solution was dissolved in $CDCl_3$. The Cp resonance positions and peak intensities in the ^1H NMr spectrum showed that the products arising from the reaction of tungsten tricarbonyl anion and methanesulfinyl chloride are $[CpW(CO)_3]_2$ (50%), $CpW(CO)_3SMe$ (40%), $CpW(CO)_3Cl$ (7%), and $CpW(CO)_3SO_2Me$ (3%) (relative amounts from ^1H NMR analysis in parentheses).

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Supplementary Material Available: A table of infrared frequencies associated with various sulfur-oxygen ligands in metal complexes used to compile Figure 1 (8 pages). Ordering information is given on any current masthead page.

Contribution from the Research School of Chemistry, The Australian National University, Canberra 2601, Australia, and Crystallography Centre, University of Western Australia, Nedlands 6009, Australia

Synthesis and Characterization of Encapsulated Cobalt(III) Hydroxylamine Complexes

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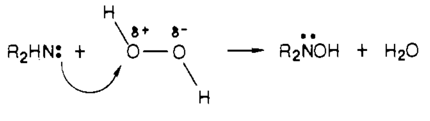
On treatment of two Co(III) cage complexes with H_2O_2 in basic solution, up to three coordinated N sites were oxidized to hydroxylamine groups. The complexes isolated and characterized were [(1,8-dinitro-3-hydroxy-3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane)cobalt(III)](3+), [(1,8-dinitro-3,10,16-trihydroxy-3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane)cobalt(III)](3+), [(1,8-dinitro-3,13,16-trihydroxy-3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane)cobalt(III)](3+), [(1,8-dichloro-3-hydroxy-3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane)cobalt(III)](3+), and [(1,8-dinitro-3,10-dihydroxy-3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane)cobalt(III)](3+). For the last of these complexes, the type and sites of oxidation were established by an X-ray structure determination (orthorhombic, space group $P2_12_12_1$, with a = 16.414 (5) Å, b = 15.122 (7) Å, c = 9.624 (3) Å, Z = 4, 1759 reflections, R = 0.059). The hydroxylamine groups are rather acidic (pK_a 2.8-6), and deprotonation leads to a profound change in redox potential (~-0.5 V). Reduction back to the secondary amine is not a fast process with one-electron reagents. V^{2+}(aq), however, instantly reduces the hydroxylamine back to the coordinated secondary amine by oxygen atom transfer to V^{2+}(aq) generating directly VO^{2+}(aq) ion.

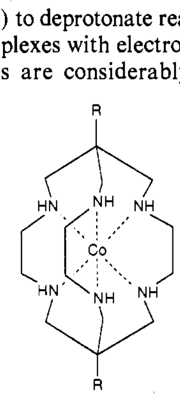
Introduction

Secondary alkylamines are readily oxidized to hydroxylamines by hydrogen peroxide in aqueous solution,[2] but yields of hydroxylamines are usually low due to further oxidation. The mechanism involves attack by the electrophilic peroxidic oxygen on the free amine by direct atom transfer (eq 1). When the amine



(1)

is coordinated to Co(III), this mechanism is not feasible unless the amine is deprotonated first. In most cases, coordinated amines are too basic (pK_a > 14) to deprotonate readily in aqueous solution, but for some cage complexes with electronegative substituents on the caps (I) the pK_a's are considerably less (pK_a = 9.87 for $[Co(dinosar)]^{3+}$, and pK_a = 10.36 for $[Co(dichlosar)]^{3+}$ at 25 °C and μ = 1.0 M;[3] dinosar = ligand in I with R = NO_2; dichlosar = ligand in I with R = Cl). This property renders them more susceptible to attack by H_2O_2 in basic solutions, and this paper records the results of such reactions.



