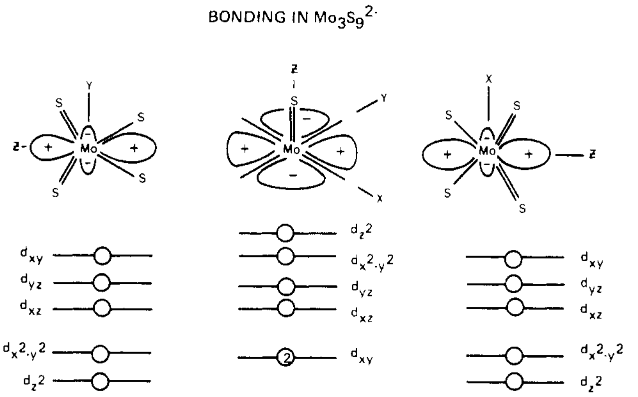

Figure 5. Molecular orbital picture of the Mo–Mo interactions in $Mo_3S_9^{2-}$.

molybdenyl complexes.[26] The splitting expected on the basis of coordinate system shown places the $4d_{xy}$ level lowest in energy, and the diamagnetism of the complex would require both d electrons of the central Mo(IV) to occupy that level. However, the $(4d_{xy})^2$ configuration may be significantly stabilized by the thiomolybdate ligands. Recent studies[7] indicate that MoS_4^{2-} may function as an acceptor ligand, moving electron density from the $(4d_{xy})^2$ configuration to empty MoS_4^{2-} levels. If the MoS_4^{2-} ion is oriented with its z axis bisecting S–Mo–S angles and roughly in the Mo–Mo direction, then, as shown in Figure 5, strong overlap is possible between the central Mo d_{xy} orbital and the d_{z^2} levels on the terminal Mo atoms. The $4d_{xy} \rightarrow 4d_{z^2}$ bonding is not of π character as there is no nodal plane containing the bond axis. However, the acceptor ability of MoS_4^{2-} may nonetheless be an effective stabilizing feature of the $Mo_3S_9^{2-}$ complex. That there may be interaction between the central Mo and terminal Mo is indicated by the short Mo–Mo distance and more so by the small folding along the bridging sulfurs, S3–S6 and S2–S7.

Conclusion

The trinuclear clusters $M_3S_9^{2-}$ can readily be prepared by heating $(NH_4)_2MS_4$ in DMF. The structure of $(PPh_4)_2Mo_3S_9$ shows ligating MoS_4 groups and a central thiomolybdenyl group. The complexes are formulated as $(M^{VI}S_4)_2M^{IV}S^{2-}$, i.e., a mixed-valence formulation. The Mo–Mo distances may be indicative of inter-molybdenum charge transfer mediated by the d orbitals of the Mo atoms. Spectroscopically, the $M_3S_9^{2-}$ complexes behave similarly to $M'(MS_4)_2^{2-}$ (M′ = Ni, Pd, Pt) complexes. The dinuclear complexes $M_2S_4(edt)_2^{2-}$ and $M_2S_4(abt)_2^{2-}$ can be prepared by heating MS_4^{2-} and $edtH_2$ or $abtH_2$ in DMF. The formation of the di- and trinuclear complexes from MS_4^{2-} may involve a common mechanism in which initial formation of the intermediate species $M_2S_7^{2-}$ is followed by internal redox processes leading to disulfide formation. Future studies will address both electronic structural features of these complexes and mechanistic aspects of their reactions.

Supplementary Material Available: Listings of cation bond lengths and angles, least-squares planes, structure factor amplitudes, anisotropic thermal parameters for non-hydrogen atoms, and calculated positional parameters for H atoms (37 pages). Ordering information is given on any current masthead page.

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Nitration of Metal Ion Coordinated Imidazole and the Crystal Structure of Pentaammine(4-nitroimidazolato)cobalt(III) Chloride

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The title complex, $[Co(NH_3)_5(NO_2Im)]Cl_2$, was prepared by the action of a standard HNO_3–H_2SO_4 nitrating mixture on $Co(NH_3)_5(ImH)^{3+}$. The complex has been characterized by ^1H NMR and UV–vis spectroscopy and a single-crystal X-ray structure determination. The pH dependence of the ^1H NMR spectra has been determined, and the pK_a of the coordinated NO_2Im is 1.66. Crystal data for $[Co(NH_3)_5(NO_2Im)]Cl_2$ is as follows: space group $P2_1/n$; $Z = 4$; $a = 9.434$ (2), $b = 13.679$ (3), $c = 10.457$ (3) Å; $\beta = 93.65$ (2)°; $V = 1346.7$ (5) Å^3; $R = 4.5\%$ for 2135 reflections.

