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Electrophilic Substitution Reactions in Heterocycles Complexed to Exchange-Inert Metal Ions. (Ethylenediamine)cobalt(III) Complexes of Imidazole and Histidine

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(Ethylenediamine)cobalt(III) complexes of imidazole and histidine are nitrated under mild conditions with a standard HNO_3–H_2SO_4 nitrating mixture. In contrast to the more robust pentaamminecobalt(III) complexes, the nitrated imidazole ligand readily dissociates, providing an excellent synthetic route to a variety of nitroimidazoles. Pyridine coordinated to either $Co(NH_3)_5^{3+}$ or $Co(en)_2Cl^{2+}$ is not nitrated, even under conditions that destroy the complex. The difference in reactivity is evidently a reflection of the Co(III) d electron interaction with the lowest unoccupied molecular orbital (LUMO) of the ligand. The nucleophilic displacement of a nitro group by chloride in a coordinated nitroimidazole is also observed. Crystal data for bis(ethylenediamine)(benzimidazole)chlorocobalt(III) perchlorate, space group $P\bar{1}$, $Z = 4$, $a = 8.168$ (4) Å, $b = 11.570$ (4) Å, $c = 21.162$ (8) Å, $\alpha = 78.93$ (2)°, $\beta = 78.87$ (2)°, $\gamma = 69.24$ (2)°, and $R = 6.67\%$ for 3437 reflections; for bis(ethylenediamine)(pyridine)chlorocobalt(III) chloride, space group $P2_1/n$, $a = 8.489$ (3) Å, $b = 14.021$ (6) Å, $c = 12.670$ (6) Å, $\alpha = 90.0°$, $\beta = 91.63$ (2)°, $\gamma = 90.0°$, and $R = 4.11\%$ for 2185 reflections; for bis(ethylenediamine)(4-nitroimidazolato)chlorocobalt(III) chloride hydrate, space group $P\bar{1}$, $a = 8.603$ (5) Å, $b = 7.358$ (3) Å, $c = 14.287$ (7) Å, $\alpha = 95.82$ (2)°, $\beta = 86.79$ (2)°, $\gamma = 115.39$ (2)°, and $R = 5.21\%$ for 5903 reflections; for bis(ethylenediamine)(4-chloroimidazole)chlorocobalt(III) chloride, space group $C2/c$, $Z = 8$, $a = 23.550$ (6) Å, $b = 11.805$ (2) Å, $c = 12.128$ (3) Å, $\alpha = 90.0°$, $\beta = 115.92$ (2)°, $\gamma = 90.0°$, and $R = 4.34\%$ for 2377 reflections; and for (ethylenediamine)(4-nitrohistidinato-*O,N,N′*)chlorocobalt(III) hydrate, space group $P2_1/n$, $a = 8.544$ (3) Å, $b = 17.382$ (5) Å, $c = 10.256$ (3) Å, $\alpha = 90.0°$, $\beta = 107.50$ (2)°, $\gamma = 90.0°$, and $R = 5.60\%$ for 2556 reflections, are reported.

Introduction

Nitroimidazoles and substituted nitroimidazoles are an important class of nitroaromatics with a wide range of applications. They are used as intermediates in organic syntheses,[2] their radicals are potential intermediates in ionizing radiation reactions and electron-transfer reactions,[3,4] and their derivatives are used as antiprotozoal or antimalarial drugs[5] or as sensitizing reagents in chemotherapy.[6–8] Improved methods for the nitration of histidine would be of interest in monitoring structure and reactivity properties for this amino acid.[9] For instance, if suitably mild conditions could be found, histidines already in peptides could be coordinated and subsequently nitrated, in a manner analogous to the in situ modification of tyrosine.[10]

In general, electrophilic reactions involving imidazole or pyridine require extreme reaction conditions and give low yields of a mixture of products. Metal ion coordination has been shown to enhance the rate of substitution reactions of aromatic heterocycles such as imidazole and pyrazole by several orders of magnitude and to give high yields of isomerically pure nitrated derivatives.[11–15] In these studies, it was found that much milder conditions could be used than those required to nitrate uncoordinated imidazole. The general applicability of the method was established by using a variety of methyl-substituted imidazoles,[11,15] histidine,[11,15,16] and pyrazole,[13–15] while it was established that this approach did not work for the six-membered aromatic heterocycle pyridine.[16]

This novel nitration method is extended here to the less robust (ethylenediamine)cobalt(III) complexes of imidazole and histidine to assess the effect of changing the nature of the coordinated amine. One consequence of using the less robust ethylenediamine complexes is that the nitroimidazole ligand readily dissociates from the complex, thus providing a simple synthetic route to a variety of isomerically pure nitroimidazoles. The structures of bis(ethylenediamine)(4-nitroimidazolato)chlorocobalt(III) chloride (*cis*-[$Co(en)_2Cl(4\text{-}NO_2Im)$]Cl), and (ethylenediamine)(4-nitrohistidinato-*O,N,N′*)chlorocobalt(III) (*cis*-[$Co(en)Cl(4\text{-}NO_2Hist)$]) are presented as evidence of the utility of this method. Extension of this method to produce chlorinated imidazole is established by the structure of bis(ethylenediamine)(4-chloroimidazole)chlorocobalt(III) chloride (*cis*-[$Co(en)_2Cl(4\text{-}ClImH)$]$Cl_2$). In addition, the structure of the precursor molecule bis(ethylenediamine)(pyridine)chlorocobalt(III) chloride (*cis*-[$Co(en)_2Cl(py)$]Cl_2) is reported as is that of bis(ethylenediamine)(benzimidazole)chlorocobalt(III) perchlorate (*cis*-[$Co(en)_2Cl(benzImH)$]$(ClO_4)_2$) for general structural comparison.

Experimental Section

The precursor compounds for this nitration study, *cis*-$Co(en)_2Cl(N\text{MeIm})^{2+}$, *cis*-$Co(en)_2Cl(4\text{-}MeIm)^{2+}$, *cis*-$Co(en)_2Cl(ImH)^{2+}$, and $Co(en)Cl(HisH)^{+}$ (en = ethylenediamine, ImH = imidazole, HisH = monodeprotonated histidine) were all synthesized as described previously.[11,18–20] Initial nitration reactions were carried out by using the earlier procedure[11] and produced mainly the nitrated but uncoordinated heterocycle as well as the aquation product $Co(en)_2(H_2O)_2^{3+}$. To obtain an optimum recovery of the nitrated but uncomplexed samples of the imidazoles isolated in this study the following procedure was used. After the 20-min reaction period[11] the solution was warmed to room temperature and diluted with 100 mL of distilled water. The pH of the resulting solution was then adjusted to 8.0 with $NaHCO_3$ and extracted with three 200-mL portions of diethyl ether. The ether portions were combined and evaporated to dryness. The resulting white solid was recrystallized from ethanol and shown by ^1H NMR to be the nitrated product. To produce

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coordinated, nitrated heterocycles the above procedure was modified as outlined below.