I, R = NO_2, Cl

Experimental Section

^1H-decoupled ^{13}C NMR spectra were obtained with a JEOL JNM-FX-200 spectrometer using D_2SO_4-D_2O solutions (pD ~1.5) and dioxane as a reference. Electronic spectra were recorded with a Hewlett-Packard 8450A UV/vis spectrophotometer using 0.1 M HCl and a pH 8.2, 0.05 M Tris/$HClO_4$ buffer. pK_a's were obtained by potentiometric titrations at μ = 0.1 and 25 °C with an Action 108 pH meter and an Orion Ross combination electrode. The computer program MINIQUAD[4] was used for the calculations. Cyclic voltammetry measurements were performed with a three-electrode iR-compensated system having a Pt auxiliary electrode and a PAR Model 170 electrochemistry system together with an EG&G Model 303 mercury electrode in the HMDE mode vs. a saturated calomel electrode (SCE) and with a BAS-100 electrochemical analyzer with a glassy-carbon electrode vs. a Ag/AgCl, saturated NaCl electrode.

Reaction of $[Co(dinosar)]^{3+}$ with H_2O_2 in Basic Solution. $[Co(dinosar)]Cl_3$[5] (25 g, 4.5 × 10^{-2} mol) was dissolved in water (~1 L). NaOH solution (130 mL of a 1 M solution) was added followed by 30% H_2O_2 (40 mL, 0.46 mol). The mixture was left at 20 °C for 1 h and absorbed on a Dowex 50W-X2 cation-exchange column, and the column was washed with H_2O and eluted with 1 M HCl to remove Na^+. This was followed by 3 M HCl to elute the complexes. The eluate was taken down to dryness on a vacuum evaporator and the solid dissolved in water and absorbed on a SP Sephadex C-25 cation-exchange column. On elution with 0.3 M NaH_2PO_4 three orange bands (A small, B large, C small) separated. Each fraction was collected, and the complexes were isolated from Dowex 50W-X2 columns after elution with 1 M HCl to remove Na^+ and then with 3 M HCl and evaporation of the solvent. When band B (yield 40%) was resorbed on Dowex 50W-X2 resin and eluted with dilute NH_3, a band separated and was isolated via Dowex 50W-X2. On sorption on Dowex 1-X8 anion-exchange resin and elution with dilute NH_3 the band moved through the column. This suggested a neutral charge of the complex in the basic medium. A similar treatment of band

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(1) (a) The Australian National University. (b) University of Western Australia.

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Table I. Non-Hydrogen Atom Coordinates