Introduction

The electrophilic aromatic nitration of nitrogen heterocycles is a useful route to nitro, amino, and fluoro derivatives for these compounds. These derivatives have many uses as drugs, synthetic intermediates, or analogues in structure–activity investigations. The amino acid histidine occurs in most proteins and is of considerable importance in protein structure and function. The imidazole functional group of histidine is widely used as an intrinsic probe of protein structure–activity relationships[3] and is quite suitable for chemical modification for both large and small perturbations on its chemical and spectroscopic properties.[4]

The coordination of a ligand to a metal ion can cause an appreciable change in reactivity of the ligand.[2] Metal ion coordinated imidazole has been shown to have a pK_a of 10.0 and to have a much reduced rate of C-2 H exchange and ^1H and ^{13}C NMR spectra quite different from free imidazole.[5,6] We wish to report here the regiospecific nitration, under very mild conditions, of imidazole coordinated to Co(III). The facile nitration and the pK_a of the resulting complex support

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(1) (a) Howard University. (b) American University. (c) University of Virginia.
(2) Busch, D. H. "Reactions of Coordinated Ligands"; American Chemical Society: Washington, DC, 1963; Adv. Chem. Ser. No. 37.
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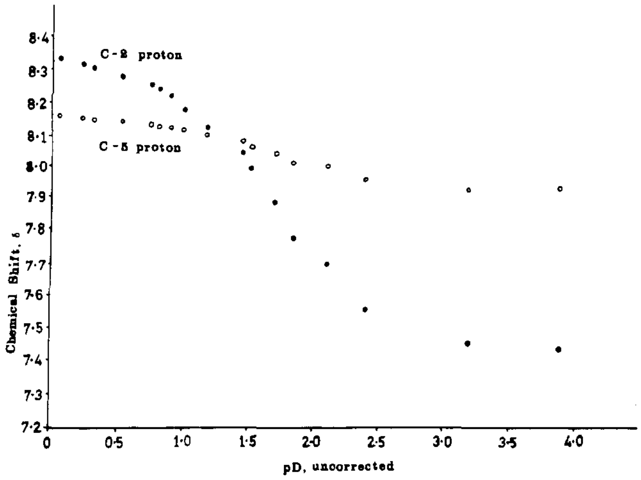

Figure 1. Chemical shift of the C-2 H and C-5 H of $Co(NH_3)_5(NO_2Im)(NO_3)_2$ as a function of pD.

the electronic effect of the $Co(NH_3)_5^{3+}$ functional group reported previously.[5,6]

Experimental Section

Synthesis of $[Co(NH_3)_5(NO_2Im)]Cl_2$. A nitrating mixture was prepared by adding 0.6 mL of concentrated HNO_3 to 3.5 mL of concentrated H_2SO_4 in an Erlenmeyer flask cooled in an ice bath. After the mixture reached 12 °C, 0.5 g of $[Co(NH_3)_5(ImH)](ClO_4)_3$ (prepared by the method of Harrowfield et al.)[5] was added rapidly. Even with stirring and grinding, all of the complex did not dissolve in the nitrating mixture. After approximately 20 min at 10–15 °C the reaction is complete. The yield is about the same whether the product is isolated at this point or warmed to room temperature and left overnight before isolation.

For isolation of the product the reaction solution was diluted by adding 20 g of ice and 112 mL of water to give a solution 1 M in H^+. A small amount of orange precipitate formed while the solution was still in ice but dissolved as the solution warmed to room temperature. The resulting solution was poured onto a Dowex 50-X4 50–100 mesh H^+ column (2 × 35 cm) and washed with several volumes of 1 M HCl and then distilled water. The product was eluted as an orange band with 3 M HCl at an elution rate of 2 mL/min. The orange fraction was taken to dryness on a rotary evaporator. A minor fraction (red) was obtained with the 1 M HCl. The yield of $[Co(NH_3)_5(NO_2Im)]Cl_2 \cdot H_2O$ was 97%. The complex has a λ_{max} at 475 nm; $\epsilon = 64$ M^{-1} cm^{-1}.