***cis*-Co(en)$_2$Cl(L)$^{2+}$ (L = Substituted 4-Nitroimidazoles).** The conditions used for the Co(NH$_3$)$_5$(L)$^{3+}$ complexes when attempted for the *cis*-Co(en)$_2$Cl(L)$^{2+}$ complexes, while achieving nitration of the heterocycle, proved to be too severe to leave the nitrated heterocycle coordinated to the cobalt, and the following modifications were made. The nitrating mixture was precooled to 0.5 °C and the starting complex added. The reaction was allowed to proceed for 10 min (5 min for *cis*-Co(en)$_2$Cl(4-MeIm)$^{2+}$), and then 20 g of ice and 500 mL of cold distilled water (0.5 °C) were added to the reaction mixture. The diluted solution was warmed to room temperature and added to an ion-exchange column (Dowex 50-X2, 50–100 mesh) and eluted with 1, 3, and 6 M HCl. Each colored fraction was characterized by UV–vis and NMR spectra and by cobalt(II) analyses. X-ray quality crystals were obtained by vapor diffusion of ethanol into aqueous solutions of the complex.

***cis*-Co(en)Cl(L)$^{2+}$ (L = 4-Nitrohistidine), C$_8$H$_{16}$N$_6$O$_5$ClCo (Mol Wt 368.66).** To the normal nitrating mixture, [Co(en)(HisH)Cl]Cl was added and the temperature maintained at 1 °C for 10 min. The reaction solution was then quenched by adding 20 g of ice and 500 mL of cold distilled water (1 °C). The resulting solution was then warmed to room temperature and chromatographed as above. All colored fractions were evaporated to dryness and recrystallized from distilled H$_2$O. The contents of each fraction were determined by UV–vis and NMR spectra and by cobalt(II) analyses. X-ray quality crystals were obtained by vapor diffusion of ethanol into aqueous solutions of the complex.

***cis*-Co(en)$_2$Cl(L)$^{2+}$ (L = 4-Chloroimidazole), C$_7$H$_{19}$N$_6$Cl$_4$Co (Mol Wt 388.06).** The precursor complex, *cis*-Co(en)$_2$(ImH)Cl^{2+} was dissolved in sulfolane, maintained at 0 °C, and a stoichiometric quantity of nitronium tetrafluoroborate dissolved in sulfolane added. The resulting solution was stirred at the same temperature for 1 h and then allowed to warm to room temperature. The resulting solution was absorbed on a Sephadex C-25 column and eluted with NaCl. The desired material was recovered after evaporation of the resulting colored fractions and recrystallized from distilled water. The contents of each fraction were determined by UV–vis and NMR spectra and by cobalt(II) analyses. X-ray quality crystals were obtained by vapor diffusion of ethanol into aqueous solutions of the complex.

(Benzoato)pentaamminecobalt(III) (CoA$_5$Bz^{2+}) perchlorate was prepared by the method of Sebera and Taube.[14a,b] The CoA$_5$Bz^{2+} was nitrated in concentrated H$_2$SO$_4$ with 70% HNO$_3$ at 0 °C, a 3-fold volume of ice added, the solution warmed to room temperature, and the *m*-nitrobenzoic acid isolated by ether extraction and identified by ^{1}H NMR. For the competitive nitration equimolar amounts of methyl benzoate and (CoA$_5$Bz)(ClO$_4$)$_2$ were dissolved in concentrated H$_2$SO$_4$ at 0 °C, 1 equiv of 70% HNO$_3$ was added, the reaction mixture was stirred for 1 h, cooled to −40 °C, and extracted with ether, and the methyl *m*-nitrobenzoate was isolated and identified by ^{1}H NMR.

Spectroscopic Methods. UV–vis spectra were recorded on a Varian DMS90 spectrophotometer for samples freshly eluted from the ion-exchange column or from samples prepared from weighed amounts of recrystallized solid. ^{1}H NMR spectra were determined in D$_2$O solutions containing sodium (trimethylsilyl)propionate (TSP) as a standard and recorded on either a Bruker WP80 or a Nicolet NT-200 NMR spectrometer.

X-ray Methods. Data for the individual molecules were gathered with Mo Kα radiation on a Nicolet P3m automatic diffractometer by using a graphite monochromator on the incident beam. Crystal, data collection, and refinement data for the five molecules are given in Table I. Cell dimensions were determined from a least-squares refinement of 15 independently measured reflections between 30 and 35°.

All space groups were unambiguously obtained from a statistical examination of the intensities of the collected data set for each molecule. Corrections for decay, absorption, and extinction were applied where noted in Table I. Data were collected to the limits of availability.

All structures were solved by direct methods[22] as implemented in the Texray system[23] of computer programs. The structures were refined to convergence by full-matrix least-squares methods on a PDP 11/73 minicomputer. All hydrogen atoms were found and their positional parameters refined. Atomic scattering factors used were those from ref 24.

The criterion for data used in the refinement is indicated in Table I and the function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/[\sigma^2(|F_o| + p(F_o)^2)]$ with values for w for each structure indicated in Table I. Final R factors, R and R_w, as well as goodness-to-fit values, largest shift to error ratios, and final difference Fourier excursions for each structure are given in Table I.

Table II lists the refined coordinates and equivalent isotropic thermal parameters for the heavy atoms in the molecules studied. Standard

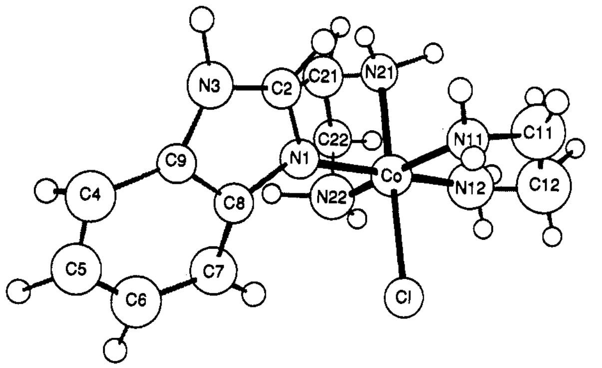

Figure 1. Atomic arrangement of the bis(ethylenediamine)(benzimidazole)chlorocobalt(III) cation and the numbering scheme for the complex.

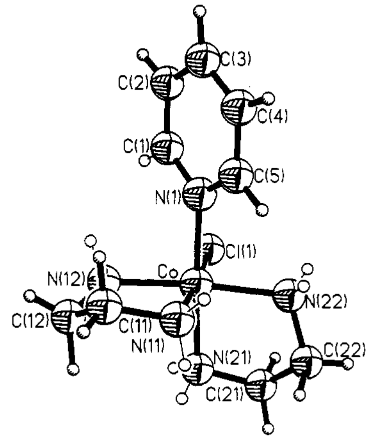

Figure 2. Atomic arrangement of the bis(ethylenediamine)(pyridine)chlorocobalt(III) cation and the numbering scheme for the complex.

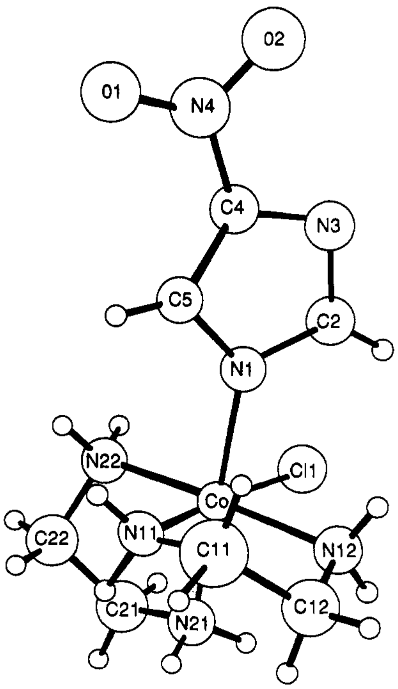

Figure 3. Atomic arrangement of the bis(ethylenediamine)(4-nitroimidazolato)chlorocobalt(III) cation and the numbering scheme for the complex.