	ligand section 1								
	a			b			c		
atom	x	y	z	x	y	z	x	y	z
				Cobalt Atom					
Co	0.04469 (9)	0.31386 (8)	0.32166 (12)						
				Ligand					
O(11)	−0.1297 (6)	0.2886 (6)	0.7728 (8)	−0.0665 (6)	0.1656 (6)	0.7761 (9)			
N(1)	−0.0835 (6)	0.2351 (6)	0.7227 (8)						
C(2)	−0.0398 (7)	0.2597 (6)	0.5867 (9)						
C(13)	0.0315 (6)	0.3172 (7)	0.6312 (9)	−0.0180 (6)	0.1745 (6)	0.5144 (10)	−0.1026 (6)	0.3149 (7)	0.5021 (10)
N(14)	0.0718 (5)	0.3606 (5)	0.5089 (8)	0.0366 (5)	0.1903 (5)	0.3910 (7)	−0.0704 (5)	0.3276 (5)	0.3589 (8)
O(14)				0.0083 (4)	0.1344 (4)	0.2832 (6)			
C(15)	0.0563 (7)	0.4562 (6)	0.5070 (10)	0.1219 (6)	0.1634 (6)	0.4227 (10)	−0.1194 (7)	0.2788 (6)	0.2548 (10)
C(15′)	0.0932 (7)	0.4910 (6)	0.3758 (11)	0.1734 (6)	0.1880 (6)	0.3008 (10)	−0.0774 (6)	0.2920 (7)	0.1168 (10)
N(14′)	0.0601 (5)	0.4398 (5)	0.2566 (8)	0.1592 (5)	0.2869 (5)	0.2756 (8)	0.0109 (5)	0.2775 (5)	0.1343 (8)
O(14′)	−0.0211 (4)	0.4720 (4)	0.2253 (8)						
C(13′)	0.1107 (8)	0.4534 (7)	0.1313 (12)	0.1944 (7)	0.3110 (7)	0.1387 (10)	0.0572 (7)	0.3159 (7)	0.0133 (9)
C(2′)	0.1314 (7)	0.3677 (7)	0.0589 (9)						
N(1′)	0.1747 (6)	0.3955 (6)	−0.0778 (9)						
O(11′)	0.1326 (6)	0.4764 (6)	−0.1612 (8)	0.2466 (5)	0.3814 (7)	−0.0926 (9)			
				Anions					
F(1)	0.2826 (4)	0.0309 (5)	−0.1862 (9)	0.2682 (4)	0.1066 (5)	−0.0016 (8)	0.2238 (5)	−0.0254 (4)	−0.0085 (9)
C	0.2317 (8)	0.0494 (8)	−0.0826 (13)						
S	0.1346 (2)	0.0896 (2)	−0.1446 (3)						
O(1)	0.0908 (5)	0.1059 (6)	−0.0178 (8)	0.1562 (5)	0.1665 (5)	−0.2185 (8)	0.1057 (6)	0.0185 (6)	−0.2261 (9)
C	0.7654 (2)	0.1293 (2)	0.4950 (3)						
				Refined H(14(′)) Atoms					
H(14)	0.141 (5)	0.358 (5)	0.525 (8)				−0.074 (5)	0.384 (6)	0.332 (9)
H(14′)	−0.020 (5)	0.543 (5)	0.227 (9)	0.184 (6)	0.314 (6)	0.333 (10)	0.022 (5)	0.221 (5)	0.173 (9)

Table II. Cobalt Environment[a]

atom	$r_{\text{Co–N}}$	N(a4′)	N(b4)	N(b4′)	N(c4)	N(c4′)
N(a4)	1.986 (8)	85.3 (3)	92.6 (3)	93.7 (3)	90.7 (3)	174.5 (3)
N(a4′)	2.020 (8)		176.3 (3)	90.3 (3)	94.5 (3)	90.8 (3)
N(b4)	1.988 (7)			86.8 (7)	88.5 (3)	91.5 (3)
N(b4′)	1.974 (8)				173.7 (3)	90.3 (3)
N(c4)	1.935 (8)					85.7 (3)
N(c4′)	1.965 (8)					

[a] $r_{\text{Co–N}}$ (Å) is the cobalt–nitrogen distance. Other entries in the table are the angles (deg) subtended by the atoms at the head of the relevant row and column. Features of interest in the ligand are chiefly concerned with N(a4′)–O(a4′) = 1.45 (1) Å and N(b4)–O(b4) = 1.42 (1) Å, N(a4′) and N(b4) being trans in the coordination sphere. Hydrogen atoms have been refined in x, y, z for all N(4) atoms that do not carry oxygen; only one hydrogen has been located in association with the oxygen atoms (H(a4′)) disposed about halfway between symmetry-related molecules (H(a4′)–O-(a4′) = 1.08 (8) Å, H(a4′)–O(b4) = 1.39 (8) Å ($\bar{x}$, $^1/_2 + y$, $^1/_2 - z$), with O···H···O = 172 (8)°). Intracation hydrogen bonds H(c4′)···O(b4) = 1.69 (8) and H(c4)···O(a4′) = 1.89 (9) Å are found (see Figure 1). Cl is chelated at 2.05 (8) and 2.29 (9) Å by H(a4) and H(b4′) of the cation at $^1/_2 + x$, $^1/_2 - y$, $1 - z$.