pK_a Determination. The pK_a of the complex was determined from the pH dependence of the C-2 H and C-5 H chemical shifts. The proton NMR spectra were obtained in ^2H_2O solvent at 25 °C on a Nicolet NT-200 NMR spectrometer operating at 200 MHz. The pHs of the solutions were measured directly in the 5-mm NMR tube with use of an Ingold microelectrode, and pH values are reported as uncorrected pD values. The pH was adjusted by the addition of NaOD. Sodium 3-(trimethylsilyl)propionate (TSP) was used as an internal standard, and chemical shifts are reported on the δ scale. $[Co(NH_3)_5(NO_2Im)]Cl_2$ is very insoluble and was converted to the nitrate salt for the NMR studies by chromatography on Dowex 50-X4, eluting with 3 M HNO_3, and removal of the solvent on a rotary evaporator. The chemical shift of the C-2 H and C-5 H as a function of pD are shown in Figure 1. The chemical shifts were fit to the profile by a nonlinear least-squares program, and the pK_a was derived from that analysis. The pK_a for the C-2 H is 1.68 and for the C-5 H is 1.64.

Structure Determination and Crystal Data. Crystals of the title compound were grown by slow evaporation of an aqueous solution. A well-shaped bright orange crystal of approximate dimensions 0.74 × 0.62 × 0.48 mm was chosen, fixed to a glass fiber with 5-min epoxy resin, and mounted on a goniometer head. The X-ray measurements were performed on a microprocessor-controlled Nicolet P3m diffractometer with niobium-filtered Mo $K\bar{\alpha}$ radiation ($\lambda(\alpha_1) = 0.709\,26$ Å, $\lambda(\alpha_2) = 0.713\,554$ Å). After optical alignment of the crystal, 15 independent reflections, chosen from a Polaroid rotation photograph, were computer centered. The angular coordinates thus obtained were autoindexed, from which a monoclinic cell was found and confirmed by axial photographs. Least-squares refinement gave an approximate orientation matrix from which angle settings for all reflections could be generated. ω scans of a few reflections showed well-defined peaks with peak widths at half-height measured to be less than 0.2°. At this point a short data set in the range $30° \leq 2\theta \leq 35°$ was obtained, and 15 independent medium-intensity reflections scattered evenly throughout reciprocal space were recentered to obtain a precise orientation matrix and accurate cell parameters together with their associated standard errors.

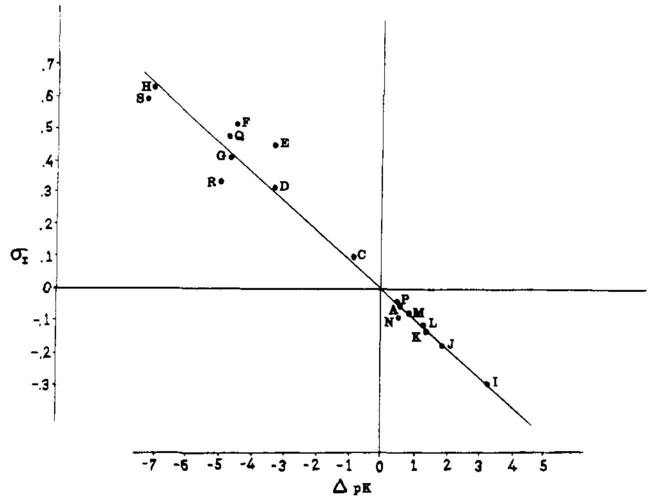

Figure 2. Plot of the p*K* values of various substituted imidazoles as a function of the σ_I values of the substituent(s). The values are taken from Table II, and the p*K* of imidazole is corrected by log 2 for comparison to those for 1-substituted imidazoles. The letters refer to compounds in Table II.

Crystal Data: $CoCl_2O_3N_8C_3H_{19}$; mol wt = 345.07; $F(000) = 712$; monclinic; $a = 9.434$ (2), $b = 13.679$ (3), $c = 10.457$ (3) Å; $\beta = 93.65$ (2)°, $V = 1346.7$ (5) Å^3; $D_m = 1.80$ (1), $D_c = 1.79$ g/cm^3; space group $P2_1/n$ (a nonstandard setting of $P2_1/c$, No. 14, in ref 7); μ(Mo $K\bar{\alpha}$) = 19.2 cm^{-1}; $Z = 4$. For 2315 independent reflections with $I > 3\sigma(I)$, $R = 4.5\%$ and $R_w = 5.3\%$. The experimental density was determined by a pycnometric method with chlorobenzene and bromobenzene for flotation.