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Table I. Crystal Data for $[Co(en)_m(Cl)(L)]^{n+}$ Compounds

param	L = benzimidazole	L = py	L = NO_2Im	L = ClIm	L = NO_2Hist
formula	$C_{11}H_{21}N_6Cl_3Co$	$C_9H_{21}N_5Cl_3Co$	$C_7H_{20}N_7O_3Cl_2Co$	$C_7H_{19}N_6Cl_4Co$	$C_8H_{16}N_6O_5ClCo$
M_r	402.66	364.63	378.16	388.06	368.66
a, Å	8.168 (4)	8.489 (3)	8.603 (5)	23.550 (6)	8.544 (3)
b, Å	11.570 (4)	14.021 (6)	7.358 (3)	11.805 (2)	17.382 (5)
c, Å	21.162 (8)	12.670 (6)	14.287 (7)	12.128 (3)	10.256 (3)
α, deg	78.93 (2)	90.0	95.82 (2)	90.0	90.0
β, deg	78.87 (2)	91.63 (2)	86.79 (2)	115.92 (2)	107.50 (2)
γ, deg	69.24 (2)	90.0	115.39 (2)	90.0	90.0
Vol, $Å^3$	1822 (2)	1507 (2)	812 (1)	3032 (2)	1452 (2)
Z	4	4	2	8	4
space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$C2/c$	$P2_1/n$
d_{calc}, g/cm^3	2.94	1.61	1.70	1.70	1.65
radiation	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα
abs coeff, cm^{-1}	27.7	16.64	15.69	18.34	13.88
abs cor	empirical	none	none	empirical	empirical
min transm factor	0.76			0.82	0.66
max transm factor	1.33			1.18	1.42
P-factor	0.08	0.04	0.075	0.03	0.07
goodness of fit	1.70	1.28	1.36	1.33	1.39
max shift/error	0.42	0.17	0.02	0.17	0.38
$F(000)$	1664	752	428	1584	740
T, °C	23	23	23	23	23
R	6.67	4.11	5.21	4.34	5.60
R_w	9.87	4.53	6.75	4.27	7.07
no. of Observns	6345	3622	8863	4430	4242
no. of observns used > 3σ	3437	2185	5903	2377	2556
no. of var	505	247	262	239	274
sin $(\theta/\lambda)_{max}$	0.7054	0.6511	0.8585	0.7048	0.7048

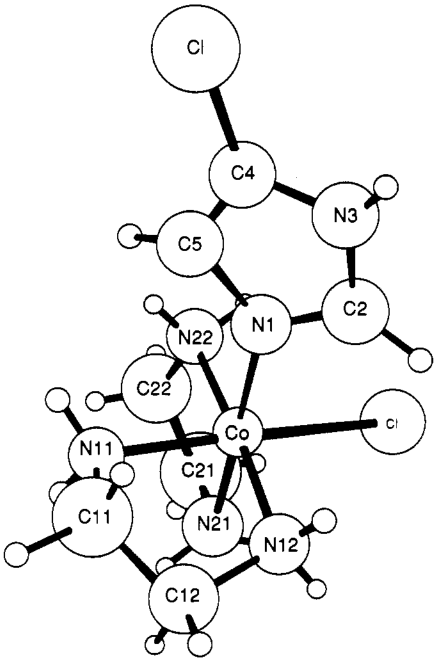

Figure 4. Atomic arrangement of the bis(ethylenediamine)(4-chloroimidazole)chlorocobalt(III) cation and the numbering scheme for the complex.

deviations, given in parentheses, are based solely on the least-squares results. Full tables of bond lengths and angles and of hydrogen coordinates are available in the supplementary material, as are tables of comparisons between observed and calculated structure factors. Figures 1–5 show the atomic arrangement and numbering scheme for the cations.

Results and Discussion

For the *cis*-$Co(en)_2Cl(L)^{2+}$ complexes where L = imidazole, *N*-methylimidazole or 4-methylimidazole, when the same conditions[11] as used for the nitration of the corresponding pentaammine complexes are used, mostly the *free nitrated* imidazole and $Co(en)_2(H_2O)_2^{3+}$ are produced. In all cases, the yield of uncoordinated nitrated imidazole is at least 75% and the yield of coordinated nitrated imidazole is less than 25% (see Table V). There is no evidence for any unnitrated imidazole, either coordinated or uncoordinated, for any of the complexes, which indicates that coordinated imidazole is nitrated prior to the aquation reaction to produce $Co(en)_2(H_2O)_2^{3+}$. The experimental procedure has been modified to allow the nitrated imidazole to be isolated from the rest of the mixture and subsequently purified for further use (see Experimental Section). These nitrated imidazoles were characterized by ^{1}H NMR and UV–vis spectroscopy. The ^{1}H NMR chemical shifts for the isolated products are given in Table III and show that the ring has been nitrated in the 4(5)-position but not in the 2-position.[21] For the coordinated nitrated heterocycles, UV–vis spectral data are given in Table IV, and NMR chemical shifts are given in Table V.

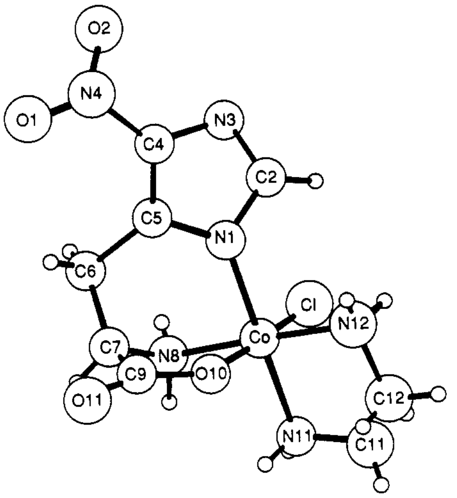

Figure 5. Atomic arrangement of (ethylenediamine)(4-nitrohistidinato-*O,N,N'*)chlorocobalt(III) and the numbering scheme for the complex.

In order to obtain products in which the nitrated heterocycle remained coordinated to the cobalt, the reaction procedures were modified by reducing the reaction time and lowering the temperature to 0.5 °C. The UV–vis spectra of the resulting nitrated complexes show absorption maxima at ca. 500 nm, which are in the same region as those found for the chloro imidazole complexes. For *cis*-$Co(en)_2Cl(ImH)^{2+}$ and *cis*-$Co(en)_2Cl(NMeImH)^{2+}$ the yield of coordinated nitrated complex produced by the modified procedure was higher (see Table V). However, even shortening the reaction time to less than 5 minutes did not improve the yield of the nitrated 4-methylimidazole complex.

