do not. Thus, the $CoCl^{2+}$ result will be less than that for $CoOH_2^{3+}$ if no stereochemical change occurs on anation (±1%). However, because of the competing stereochemical change in the water-exchange process, this result is less certain than the others. Thus, the 2.8 ± 0.4% change to *cis*-$CoOH_2^{3+}$ found in the aquation reaction of $CoBr^{2+}$ over 6 days (experiment 16, Table I) arises largely, or entirely, from subsequent stereochemical change in $CoOH_2^{3+}$. The larger amounts of stereochemical change accompanying

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anation in the solid state of $[Co(NH_3)_4(^{15}NH_3)OH_2]Cl_3$ (8%), however, demonstrate that back-side entry of Cl^- and front-side expulsion of coordinated OH_2 are more likely in the crystalline lattice than in aqueous solution.

Summary

The following represents a summary of the findings of this study: (1) Small, but real, stereochemical change occurs in the $CoOH_2^{3+}$ products derived from the Hg^{2+}- and Ag^+-induced reactions (2-3%). (2) Probably no stereochemical change occurs during production of $CoONO_2^{2+}$ in the same reactions. (3) No stereochemical change occurs in the formation of $CoCl^{2+}$ by $Cl_2(g)$ oxidation of $CoBr^{2+}$. (4) Some stereochemical change (1.4%) accompanies water exchange in $CoOH_2^{3+}$. (5) No significant stereochemical change accompanies anation (by Cl^- or Br^-) of $CoOH_2^{3+}$ in acidic solution, but this result is less certain than the others due to process 4 occurring at the same time.

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A Water-Stable Gadolinium(III) Complex Derived from a New Pentadentate "Expanded Porphyrin" Ligand

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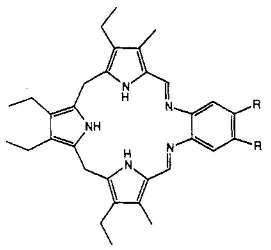
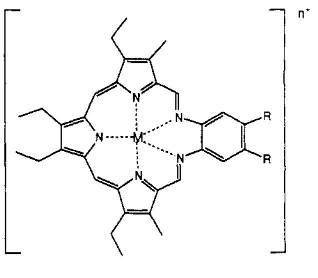
Gadolinium(III) complexes derived from strongly binding anionic ligands, such as diethylenetriaminepentaacetic acid (DTPA),[1-3] 1,4,7,10-tetraazacyclododecane-*N*,*N*′,*N*″,*N*‴-tetraacetic acid (DOTA),[1,4,5] and 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane-*N*,*N*′-diacetic acid (dacda),[1,6] are among the most promising of the paramagnetic contrast agents currently being developed for use in magnetic resonance imaging (MRI).[1] Indeed, $[Gd(DTPA)]^-$ is now being used clinically in the United States in certain enhanced tumor detection protocols. Nonetheless, the synthesis of other gadolinium(III) complexes remains of interest, since such systems might have greater kinetic stability, superior relaxivity, or better biodistribution properties than the existing carboxylate-based contrast agents. One approach currently being pursued is based on using water-soluble porphyrin derivatives, such as tetrakis(4-sulfonatophenyl)porphyrin (TPPS) or tetrakis(*N*-methyl-4-pyridiniumyl)porphyrin (TMPyP).[7-9] Unfortunately, the large gadolinium(III) cation cannot be accommodated completely[10] within the relatively small porphyrin binding core ($r \cong 2.0$ Å[11]), and as a consequence, gadolinium porphyrin complexes are invariably hydrolytically unstable.[7,8,12,13] Larger porphyrin-like ligands, however, might offer a means of circumventing this problem.[14-22]

We have recently reported[23] the synthesis of a novel "expanded porphyrin" system, **1**,[24] and the structure of the bis(pyridine) adduct of its cadmium(II) complex **2**. The presence in this structure of a near circular pentadentate binding core, which is roughly 20% larger than that of the porphyrins,[23] coupled with the realization that almost identical ionic radii pertain for hexacoordinate Cd^{2+} ($r = 0.92$ Å) and Gd^{3+} ($r = 0.94$ Å),[25] prompted us to explore the general lanthanide-binding properties of this new monoanionic porphyrin-like ligand. We report here the synthesis and characterization of a water-stable gadolinium(III) complex (**7**) derived formally from a new 16,17-dimethyl-substituted analogue (**6**)[24] of our original "expanded porphyrin" system, as well as the preparation and characterization of the corresponding europium(III) and samarium(III) complexes **8** and **9**.



10 R = H
11 R = CH_3



1 M = H, R = H, n = 0
2 M = Cd, R = H, n = 1
3 M = Nd, R = H, n = 2
4 M = Sm, R = H, n = 2
5 M = Eu, R = H, n = 2
6 M = H, R = CH_3, n = 0
7 M = Gd, R = CH_3, n = 2
8 M = Eu, R = CH_3, n = 2
9 M = Sm, R = CH_3, n = 2

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