Intensity Measurements and Data Reduction. The θ–2θ scan technique was used to measure 2501 intensities with a variable scan speed in 2θ of 2.93–29.3°/min from 0.8° below $K\alpha_1$ to 0.8° above $K\alpha_2$ and with stationary-crystal–stationary-counter background counting at both extremes of the scan for half of the total scan time. The actual scan speed for each reflection was automatically determined from an initial 3-s scan over the central one-third of the peak. Reflections were scanned at the slowest rate if in the prescan the counting rate did not exceed 1000 counts/s. The intensities of three standard reflections (800; 0,12,0; 0,0,10) measured after every 97 data showed no evidence of significant crystal decay during the entire data collection. Data, sampled once in the reciprocal lattice octants hkl and $hk\bar{l}$ for $4.5° \leq 2\theta \leq 60.00°$, were reduced to $|F_o|$ and $\sigma(F_o)$,[8] and Lorentz–polarization corrections were included.

Observed systematic absences for $\{hkl\}$ data of $h + L = 2n + 1$ and $0k0 = 2n + 1$ indicated $P2_1/n$ as the space group, and this was subsequently confirmed by the successful solution and refinement of the crystal structure. An absorption correction[8] was made on the basis of a calculated linear absorption coefficient of 19.2 cm^{-1} for Mo $K\bar{\alpha}$ radiation for a crystal bounded by 8 faces (with distances from the crystal centroid in mm in parentheses): 101 (0.31), $\bar{1}0\bar{1}$ (0.31), $10\bar{1}$ (0.37), 011 (0.24), $0\bar{1}\bar{1}$ (0.24), $\bar{1}01$ (0.37), $01\bar{1}$ (0.22), $0\bar{1}1$ (0.22). Transmission factors varied from 0.65 for the $15\bar{3}$ reflection to 0.48 for the 10,4,1 reflection. After data reduction and absorption corrections had been applied, there were 2315 reflections with $I > 3\sigma(I)$.

Structure Determination and Refinement. The structure was solved via the heavy-atom method, and the cobalt atom was located from the Patterson function calculated on the basis of all data.[8] Subsequent

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(7) Henry, F. M. H., Lonsdale, K., Eds. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1952; Vol. I.

(8) All computing methods and programs used as described in: Freyberg, D. P.; Mocker, G. M.; Sinn, E. *J. Chem. Soc., Dalton Trans.* **1976**, *447*.