Table II. Final Least-Squares Positional Parameters for C, N, Cl, and Co (×10⁴), the Equivalent Isotropic Thermal Parameters B_{eq} (Å^2), and Their Estimated Standard Deviations for the Five Complexes

atom	*x*	*y*	*z*	B_{eq}	atom	*x*	*y*	*z*	B_{eq}
a. Bis(ethyenediamine)(benzimidazole)chlorocobalt(III) Perchlorate									
Co	9010 (1)	1978.9 (8)	0851.6 (5)	2.21 (2)	C2′	10880 (10)	1956 (7)	5471 (4)	2.9 (2)
Co′	11840 (1)	3012.2 (8)	4148.4 (5)	2.21 (2)	C4	12120 (20)	2761 (9)	−1648 (5)	5.0 (3)
Cl	5789 (4)	3857 (3)	2521 (1)	4.94 (6)	C4′	13250 (10)	2200 (9)	6662 (4)	5.3 (2)
Cl′	11819 (3)	4967 (2)	4204 (1)	3.53 (4)	C5	13830 (10)	2270 (10)	−1534 (5)	5.5 (3)
Cl$_1$	12174 (3)	1141 (2)	2478 (1)	4.88 (5)	C5′	14510 (10)	2796 (9)	6512 (4)	5.5 (2)
Cl$_2$	10992 (3)	33 (2)	797 (1)	3.50 (4)	C6	14220 (10)	1732 (9)	−906 (5)	5.8 (2)
Cl$_3$	7999 (3)	1196 (2)	4641 (1)	3.92 (5)	C6′	15000 (10)	3282 (8)	5913 (4)	4.6 (2)
Cl$_4$	13839 (3)	3800 (2)	361 (1)	3.96 (5)	C7	12900 (10)	1703 (9)	−372 (4)	4.4 (2)
N1	9544 (8)	2475 (6)	−92 (3)	2.9 (1)	C7′	14250 (10)	3288 (8)	5376 (4)	3.9 (2)
N1′	11907 (8)	2533 (5)	5091 (3)	2.9 (1)	C8	11160 (10)	2259 (7)	−498 (4)	3.0 (2)
N3	897 (1)	3269 (6)	−1101 (3)	3.4 (2)	C8′	12910 (10)	2738 (7)	5495 (4)	3.1 (2)
N3′	11128 (9)	1740 (6)	6098 (4)	3.5 (2)	C9	10800 (10)	2767 (7)	−1133 (4)	2.8 (2)
N22	7127 (8)	1408 (6)	716 (3)	3.0 (1)	C9′	12440 (10)	2245 (7)	6120 (4)	3.2 (2)
N22′	9248 (9)	3599 (6)	4286 (3)	3.3 (1)	C22	6190 (10)	1080 (10)	1335 (6)	6.7 (3)
N21	8393	1424 (6)	1779 (3)	3.0 (1)	C22′	8580 (10)	3940 (20)	3672 (7)	6.0 (4)
N21′	11609 (8)	3563 (6)	3222 (3)	3.1 (1)	C21	7320 (20)	650 (10)	1847 (6)	7.0 (3)
N11	7371 (8)	3669 (5)	941 (3)	2.3 (1)	C21′	9770 (20)	4310 (10)	3158 (5)	6.2 (3)
N11′	11976	1297 (6)	4080 (3)	2.9 (1)	C11	8420 (10)	4514 (7)	921 (4)	3.1 (2)
N12	10787 (8)	2577 (6)	1072 (3)	2.9 (1)	C11′	13860 (10)	498 (7)	4062 (4)	3.3 (2)
N12′	14425 (8)	2434 (6)	3929 (3)	3.0 (1)	C12	9820 (10)	3805 (7)	1334 (4)	3.2 (2)
C2	8310 (10)	3042 (7)	−473 (4)	3.0 (2)					
b. Bis(ethylenediamine)(pyridine)chlorocobalt(III) Chloride									
Co	0.80094 (6)	0.21970 (5)	0.05387 (4)	1.602 (9)	C1	0.9168 (5)	0.4065 (3)	0.1207 (4)	2.45 (9)
Cl1	0.6199 (1)	0.32519 (8)	−0.0067 (1)	2.63 (2)	C2	1.0219 (5)	0.4800 (3)	0.1378 (4)	2.62 (9)
Cl2	1.3580 (1)	0.16459 (9)	0.19484 (9)	2.93 (2)	C3	1.1763 (5)	0.4701 (3)	0.1078 (4)	2.65 (9)
Cl3	0.7060 (1)	0.41157 (9)	0.3863 (1)	3.48 (3)	C4	1.2191 (5)	0.3847 (3)	0.0619 (4)	2.49 (9)
N1	0.9584 (4)	0.3230 (2)	0.0754 (3)	1.75 (6)	C5	1.1086 (5)	0.3134 (3)	0.0465 (4)	2.26 (8)
N11	0.0518 (4)	0.1280 (3)	0.1164 (3)	2.08 (7)	C11	0.9577 (6)	0.1386 (4)	0.2320 (4)	3.3 (1)
N12	0.7226 (4)	0.2323 (3)	0.1978 (3)	2.19 (7)	C12	0.7927 (6)	0.1563 (4)	0.2657 (4)	3.7 (1)
N21	0.6447 (4)	0.1189 (3)	0.0247 (3)	2.23 (7)	C21	0.6299 (6)	0.1010 (4)	−0.0898 (4)	3.6 (1)
N22	0.8691 (4)	0.1959 (3)	−0.0903 (3)	2.18 (7)	C22	0.7887 (6)	0.1106 (4)	−0.1346 (4)	4.1 (1)
c. Bis(ethylenediamine)(4-nitroimidazolato)chlorocobalt(III) Chloride Hydrate									
Co	0.35403 (3)	0.20713 (3)	0.21859 (2)	1.389 (4)	N12	0.1425 (2)	0.2426 (2)	0.2036 (1)	1.93 (3)
Cl1	0.24297 (7)	−0.09340 (7)	0.13279 (4)	2.266 (9)	N21	0.4522 (2)	0.3290 (3)	0.1011 (1)	2.09 (3)
Cl2	0.7364 (1)	0.4893 (1)	0.4283 (1)	3.12 (1)	N22	0.5727 (2)	0.1895 (2)	0.2314 (1)	1.98 (3)
Cl3	0.3253 (1)	0.1868 (1)	0.8611 (1)	3.21 (1)	C2	0.1090 (3)	−0.0928 (3)	0.3386 (2)	2.01 (3)
O	0.0756 (3)	0.2599 (3)	0.0108 (3)	4.45 (5)	C4	0.2165 (2)	−0.0294 (3)	0.4774 (1)	1.87 (3)
O1	0.3659 (3)	0.0527 (4)	0.6125 (2)	4.01 (5)	C5	0.3298 (2)	0.1107 (3)	0.4215 (1)	1.86 (3)
O2	0.0931 (3)	−0.1556 (3)	0.6150 (1)	3.59 (4)	C11	0.2921 (3)	0.5236 (3)	0.3167 (2)	2.57 (4)
N1	0.2601 (2)	0.0689 (2)	0.3339 (1)	1.70 (3)	C12	0.1729 (3)	0.4536 (3)	0.2342 (2)	2.73 (4)
N3	0.0775 (3)	−0.1553 (3)	0.4251 (1)	2.06 (3)	C21	0.6075 (3)	0.2928 (3)	0.0745 (2)	2.60 (4)
N4	0.2263 (3)	−0.0448 (3)	0.5750 (1)	2.48 (3)	C22	0.7016 (3)	0.3167 (3)	0.1640 (2)	2.53 (4)
N11	0.4389 (2)	0.4734 (2)	0.2894 (1)	1.85 (3)					
d. Bis(ethylenediamine)(4-chloroimidazole)chlorocobalt(III) Chloride									
Co	0.13509 (2)	0.19098 (5)	0.12863 (4)	1.962 (9)	N21	0.1533 (1)	0.0278 (3)	0.1437 (3)	2.75 (8)
Cl	0.07978 (5)	0.16517 (9)	−0.07454 (9)	3.21 (2)	N22	0.0617 (1)	0.1526 (3)	0.1551 (3)	2.66 (8)
Cl′	0.05944 (6)	0.6388 (1)	0.1945 (1)	5.59 (3)	C2	0.1083 (2)	0.4201 (4)	0.0232 (4)	3.1 (1)
Cl1	0.08824 (5)	0.2412 (1)	0.42611 (9)	3.49 (2)	C4	0.0820 (2)	0.5205 (4)	0.1425 (4)	2.79 (9)
Cl2	0.75550 (6)	0.0202 (1)	0.5446 (1)	4.34 (3)	C5	0.0948 (2)	0.4160 (4)	0.1883 (3)	3.2 (1)
N1	0.1115 (1)	0.3510 (3)	0.1110 (3)	2.33 (7)	C11	0.2475 (2)	0.2720 (4)	0.3195 (4)	3.9 (1)
N3	0.0906 (2)	0.5243 (3)	0.0395 (3)	3.03 (8)	C12	0.2673 (2)	0.2176 (5)	0.2297 (4)	3.9 (1)
N11	0.1886 (1)	0.2137 (3)	0.3042 (3)	2.45 (7)	C21	0.0988 (2)	−0.0338 (4)	0.1411 (5)	4.9 (1)
N12	0.2115 (2)	0.2215 (3)	0.1081 (3)	3.05 (8)	C22	0.0640 (2)	0.0322 (4)	0.1879 (5)	5.0 (1)
e. (Ethylenediamine)(4-nitrohistidinato-*O*,*N*,*N*′)chlorocobalt(III) Hydrate									
Co	0.59618 (7)	0.20418 (3)	0.88899 (5)	1.634 (9)	O11	0.6936 (5)	0.2480 (3)	0.5487 (3)	3.62 (8)
Cl	0.6393 (2)	0.18335 (8)	1.1137 (1)	2.85 (2)	N1	0.6159 (4)	0.3158 (2)	0.9099 (4)	2.02 (7)
O1W	0.000	0.000	0.000	2.67 (9)*	N3	0.5627 (5)	0.4370 (2)	0.9567 (4)	2.90 (8)
O1	0.9039 (5)	0.4966 (2)	0.8579 (4)	3.54 (8)	N4	0.7798 (6)	0.5030 (3)	0.8937 (5)	3.6 (1)
O2	0.7278 (7)	0.5649 (3)	0.9172 (6)	7.6 (1)	N8	0.8283 (4)	0.2015 (2)	0.9044 (4)	2.27 (7)
O2W	−0.055 (2)	0.0513 (8)	−0.129 (1)	4.2 (2)*	N11	0.5713 (5)	0.0938 (2)	0.8621 (4)	2.47 (8)
O3W	−0.174 (2)	−0.018 (1)	−0.054 (2)	3.8 (4)*	N12	0.3589 (4)	0.2050 (2)	0.8525 (4)	2.24 (7)
O4W	−0.102 (3)	0.041 (1)	0.106 (2)	4.9 (5)*	C2	0.5195 (6)	0.3636 (3)	0.9522 (5)	2.54 (9)
O5W	−0.131 (3)	0.029 (1)	−0.087 (2)	4.6 (4)*	C4	0.6971 (6)	0.4348 (3)	0.9106 (5)	2.51 (9)
O6W	−0.011 (4)	0.081 (2)	0.119 (3)	4.3 (6)*	C5	0.7311 (5)	0.3612 (3)	0.8801 (4)	1.98 (8)
O7W	0.132 (4)	0.068 (2)	0.055 (3)	6.0 (7)*	C6	0.8647 (6)	0.3322 (3)	0.8260 (5)	2.36 (9)
O8W	0.024 (5)	0.074 (2)	−0.033 (4)	5.4 (8)*	C7	0.8471 (5)	0.2468 (3)	0.7888 (5)	2.26 (8)
O9W	0.149 (4)	0.008 (2)	−0.018 (3)	3.5 (6)*	C9	0.6939 (6)	0.2353 (3)	0.6672 (5)	2.31 (8)
O10W	0.0066 (9)	−0.0125 (4)	−0.0459 (6)	3.0 (1)*	C11	0.4057 (7)	0.0697 (3)	0.8639 (6)	3.5 (1)
O10	0.5634 (4)	0.2151 (2)	0.6975 (3)	2.18 (6)	C12	0.2910 (7)	0.1300 (3)	0.7922 (6)	3.5 (1)