C gave the same result, while band A did not move with dilute NH_3 on either resin. Band A (A-2NOH) was isolated from acid solution as the chloride salt and from neutral solution as the $CF_3SO_3^-/Cl^-$ salt, yield 10%. Anal. Calcd for $CoN_8C_{14}H_{30}O_6Cl_3 \cdot H_2O$: C, 27.67; H, 5.63; N, 18.44; Cl, 17.50. Found: C, 28.1; H, 5.9; N, 17.5; Cl, 17.8. ^{13}C NMR: δ +19.9, +2.8, +0.6, −11.2, −13.2, −14.1, −14.8. Electronic spectrum (λ_{max}, nm (ϵ_{max})): in 0.1 M HCl, 488 (212), 351 (255), 250 (16 800); at pH 8.2, 460 (s) (300), 353 (7760). pK_a's: 5.05, 2.86.

The complex in the NH_3 extract of band B (B-3NOH) was isolated as the $ZnCl_4^{2-}/Cl^-$ salt. Anal. Calcd for $CoN_8C_{14}H_{30}ZnCl_5O_7 \cdot 2^1/_2H_2O$: C, 21.87; H, 4.58; N, 14.57; Zn, 8.50; Cl, 23.05. Found: C, 22.2; H, 4.4; N, 14.5; Zn, 8.6; Cl, 23.0. ^{13}C NMR: δ +19.8, +19.2, +1.5, +1.1 (2 C), +0.3, −0.1, −0.3, −10.4, −11.4, −11.9, −13.3, −15.0, −15.2. Electronic spectrum (λ_{max}, nm (ϵ_{max})): in 0.1 M HCl, 494 (254), 355 (292), 257 (18 800); at pH 8.2, 455 (s) (275), 332 (9300). pK_a's: 6.35, 4.88, 2.88.

The complex in band C (C-3NOH) was isolated as the Cl^- salt, yield 10%. Anal. Calcd for $CoN_8C_{14}H_{30}O_7Cl_3 \cdot H_2O$: C, 27.75; H, 5.32; N, 18.50; Cl, 17.56. Found: C, 28.2; H, 5.7; N, 18.0; Cl, 17.4. ^{13}C NMR: δ +20.9, +18.8, +0.8 (2 C), +0.1 (3 C), −10.7 (3 C), −16.2 (3 C). Electronic spectrum (λ_{max}, nm (ϵ_{max})): in 0.1 M HCl, 494 (285), 358 (450), 257 (19 500); at pH 8.2, 464 (s) (260), 351 (4900). pK_a's: 6.59, 4.88, 3.05.

[Co(dinosar)]$(CH_3COO)_3$ (6.1 g, 10^{-2} mol) was dissolved in water (150 mL), 30% H_2O_2 (0.86 mL, 10^{-2} mol) and NaOH solution (10 mL of a 1 M solution) were added, and the mixture was left at 20 °C for 3 h and treated as above. On elution with 0.3 M NaH_2PO_4 solution only one major band was observed, which finally yielded the complex as the Cl^- salt by the treatment above; yield 74%. Anal. Calcd for $CoN_8C_{14}H_{30}O_5Cl_3 \cdot 3H_2O$: C, 27.58; H, 5.92; N, 18.38; Cl, 17.44. Found: C, 27.5; H, 5.6; N, 18.5; Cl, 17.4. ^{13}C NMR: δ +21.3, +20.1, +2.4, +1.7, −9.9, −10.8, −11.5, −12.5, −12.9, −14.6, −14.8, −14.9, −15.6, −16.1. Electronic spectrum (λ_{max}, nm (ϵ_{max})): in 0.1 M HCl, 484 (197), 348 (172), 246 (17 500); at pH 8.2, 465 (s) (270), 350 (5090). pK_a's: 10.80 (secondary amine), 3.62.