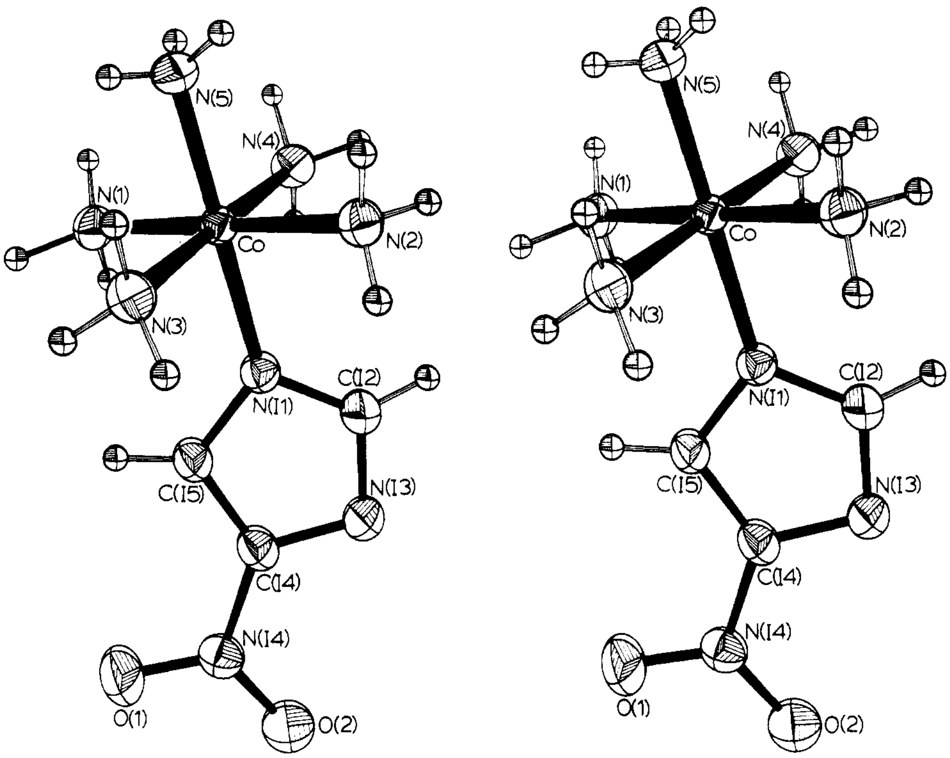


Figure 3. Atomic arrangement of the $[Co(NH_3)_5(NO_2Im)]^{2+}$ cation and the numbering scheme for the complex.

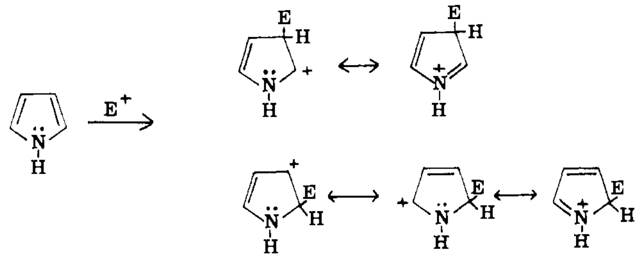
refinement of atomic positions followed by difference Fourier synthesis revealed the positions of all atoms. After all non-hydrogen atoms had been refined, hydrogen atoms, in positions located from difference Fourier analysis, were refined isotropically for three cycles and subsequently held fixed. All non-hydrogen atoms were refined anisotropically, and the model converged with $R = 4.5\%$ and $R_w = 5.3\%$. Positional parameters and their esd's are listed in Table I. The atomic scattering factors for non-hydrogen atoms were taken from Cromer and Waber,[35] and those for hydrogen were taken from Stewart et al.[36] The effects of anomalous dispersion for all non-hydrogen atoms were included in F_c by using the values of Cromer and Ibers[37] for $\Delta f'$ and $\Delta f''$.

Results and Discussion

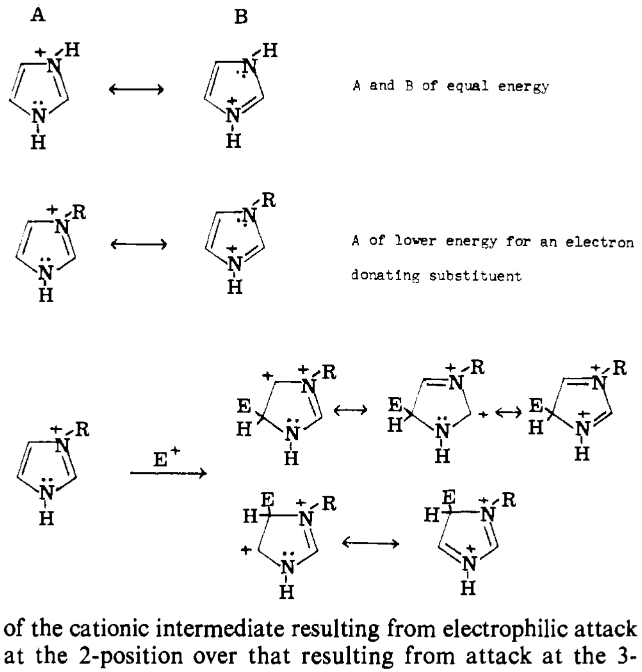
Regiospecificity. The nitration of $Co(NH_3)_5ImH^{3+}$ takes place under very mild conditions and produces only the 4-nitro-substituted isomer (see Figure 3 for numbering scheme). This is in marked contrast to the case for 1-methylimidazole. When 1-methylimidazole is nitrated by "boiling gently for 2 hours" in a 1:1 mixture of concentrated nitric and sulfuric acids, the 4-nitro and 5-nitro derivatives are formed in a 2.6:1 ratio and a 29% total yield.[9,10] When 1,2-dimethylimidazole is nitrated under similar conditions at 100 °C for 4 h, the 4-nitro and 5-nitro derivatives are formed in a 2:1 ratio.[11]

The $(NH_3)_5Co^{3+}$ functional group is certainly much larger than the methyl group and will hinder substitution at the adjacent 5-position. The electronic nature of the cobalt substituent will also strongly favor the substitution at the 4-position. This electronic effect is perhaps best understood by comparing the reactivity of imidazole and pyrrole. Pyrrole undergoes electrophilic aromatic substitution under mild conditions exclusively in the 2-position. The regioselectivity for the 2-position is the result of the resonance stabilization of the cationic intermediate resulting from electrophilic attack at the 2-position over that resulting from attack at the 3-position (see Scheme I).