Previously a crystal structure determination[11] of the nitrated product obtained from $Co(NH_3)_5(ImH)^{3+}$ confirmed that the nitro group was in the 4-position of the imidazole ring. For the nitrated product from the reaction with *cis*-$Co(en)_2Cl(NMeImH)^{2+}$, NMR

Table III. ^{1}H NMR Chemical Shifts for Uncomplexed Nitroimidazoles

compound	C-4(5) H	C-2 H	methyl H	ref
4(5)-nitroimidazole	8.17	7.79		*a*
1-methyl-5-nitroimidazole	8.15 (C-4 H)	7.74	3.80	*a*
1-methyl-4-nitroimidazole	7.87 (C-5 H)	7.54	3.90	*b*
	8.19 (C-5 H)	7.74	*d*	*c*
1-methyl-5-nitroimidazole	8.09 (C-4 H)	7.64	4.05	*b*
	8.11 (C-4 H)	7.92	*d*	*c*
4-methyl-5-nitroimidazole		8.15	2.65	*a*

[a] This work, D_2O solvent, TSP reference. [b] Barlin, G. B.; Batterham, T. J. *J. Chem. Soc. B* **1967**, 516. $CDCl_3$ solvent, TMS reference. [c] Takeuchi, Y.; Kirk, K. L.; Cohen, L. A. *J. Org. Chem.* **1978**, *43*, 3570. D_2O solvent. [d] Not reported.

Table IV. UV–Vis Data for Nitrated Complexes

complex	λ_{max}, nm	ϵ, M^{-1}, cm^{-1}
$[Co(en)_2Cl(NO_2Im)]^+$	475	64
$[Co(en)_2Cl(NO_2\text{-}N\text{-}MeIm)]^{2+}$	520	73
$[Co(en)_2Cl(NO_2\text{-}4\text{-}MeIm)]^+$	480	99
$[Co(en)Cl(NO_2His)]$	560	77
	450	40

methods[21] show that the nitro group is in the 4-position as the C-5 proton shows a positive nuclear Overhauser effect (NOE) when the ethylenediamine NH's are irradiated. That the *cis*-$Co(en)_2Cl(ImH)^{2+}$ nitrates in the 4-position as well is confirmed by the X-ray structure of this complex (Figure 3).