[Co(dichlosar-NOH)]Cl_3. [Co(dichlosar)]Cl_3[5] (5.2 g, 10^{-2} mol) was dissolved in water (150 mL). NaOH solution (10 mL of a 1 M solution) was added followed by 30% H_2O_2 (0.86 mL, 10^{-2} mol) and the mixture kept at 20 °C for 3 h. When the system was treated as above, only one major band was observed. The same result was observed when 3 mol of NaOH and excess H_2O_2 were used; yield 70%. Anal. Calcd for $CoN_6C_{14}H_{30}OCl_5 \cdot 2H_2O$: C, 29.47; H, 5.99; N, 14.73; Cl, 31.06. Found: C, 29.3; H, 6.1; N, 14.4; Cl 30.9. ^{13}C NMR: δ +5.5, +2.0, −4.9, −6.4, −10.3 to −13.3 (10 signals). Electronic spectrum (λ_{max}, nm (ϵ_{max})): in 0.1 M HCl, 478 (164), 347 (155), 248 (16 700); at pH 8.2, 468 (216), 346 (4810). pK_a's: 11.80 (secondary amine), 4.06.

Structure Determination of the Band A $CF_3SO_3^-/Cl^-$ Salt. A unique data set was measured at ~295 K within the limit $2\theta_{max} = 50°$ with a Syntex P$\bar{1}$ four-circle diffractometer in the conventional $2\theta/\theta$ scan mode. A total of 1974 independent reflections were obtained, 1759 with $I > 3\sigma(I)$ being considered "observed" and used in the full-matrix least-squares refinement after analytical absorption correction and solution of the structure by direct methods. Anisotropic thermal parameters were refined for the non-hydrogen atoms; x, y, z, and U_{iso} for hydrogen atoms were included constrained at estimated values, excepting those attached to nitrogen and oxygen, which were refined in x, y, z (see Table II).

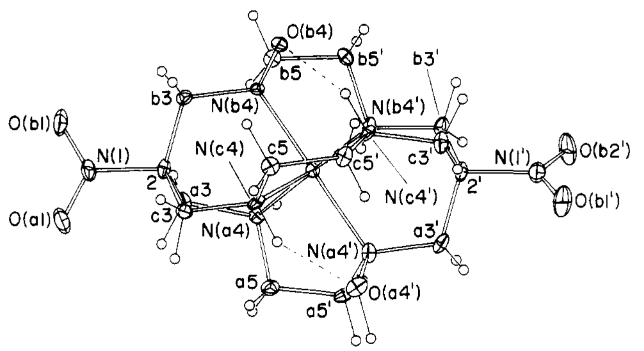


Figure 1. The complex hydroxylamido cation from band A (A-2NOH), projected down its pseudotwofold axis, showing atom labeling and 20% thermal ellipsoids for the non-hydrogen atoms. Hydrogen atoms have arbitrary radii of 0.1 Å.

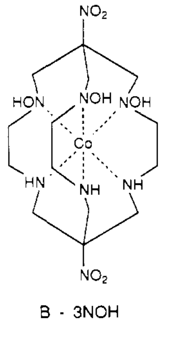
Residuals on $|F|$ at convergence, R and R' (statistical weights derived from $\sigma^2(I) = \sigma^2(I)_{\text{diff}} + 0.0003\sigma^4(I_{\text{diff}})$), were 0.059 and 0.062, respectively (preferred chirality). Neutral-complex scattering features were used;[6] the computation used the XTAL program system[7] implemented by Hall on a Perkin-Elmer 3240 computer.

Crystal Data: $C_{15}H_{29}ClCoF_3N_8O_9S$, $M_r = 648.9$, orthorhombic, space group $P2_12_12_1$ (D_2^4, No. 19), $a = 16.414$ (5) Å, $b = 15.122$ (7) Å, $c = 9.624$ (3) Å, $U = 2389$ (2) Å^3, D_{calcd} ($Z = 4$) = 1.81 g cm^{-3}, $F(000) = 1336$, monochromatic Mo Kα radiation ($\lambda = 7106_9$ Å), $\mu_{\text{Mo}} = 9.7$ cm specimen 0.26 × 0.25 × 0.33 mm, $A^*_{\text{min}} = 1.22$, $A^*_{\text{max}} = 1.43$.