Scheme I



Scheme II



Imidazole is strongly deactivated toward electrophilic attack because of its protonation in acid. In N-1 derivatives of imidazole, which are also protonated in acid solution, the C-4

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(9) Hazeldine, C. E.; Pyman, F. L.; Winchester, J. *J. Chem. Soc.* **1924**, *125*, 1431.

(10) Takeuchi, Y.; Yeh, H. J. C.; Kirk, K. L.; Cohen, L. A. *J. Org. Chem.* **1978**, *43*, 3565.

(11) Bhagwat, V. K.; Pyman, F. L. *J. Chem. Soc.* **1925**, *127*, 1832.

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(14) Hofmann, K. "Imidazole and its Derivatives"; Interscience: New York, 1953; p 15.

Table I. Positional Parameters and Their Estimated Standard Deviations for $[Co(NH_3)_5(NO_2Im)]Cl_2$[a]

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Co	0.24212 (4)	0.13817 (3)	0.26365 (4)	H(12)	0.127 (7)	0.001 (5)	0.359 (7)
Cl(1)	0.34296 (9)	0.36446 (6)	0.97333 (8)	H(13)	−0.007 (10)	0.052 (7)	0.319 (9)
Cl(2)	0.33903 (9)	0.39587 (6)	0.48158 (8)	H(21)	0.400 (7)	0.266 (5)	0.320 (6)
O(1)	0.1577 (3)	0.1092 (2)	0.7988 (3)	H(22)	0.367 (8)	0.281 (6)	0.161 (7)
O(2)	0.3809 (3)	0.1079 (2)	0.8668 (2)	H(23)	0.478 (11)	0.219 (8)	0.225 (10)
O	0.1533 (3)	0.3678 (2)	0.7157 (3)	H(31)	0.152 (6)	0.278 (5)	0.389 (6)
N(1)	0.0969 (3)	0.0366 (2)	0.2850 (3)	H(32)	0.041 (9)	0.219 (7)	0.370 (8)
N(2)	0.3864 (3)	0.2390 (2)	0.2421 (2)	H(33)	0.084 (9)	0.275 (6)	0.234 (8)
N(3)	0.1148 (3)	0.2423 (2)	0.3173 (2)	H(41)	0.386 (7)	0.005 (5)	0.285 (6)
N(4)	0.3708 (3)	0.0348 (2)	0.2108 (3)	H(42)	0.454 (9)	0.057 (7)	0.178 (8)
N(5)	0.1706 (3)	0.1559 (2)	0.0844 (3)	H(43)	0.345 (8)	0.008 (6)	0.123 (8)
N(I1)	0.3122 (3)	0.1232 (2)	0.4411 (2)	H(51)	0.215 (9)	0.202 (6)	0.037 (8)
N(I3)	0.4622 (3)	0.1185 (2)	0.6188 (2)	H(52)	0.084 (10)	0.175 (7)	0.087 (9)
N(I4)	0.2863 (3)	0.1106 (2)	0.7798 (3)	H(53)	0.179 (11)	0.109 (8)	0.050 (10)
C(I2)	0.4491 (3)	0.1223 (2)	0.4917 (3)	H(I2)	0.533 (7)	0.128 (5)	0.450 (7)
C(I4)	0.3247 (3)	0.1167 (2)	0.6508 (3)	H(I5)	0.129 (8)	0.127 (6)	0.536 (7)
C(I5)	0.2315 (3)	0.1194 (2)	0.5438 (3)	H(O1)	0.186 (8)	0.370 (6)	0.629 (7)
H(11)	0.087 (7)	0.009 (5)	0.204 (6)	H(O2)	0.218 (8)	0.369 (6)	0.773 (7)

[a] The thermal parameters and their estimated standard deviations are deposited with the supplementary material for this paper.

position is analogous to the C-2 position in pyrrole. Resonance structures shown in Scheme II indicate how delocalization of positive charge would favor substitution at the 4-position for an N-1 substituent that is electron donating relative to CH_3^+. Since the pK_a of $Co(NH_3)_5IMH^{3+}$ is some three orders of magnitude more basic (see Table II) than 1-methylimidazole, one would expect a strong electronic direction at the 4-position.