In the case of the $Co(en)_2Cl(4\text{-}MeIm)^{2+}$ complex the 4-position is occupied by the methyl group and thus the imidazole must nitrate at either the 2- or the 5-position, if at all. The analogous $(NH_3)_5Co(4\text{-}MeIm)^{3+}$ complex shows no sign of nitration, even at conditions where the complex decomposes. It is assumed that this is a consequence of the steric crowding between the CH_3 and the $(NH_3)_5Co$ functional groups. We were therefore quite surprised when the $Co(en)_2Cl(4\text{-}MeIm)^{2+}$ complex nitrated in the 5-position so readily. There are at least two possible explanations. The first coordination sphere of the $Co(en)_2(Cl)^{2+}$ ion is rather different than that of the $(NH_3)_5Co^{3+}$ ion, and the steric restrictions around the coordinated Cl^- may be much less. This could permit direct nitration of the 5-position, adjacent to the methyl group. The transfer of the nitronium could even be assisted by an electron pair on the coordinated Cl^-. A second possibility involves the isomerism of the coordinated 4(5)-methylimidazole. The $(NH_3)_5Co(4(5)\text{-}MeIm)^{3+}$ complex exists as adjacent and remote isomers.[25] It has been shown[25] that the more strained adjacent isomer converts to the remote isomer without the ligand becoming free of the complex. If a similar labile isomerization exists for the $Co(en)_2Cl^{2+}$ complex, then the nitration could take place in the open remote position followed by dissociation of the nitrated ligand. We plan further study of this question.

These $Co(en)_2Cl^{2+}$ complexes of substituted imidazoles nitrate more rapidly than the corresponding $(NH_3)_5Co^{3+}$ complexes as a consequence of the $Co(en)_2Cl^{2+}$ being more electron donating. This can be seen from the fact that the pK_a[18,26] found for *cis*-$Co(en)_2Cl(ImH)^{2+}$ is higher than that for $Co(NH_3)_5(ImH)^{3+}$, indicating that the ring in the former complex is more basic. A comparison of bond lengths of the Co–N bond trans to the 4-nitroimidazole group in *cis*-$Co(en)_2Cl(4\text{-}NO_2Im)^+$ with Co the same bond in $Co(NH_3)_5(4\text{-}NO_2Im)^{2+}$ does not show any structural evidence of a trans effect, making the former complexes more labile. The pK_a value for *cis*-$Co(en)_2Cl(4\text{-}NO_2ImH)^{2+}$ appears to be similar to that found[11] for $Co(NH_3)_5(4\text{-}NO_2ImH)^{3+}$. However, the ethylenediamine complex precipitated from solution at pH values above 1.5, preventing an accurate determination of its pK_a.

As expected, the $Co(en)(HisH)Cl^+$ complex nitrated in the 4-position under the milder, modified conditions but decomposed under the original conditions (Table V). Under acidic conditions, the nitrated histidine remained fully coordinated, but as the pH of the solution was raised, a substantial amount of the complex precipitated. The crystal structure confirmed the nitration at the 4-position in the fully chelated form.

In order to increase the yield of nitrated coordinated product, nitronium salts in nonaqueous solvents such as sulfolane (in which the precursor complexes are also soluble) were investigated for the nitration reaction instead of the mixed-acid nitrating medium. This produces less severe conditions, and the resulting yields are markedly increased. The reaction mixture is quenched with distilled water, and the desired complex can be obtained by eluting on a Sephadex C-25 column with either aqueous NaCl or $NaClO_4$. When *cis*-$Co(en)_2Cl(ImH)^{2+}$ is used as the precursor complex for the nitration reaction with nitronium tetrafluoroborate and the resulting solution passed through a Sephadex column with NaCl as eluant, the resulting product is *cis*-$Co(en)_2Cl(4\text{-}ClImH)^{2+}$ (Figure 4). The Cl^- from the NaCl eluant used in the ion-exchange chromatography has displaced the nitro group from the imidazole ring. That the nitro compound was formed first was confirmed by carrying out a subsequent reaction in which $NaClO_4$ was used as eluant and the nitroimidazole complex was isolated. This must mean that the nitroimidazole ring has been activated towards a nucleophilic attack in which the nitro group is displaced by a chloride ion. It is known[27] that excess halide ion can displace a nitro group in an aromatic ring if that ring is suitably activated. Thus it appears that the $Co(en)_2Cl^{2+}$ moiety activates not only coordinated heterocycles toward electrophilic attack but also the nitro derivative toward nucleophilic attack. The question of the susceptibility of coordinated heterocycles to nucleophilic attack has been discussed by Lay.[28] This should provide a convenient route to fluoro-, chloro-, bromo-, or iodo-substituted imidazoles at the position nitrated. Further studies are underway to investigate the generality of this phenomenon.

Earlier studies[29] of the nitration of $Co(o\text{-}phen)_3^{3+}$ indicated that it nitrated some 300 times more rapidly than the free ligand. Attempts to nitrate[30] $Cr(py)_3(Cl)_3$ showed no change in the reactivity relative to the free ligand. We have prepared[17] the $(NH_3)_5Co^{3+}$ complexes of pyridine, 3-methylpyridine and 4-methylpyridine in addition to the $Co(en)Cl(py)^{2+}$ reported here and in no case found evidence of nitration, even with forcing conditions. This demonstrates that there is a dramatic difference in the nature of the metal ion–ligand interaction between the five-membered and six-membered heterocycles. Examination of the pyridine ligand orbitals[31] shows that the lowest unoccupied molecular orbital (LUMO) ($2A_2$, π^*_4) has a node at the N,C4 plane. This will prevent a metal-to-ligand d–π^* electron donation. The five-membered heterocycles do not have a LUMO node at the nitrogen adjacent to the Co(III), permitting an efficient d–π^* interaction. We note that other six-membered heterocycles, such as pyrazine, do not have LUMO nodes at the N atom adjacent to Co(III) and may well be activated toward electrophilic attack. These observations are entirely consistent with σ-withdrawing and π-back-donation effects previously described by Lay.[28]

In order to determine the electron-withdrawing or -donating effect of the $(NH_3)_5Co^{3+}$ group in a purely σ-bonding system, we examined the comparative rates of nitration of methyl benzoate and (benzoato)pentaamminecobalt(III)$^{2+}$ (CoA_5Bz^{2+}). On the basis of pK_a's of coordinated imidazole, the $(NH_3)_5Co^{3+}$ group has a Hammet σ value of −0.30, compared to −0.04 for a methyl group.[11] Nitration of CoA_5Bz^{2+} in mixed acid (H_2SO_4/HNO_3) gives an 82% isolated yield of *m*-nitrobenzoic acid, after aqueous workup.[14] An equimolar mixture of methyl benzoate and CoA_5Bz^{2+} nitrated in the same flask, with 1 equiv of HNO_3, gives

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Table V. ^{1}H NMR Chemical Shifts and Yields for Nitrated Complexes of the Type $[Co(en)_mCl(L)]^{n+}$

L	C-5 H	C-2 H	C-4 H	CH_3	yield,[a] %	yield,[b] %	yield,[c] %
imidazole	7.26	8.26	7.40				
histidine		8.20	7.25				
4(5)-nitroimidazole	8.36	8.55			15	85	70
4-chloroimidazole	7.23	8.23					72
4-nitrohistidine		8.40			dec	0	50
5-methyl-4-nitroimidazole		7.93		2.63	10	90	10
N-methyl-4-nitroimidazole	8.39	8.49		4.10	18	82	40

[a] Yield of nitrated complex by original procedure.[11] [b] Yield of nitrated free ligand using original procedure.[11] [c] Yield of nitrated complex from modified procedure; see Experimental Section, this paper.