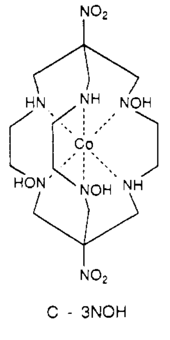
Results and Discussion

The treatment of the $[Co(dinosar)]^{3+}$ ion with a large excess of H_2O_2 and base gave a mixture of products. Three different complexes were isolated by using ion-exchange techniques. The complexes were characterized by their ^{13}C NMR spectra, electronic spectra, and elemental analysis. Also, a crystal structure of one of them (Figure 1) (deprotonated at one hydroxylamine site) showed two coordinated hydroxylamine groups at positions trans to each other, with the one associated hydrogen atom bridging oxygen atoms of independent molecules to form a chain of connected cations through the lattice. Otherwise, the bond lengths and angles appear to be rather normal (Table II). ^{13}C NMR spectroscopy of the fully protonated complex in D_2O gave a signal at +19.9 ppm relative to dioxane, which is characteristic for a quaternary carbon atom attached to a NO_2 group in a cage complex.[5] Four signals at −11.2, −13.2, −14.1, and −14.8 ppm were ascribed to four pairs of cap and ethylenediamine methylene groups[5] and two signals at +2.8 and +0.6 ppm to two pairs of methylene groups on either side of the hydroxylamine groups.

Two of the products in the reaction mixture had no charge in ammoniacal solution and were assumed to have three hydroxylamine groups that became deprotonated in the basic medium. Their ^{13}C NMR spectra were consistent with the two isomers B-3NOH and C-3NOH. After the isolation of the three products a mixture remained whose ^{13}C NMR spectrum was consistent with it being a mixture of two hydroxylamine complexes. However, all attempts to separate them were unsuccessful.

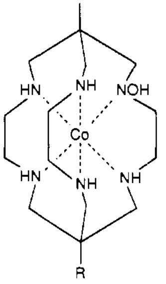


B - 3NOH



C - 3NOH

When only 1 mol of OH^-/mol of $[Co(dinosar)]^{3+}$ and 1 mol of H_2O_2/mol of $[Co(dinosar)]^{3+}$ were added, the main product was the mono(hydroxylamine) complex II. Also, $[Co(dichlosar)]^{3+}$ reacted with H_2O_2 in basic solution to give mainly the mono(hydroxylamine) complex III even with a large excess of base and H_2O_2. ^{13}C NMR signals at −4.9 and −6.4 ppm were ascribed to the quaternary carbon atoms by comparison with those for $[Co(dichlosar)]^{3+5}$ and the signals at +5.5 and +2.0 ppm were ascribed to the methylene carbon atoms next to the hydroxylamine group.



II, R = NO_2

III, R = Cl

The coordinated hydroxylamine groups exhibited quite strongly acidic properties in aqueous solution ($pK_{a_1} = 2.8$–4) similar to the analogous behavior of Pt^{II}–NH_2OH complexes.[8] By comparison the pK_a of uncoordinated NH_2OH is 13.7.[9] Complexes with one, two, and three hydroxylamine groups behaved as mono–, di–, and tribasic acids ($pK_a \approx 3$–6), respectively. The introduction of a NOH group raises the pK_a of the remaining secondary amines by approximately 1 pK_a unit. This determines how many NOH groups can be introduced into the complex by the present method. When enough NOH groups have been introduced to raise the basicity of the remaining secondary amino groups sufficiently to prevent effective deprotonation, the rate of attack by H_2O_2 falls off. The higher pK_a value of $[Co(dichlosar)]^{3+}$ relative to that of $[(Co(dinosar)]^{3+}$ points to why the mono(hydroxylamine) complex is almost the sole product, even in the presence of a large excess of base and H_2O_2.

In the electronic spectra of the fully protonated hydroxylamine complexes (in 0.1 M HCl), the first absorption band ($^1A_{1g} \rightarrow {}^1T_{1g}$ origin) is shifted toward longer wavelengths relative to that of the parent cage complexes ($\lambda_{\text{max}} = 474$ nm for both $[Co(dinosar)]^{3+}$ and $[Co(dichlosar)]^{3+}$), while for the deprotonated species the absorption is shifted equally much toward shorter wavelengths. However, the charge-transfer band of the deprotonated species extends toward longer wavelengths, partly obscuring the second d–d transition band.