pK_a of Ligand and Substituent Effects. It has been previously noted that $Co(NH_3)_5O^+$ is a very poor leaving group in ester hydrolysis,[15,16] that the pK_a of the coordinated imidazole in $Co(NH_3)_5ImH^{3+}$ is 2.87 pH units more basic than that of 1-methylimidazole[5,6] (see table II), and that the coordinated imidazolato anion is a good nucleophile in the hydrolysis of *p*-nitrophenylacetate.[5] The substituent effect of the $Co(NH_3)_5^{3+}$ functional group is also shown in the same manner in the pK_a of the coordinated 4-nitroimidazole, shifted 2.26 pH units to the basic side from 1-methyl-4-nitroimidazole (Table II). The pK_a of a series of substituted imidazoles can be correlated in a plot of the σ_I parameter against the Δp*K* of the substituted imidazole compared to that of imidazole (Figure 2). The first eight entries in Table III provide a reasonably good correlation with all of the points lying on a single line, with the exception of those for the bromo and fluoro derivatives. This permits one to assign a substituent parameter for 1-methyl- and 2-methylimidazole. With use of these parameters the calculated values for 1,2-dimethyl-, 2,4-dimethyl- and 2,4,5-trimethylimidazole fall of the same line and that for 1,4-dimethylimidazole falls somewhat below the line. This same approach assigns a σ_I value of −0.30 to the $Co(NH_3)_5^{3+}$ functional group. This is strongly electron donating, relative to H^+ or CH_3^+, and must reflect the large number of electrons in the valence shell of the cobalt complex (d^6 plus 10 electrons from the coordinated ammonias). This same electron-rich nature of the substituent must be responsible for the ease of nitration of $Co(NH_3)_5ImH^{3+}$.

Crystal Structure. The structure consists of $[Co(NH_3)_5(NO_2Im)]^{2+}$ cations, chloride anions, and water molecules, all interconnected by hydrogen bonds. Figure 3 shows the atomic arrangement of the cation plus the atom-numbering scheme.

The data set was of sufficient quality to permit the location of all the hydrogen atoms, and these are shown. This clearly shows the deprotonation of the imidazole group to form an anionic ligand. The complex consists of an extensive network of hydrogen bonds between anions, cations, and water molecules, as illustrated in the packing diagram. In the hydrogen-bonding scheme the water molecule forms two donor hydrogen bonds with Cl(1) and Cl(2) in the same asymmetric unit and also two acceptor hydrogen bonds with hydrogen atoms attached to N(2) and N(4) in different asymmetric units. The chloride anions each form six hydrogen bonds with ammonia and water hydrogen atoms in different asymmetric units.

Table II

Im substituent	pK_a	σ_I[b]	ref	code for Figure 2
4-methyl	7.56	−0.05	12	A
none	7.00	0	12	B
4-phenyl	6.10	0.10	13	C
4-carbethoxy	3.66	0.32	13	D
4-bromo	3.60	0.45	13	E
4-fluoro	2.44	0.52	12	F
4-trifluoromethyl	2.28	0.41	12	G
4-nitro	−0.15	0.63	12	H
1-$Co(NH_3)_5^{3+}$	10.0[a]	−0.30	5, 6	I
2,4,5-trimethyl	8.86	−0.18	14	J
2,4-dimethyl	8.36	−0.13	14	K
1,2-dimethyl	8.00[a]	−0.12	12	L
2-methyl	7.85	−0.08	12	M
1,4-dimethyl	7.20[a]	−0.09	12	N
1-methyl	7.13[a]	−0.04	12	P
1-methyl-4-fluoro	1.90[a]	0.48	12	Q
1-$Co(NH_3)_5^{3+}$-4-nitro	1.66[a]	0.34	this work	R
1-methyl-4-nitro	−0.60[a]	0.59	12	S

[a] The pK_a of imidazole corrected by log 2 before calculation of the Δp*K* for the plot. [b] σ_I taken from: March, J. "Advanced Organic Chemistry"; McGraw-Hill: New York, 1968; p 243. The σ_I values in the lower part of the table are either calculated from the line or are the summation of σ_I values.