Table VI. Common Bond Distances (Å) about the Cobalt and Ethylenediamine Ligands for $[Co(en)_m(Cl)(L)]^{n+}$ Compounds

type	L = benzimidazole[a]	L = py	L = Im[b]	L = NO_2Im	L = ClIm	L = Hist[c]	L = NO_2Hist
Co–Cl	2.270, 2.270 (2)	2.252 (1)	2.257 (3)	2.253 (1)	2.248 (1)	2.244 (1)	2.251 (1)
Co–N1	1.976, 1.972 (6)	1.985 (3)	1.945 (7)	1.970 (2)	1.954 (2)	1.946 (3)	1.952 (3)
Co–N11	1.961, 1.991 (6)	1.965 (4)	1.952 (6)	1.965 (2)	1.962 (3)	1.921 (2) (O)	1.907 (3) (O)
Co–N12	1.977, 1.970 (6)	1.967 (3)	1.966 (7)	1.972 (2)	1.955 (4)	1.938 (3) (NH_2)	1.948 (6) (NH_2)
Co–N21	1.971, 1.964 (6)	1.966 (3)	1.961 (7)	1.960 (2)	1.964 (3)	1.946 (3)	1.942 (4)
Co–N22	1.966, 1.965 (6)	1.961 (4)	1.963 (6)	1.960 (2)	1.946 (3)	1.949 (3)	1.944 (4)
N11–C11	1.505, 1.486 (9)	1.471 (6)	1.47 (1)	1.484 (3)	1.484 (5)		
C11–C12	1.481, 1.492 (10)	1.497 (7)	1.49 (2)	1.503 (4)	1.504 (7)		
C12–N12	1.513, 1.506 (9)	1.483 (6)	1.49 (1)	1.480 (3)	1.488 (6)		
N21–C21	1.444, 1.463 (13)	1.474 (6)	1.48 (1)	1.493 (3)	1.472 (6)	1.487 (5)	1.467 (6)
C21–C22	1.46, 1.42 (2)	1.483 (7)	1.50 (2)	1.508 (4)	1.435 (7)	1.502 (6)	1.488 (8)
C22–N22	1.44, 1.44 (2)	1.479 (6)	1.50 (1)	1.482 (3)	1.466 (5)	1.476 (6)	1.483 (7)

[a] Two molecules/asymmetric unit; same esd for both values. [b] Reference 32. [c] Reference 18.

Table VII. Bond Distances (Å) in the Attached Ligand

bond	L = benzimidazole[a]	L = Im[b]	L = NO_2Im	L = ClIm	L = NO_2Im[c]	L = Hist[d]	L = NO_2Hist	L = py[e]
N1–C2	1.322, 1.314 (11)	1.34 (1)	1.340 (2)	1.326 (5)	1.365 (3)	1.333 (4)	1.348 (5)	1.355 (5) (N1–C2)
C2–N3	1.348, 1.342 (13)	1.34 (1)	1.332 (3)	1.341 (5)	1.328 (3)	1.319 (6)	1.327 (5)	1.376 (6) (C2–C3)
N3–C4	1.393, 1.403 (11)	1.36 (1)	1.363 (2)	1.351 (4)	1.355 (3)	1.358 (6)	1.367 (6)	1.382 (6) (C3–C4)
C4–C5	1.404, 1.376 (14)	1.35 (1)	1.367 (2)	1.333 (5)	1.379 (3)	1.360 (5)	1.368 (6)	1.385 (6) (C4–C5)
C4–N4			1.419 (3)		1.419 (6)		1.418 (6)	1.381 (5) (C5–C6)
C4–Cl				1.709 (4)				1.343 (5) (C6–N1)
N4–O1			1.227 (3)		1.243 (3)		1.226 (5)	
N4–O2			1.233 (2)		1.234 (3)		1.215 (6)	
C5–N1	1.403, 1.394 (8)	1.38 (1)	1.369 (2)	1.386 (5)	1.355 (3)	1.377 (5)	1.367 (5)	
C5–C6						1.507 (5)	1.498 (6)	
C6–C7						1.525 (5)	1.530 (6)	
C7–N8						1.480 (4)	1.471 (5)	
C7–C9						1.529 (4)	1.525 (6)	
C9–O10						1.288 (4)	1.293 (5)	
C9–O11						1.231 (3)	1.235 (5)	

[a] Two molecules in asymmetric unit, same esd for both. [b] From ref 32. [c] From ref 11. [d] From ref 18. [e] Six-membered ring, thus a different atom-numbering scheme as indicated.

only methyl *m*-nitrobenzoate (42% isolated yield) after workup by cold ether extraction. This experiment confirms that, in the absence of d–π back-bonding, the $(NH_3)_5Co^{3+}$ group is strongly electron-withdrawing.

Imidazole coordinated to Co(III) is also subject to very facile electrophilic attack by bromine. For an extensive study of this reaction, the reader may consult the work of Buckingham, et al.[32,33]

The X-ray structures of the complexes *cis*-$[Co(en)_2Cl(benzImH)](ClO_4)_2$ and *cis*-$[Co(en)_2Cl(py)]Cl_2$ and the reaction products *cis*-$[Co(en)_2Cl(4\text{-}NO_2Im)]Cl$, *cis*-$[Co(en)_2Cl(4\text{-}ClImH)]Cl_2$, and *cis*-$[Co(en)Cl(4\text{-}NO_2Hist)]$ have been determined. Diagrams of the cations are shown in Figures 1–5. Tables VI and VII give the bond distances in the complexes and the attached ligands. Tables 8–12 in the supplementary material give angles and bond lengths to hydrogen. From these tables it can be seen that the distances and angles for the donor atoms subtended at the cobalt are in the normal range expected for *cis*-bis(ethylenediamine)cobalt(III) complexes and comparable to those previously reported[34] for *cis*-$[Co(en)_2Cl(ImH)]Cl_2$. The accuracy of results for the benzimidazole complex is somewhat less than those for the other complexes due to the disorder in the perchlorate groups ($R = 6.67$ and $R_w = 9.87$, compared to values ranging from 4.11 and 4.27 to 5.60 and 7.07 for the other four complexes). No major changes are found in the chromophore upon nitration of the coordinated heterocycle. However, as in the case of the pentaamminecobalt(III) complexes, upon nitration the remote imidazole nitrogen is deprotonated, reflecting the acidity of this group.

For the coordinated heterocycles, there are only minor changes in bond lengths that occur upon nitration (or chlorination in the case of imidazole). The nitro groups have there usual geometry with N–O bond lengths ranging from 1.215 (6) and 1.226 (5) Å for the 4-nitrohistidine complex to 1.243 (3) and 1.234 (3) Å for the 4-nitroimidazole complex.