The bond distances and angles found for the cation are nearly those of a regular octahedron with an average Co–N(ammonia) bond length of 1.972 (2) Å and average N(ammonia)–Co–N(ammonia) bond angles of 90.0 (2) and 179.5 (3)°. The main deviations from this regular geometry are for the Co–N(imidazole) bond length at 1.941 (1) Å (22) and for the Co–N(ammonia) bond length trans to the imidazole at 1.966 (2) Å, which indicates a small but significant shortening of this bond of the same order as found in the corresponding cyanide complex.[17]

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(17) Wang, B.-C.; Schaefer, W. P.; Marsh, R. E. *Inorg. Chem.* **1971**, *10*, 1492.

The bond lengths and angles found in the 4-nitroimidazolato ligand are similar to those found in other cobalt(III) pentaammine imidazolate complexes[18–20] although the quality of the data set obtained has allowed a more accurate determination in the present case. The geometry of the nitro group is similar to that found in the structure of another 4-nitroimidazole molecule.[21]

Results of the mean-plane calculations indicate that the imidazole ring and the nitro group are coplanar. The three equatorial N_4 donor atom planes are very nearly orthogonal to each other, making angles of 88.2, 89.6, and 89.5° to one another. The principal deviation from regular octahedral symmetry arises from the planes containing the cobalt–imidazole bond, at 88.2° to each other. The imidazole plane is not coplanar with either of the N_4 equatorial atom planes but is about equally inclined to each of them (44.2, 47.9°) as is also found in a similar cobalt(III) imidazolato complex.[18]

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Registry No. $[Co(NH_3)_5(NO_2Im)]Cl_2$, 84040-89-1; $[Co(NH_3)_5(ImH)](ClO_4)_3$, 15279-15-9.

Supplementary Material Available: Listings of thermal parameters and their esd's for the positional parameters in Table I, $Co(NH_3)_5X^{n+}$ structures and bond lengths and angles, final values for F_o and F_c for the 2315 reflections used in the refinement process, bond lengths and angles for 4-nitroimidazolate, imidazoles, and the imidazolium ion, hydrogen bond lengths and selected angles for $[Co(NH_3)_5(NO_2Im)]Cl_2$, and coefficients of least-squares planes and a figure showing the packing of the unit cell and hydrogen-bonding parameters (17 pages). Ordering information is given on any current masthead page.

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Formation of Paramagnetic Adsorbed Molecules on Thermally Activated Magnesium and Calcium Oxides. Characteristics of the Active Surface Sites

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Thermal activation of MgO, CaO, SrO, BaO, and ThO_2 yields diamagnetic active surface defects that are capable of reducing adsorbed nitrobenzene, *p*-benzoquinone, tetracyanoquinodimethane (TCNQ), tetracyanoethylene, bipyridine, pyridine, acetophenone, benzophenone, naphthalene, anthracene, and phenanthrene to radical anions at room temperature. The reduction appears to occur as a one-step process on the "reducing sites", and monolayers of many of the respective radical anions are formed. The same active sites are capable of reduction/polymerization of CO to $(CO)_x$ radical anions, dianions, and trianions. However, lower concentrations of these radical anions are formed, and this is a consequence of the need for either special steric requirements and/or higher reactivity of the sites (both reduction and polymerization are required for CO). The defect sites are highly basic and can be poisoned by Lewis acids/proton donors such as CO_2, CS_2, H_2O, H_2S, CH_3OH, HCl, NH_3, acetylene, and acetone as well as alkylating agents such as CH_3I. It is likely that the active sites are surface defects that exist because of cation vacancies, perhaps of the Schottky or Frenkel type. However, residual OH groups aid in the reduction process.

Introduction

Alkaline-earth oxides possess a multitude of structural defects.[1–3] These defects can be due to an irregularity in the crystalline lattice structure (thus, a perfect crystallite has defects at the corners and edges) or due to atom displacements, free electron centers, radiation damage sites, UV–visible absorption sites, etc. Some defects are due to ion vacancies; for example, a Frenkel defect is an ion vacancy with the ion located in an interstitial vacancy, while a Schottky defect is a pair of vacancies with opposite signs (cf. Figure 1). Frenkel and Schottky defects are the result of thermodynamics.[4,5] Thus, a vacant lattice site is higher in energy than an occupied site. However, the occurrence of point defects increases the disorder of the systems, and the entropy term increases. (Sondor and Sibley have proposed a nomenclature for defects based on an ionic crystal defect scheme).[6] The method of

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