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Registry No. 4-MeImH, 822-36-6; *N*-MeIm, 616-47-7; ImH, 288-32-4; HisH⁻, 80448-37-9; Bz⁻, 766-76-7; *cis*-$Co(en)_2Cl(N\text{-}MeIm)^{2+}$, 60314-39-8; *cis*-$Co(en)_2Cl(4\text{-}MeImH)^{2+}$, 88657-81-2; *cis*-$Co(en)_2Cl(ImH)^{2+}$, 60314-38-7; $Co(en)Cl(HisH)^{+}$, 88657-78-7; *cis*-$[Co(en)_2Cl(NO_2Im)]Cl\cdot H_2O$, 136537-78-5; *cis*-$[Co(en)Cl(NO_2His)]\cdot H_2O$, 136568-96-2; *cis*-$Co(en)_2Cl(NO_2\text{-}4\text{-}MeImH)^{2+}$, 136537-79-6; *cis*-$Co(en)_2Cl(NO_2\text{-}N\text{-}MeIm)^{2+}$, 136537-80-9; *cis*-$[Co(en)_2Cl(Cl\text{-}ImH)]Cl_2$, 136537-81-0; *cis*-$[Co(en)_2Cl(py)]Cl_2$, 21409-63-2; *cis*-$[Co(en)_2Cl(benzImH)](ClO_4)_2$, 136537-82-1; $CoAsBz^{2+}$, 30931-77-2; methyl *m*-nitrobenzoate, 618-95-1; *m*-nitrobenzoic acid, 121-92-6; methyl benzoate, 93-58-3.

Supplementary Material Available: Tables listing positional parameters and their estimated standard deviations for hydrogen atoms and the general temperature factor expressions for the five complexes and Tables 8–12, listing bond angles about the cobalt and ethylenediamine ligands and bond angles in the attached imidazole ligands, bond lengths to hydrogen in the attached ligands, and selected mean plane angles in the benzimidazole, pyridine, and chloroimidazole complexes (22 pages); tables of observed and calculated structure factors for bis(ethylenediamine)(benzimidazole)chlorocobalt(III) perchlorate, bis(ethylenediamine)(pyridine)chlorocobalt(III) chloride, bis(ethylenediamine)(4-nitroimidazolato)chlorocobalt(III) chloride hydrate, bis(ethylenediamine)(4-chloroimidazole)chlorocobalt(III) chloride, and (ethylenediamine)(4-nitrohistidinato-*O*,*N*,*N'*)chlorocobalt(III) hydrate (170 pages). Ordering information is given on any current masthead page.

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New Ionic Ozonides: Syntheses, Structures, and Properties of $N(CH_3)_4O_3$ and $N(C_2H_5)_4O_3$

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In contrast to the known alkali-metal ozonides, tetraalkylammonium ozonides can not be synthesized by reaction of ozone with the respective hyperoxides due to the oxidizability of the cation. Therefore, $N(CH_3)_4O_3$ and $N(C_2H_5)_4O_3$ have been synthesized via a new route by double reaction of their hyperoxides with alkali-metal ozonides in liquid ammonia. $N(CH_3)_4O_3$ crystallizes in the orthorhombic space group *Pmmn* (No. 59) with $a = 850.96\ (25)$ pm, $b = 689.95\ (32)$ pm, $c = 544.39\ (16)$ pm, and $Z = 2$. $N(C_2H_5)_4O_3$ crystallizes in the trigonal space group $P3_121$ (No. 152) with $a = 706.60\ (15)$ pm, $c = 1752.60\ (43)$ pm, and $Z = 3$. Diffraction data were collected on an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation. Whereas the structure of $N(CH_3)_4O_3$ shows a relationship with the CsCl type of structure, atomic arrangement in the $N(C_2H_5)_4O_3$ structure derives from the NaCl type of structure. C–H···O hydrogen bonds were found in both structures and were also evidenced by IR investigations. The decomposition of these two compounds has been studied by mass spectroscopy and DTA/TG methods. Two different mechanisms of decomposition, caused by the absence or the presence of β-hydrogen atoms, are observed for $N(CH_3)_4O_3$ and $N(C_2H_5)_4O_3$. $N(CH_3)_4O_3$ is surprisingly stable, only decomposing above 75 °C. As a consequence of their higher solubilities in commonly used solvents (e.g. acetonitrile), these new ozonides are of interest in developing a preparative chemistry involving ionic ozonides.

Introduction

In the past, ionic ozonides, salts which contain the paramagnetic bent molecular anion O_3^-, were reported only in combination with alkali-metal cations.[1] Attempts to synthesize ionic ozonides with alternative cations (NH_4^+, $N(CH_3)_4^+$, Sr^{2+}, Ba^{2+}) had been unsuccessful.[2–5] Due to their metastability and extreme sensitivity toward moisture and CO_2, the preparation of ionic ozonides is challenging. Therefore, it was not until 1985 that a general synthetic route for the preparation of pure, crystalline samples of alkali-metal ozonides in gram amounts was developed.[6] This preparative route, involving the reaction between alkali-metal hyperoxides and gaseous ozone, proved to be unsuccessful for the preparation of ozonides other than those of the alkali metals. In the present case, the oxidizability of the tetraalkylammonium cations by ozone hampered the synthesis of such ozonides. Thus, the formation of tetraalkylammonium ozonides must be carried out under very mild and nonoxidizing conditions. In the current method, the O_3^- anions are introduced via an exchange reaction between an alkali-metal ozonide and a salt of the desired cation. Recently $N(CH_3)_4O_3$ was synthesized by double reaction of KO_3 with $N(CH_3)_4O_2$ in liquid ammonia.[7] We have now been successful in preparing $N(C_2H_5)_4O_3$ by reaction of CsO_3 with $N(C_2H_5)_4O_2$; therefore, this route to ozonides of non-alkali-metal cations should prove to be general. In this paper, we report the syntheses of these two tetraalkylammonium ozonides, as well as of the reagents necessary for the preparation. Structural characterization and investigation of the thermal decomposition of $N(CH_3)_4O_3$ and $N(C_2H_5)_4O_3$ are described.

Experimental Section

General Comments. All manipulations were carried out under an atmosphere of dry argon by using Schlenk techniques. Infrared spectra were recorded by a Bruker IFS 113 spectrometer on pressed KBr disks. Pressing was effected by using a Perkin-Elmer minipellet press. The collection of Raman data was attempted by use of a Coderg LRT 800 spectrophotometer using 514.5-nm excitation of an Ar ion laser.

Thermal decomposition was studied by MS and DTA/TG investigations. MS spectra were recorded on a Kratos MS 50 high-resolution spectrometer. The ozonides were placed in a "hot box" and the evaporated gaseous products were detected. Combined DTA/TG measurements were undertaken with a NETZSCH STA 429 thermoanalyzer.

Syntheses. The synthesis of the tetraalkylammonium ozonides is depicted in eq 1. The alkali-metal ozonides were prepared as described elsewhere in a special glass apparatus[8] by reaction of gaseous ozone/oxygen mixtures with alkali-metal hyperoxides, obtained by direct oxidation of alkali metals with molecular oxygen.[9] Extraction by and recrystallization from liquid ammonia led to pure, hyperoxide-free ozonides. The most effective method of synthesizing $N(CH_3)_4O_2$ is the novel solid-state exchange reaction between tetramethylammonium hydroxide

$$\begin{gathered} NR_4O_2 + AO_3 \rightarrow NR_4O_3 + AO_2\downarrow \\ R = \text{methyl, ethyl};\ A = K, Rb, Cs \end{gathered} \tag{1}$$

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