These effects indicate a somewhat weaker ligand field for the protonated hydroxylamines vs. that for the parent complexes and a stronger ligand for the deprotonated species compared with that for the protonated parent complexes. The results are consistent with an intuitive interpretation in the sense that the anionic form of the ligand could be expected to have a higher ligand field than the neutral ligand. In this respect the property is different from that arising from deprotonation of a coordinated amine site. The latter leads to a red shift for the first ligand field band, which arises from the destabilizing effect that the N lone pair of electrons has via a π interaction with the t_{2g} electrons. With the deprotonated site more distant from the metal ion in the hydroxylamido complex, this interaction is void. The variation in charge and

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[9] Hughes, M. W.; Nicklin, H. G.; Shrimanker, K. *J. Chem. Soc. A* **1971**, 3485.

ligand field also has a substantial effect on the redox properties as indicated further on.

The hydroxylamine complexes were quite stable at room temperature, but some decomposition of the deprotonated species occurred on the cation-exchange resins and on standing in solution for long periods. Because of the geometry of the cage complexes no further oxidation of the hydroxylamine groups is possible without breaking the cage or reducing the ligand denticity, and they were found to be stable toward $Cr_2O_7^{2-}$ and Ce^{4+} in acid solution. Prolonged treatment with Zn powder and acid under nitrogen reduced the hydroxylamine groups back to the parent secondary amines. Cr^{2+}(aq) and Eu^{2+}(aq) also reconverted the complexes to the parent amines relatively slowly. However, reaction of $[Co(dichlosar\text{-}NOH)]^{3+}$ with V^{2+}(aq) in 1 M $HClO_4$ gave an immediate precipitate of $[Co(dichlosar)](ClO_4)_3$ on mixing of the reagents. This fast reaction presumably proceeds via V–O bonding between the V^{2+} ion and the hydroxylamine oxygen atom followed by rapid oxygen atom transfer from N to V to yield the secondary amine–VO^{2+} ion. The higher bond order in the formation of VO^{2+} is the driving force for this rapid process.[10] Cyclic voltammetry of the $[Co(dichlosar\text{-}NOH)]^{3+}$ complex in 0.1 M CF_3SO_3H on a glassy-carbon electrode showed only a one-electron reversible wave between 0 and −1.2 V (100 mV, 77 mV peak to peak, $E_{1/2} = -0.31$ V vs. Ag/AgCl, saturated NaCl, and $E = -0.12$ V (NHE)). In 0.1 M NaOH $E_{1/2} = -0.79$ V vs. Ag/AgCl, saturated NaCl, and $E = -0.60$ V (NHE) at 100 mV/s and 59 mV peak to peak corresponding to the Co^{II}/Co^{III} redox reaction. Presumably the reduction of the coordinated NOH groups is too slow for the electrochemical time scale. The cyclic voltammograms of the Co(dinosar-NOH) complexes were complicated by the characteristic reduction of the NO_2 groups on the caps.[11]

Only a few Co(III) hydroxylamine complexes appear in the literature. $[Co(NH_2OH)_6]^{3+}$ is reported[12] to be relatively stable in acid solution but decomposes rapidly in neutral and basic solution. Also the last two solutions were light-sensitive and small amounts of impurities accelerated the decomposition of the complexes. $[Co(en)_2(NH_2OH)Cl]^{2+}$ also undergoes spontaneous reduction to a labile Co(II) complex in neutral and basic solutions.[13] The present hydroxylamine complexes, as well, were found to be somewhat less stable in basic solutions than in acid, but they could be handled on chromatography columns by using basic eluents without appreciable decomposition. Their increased stability over the unsubstituted hydroxylamine complexes is probably due to the stability of the cage ligand itself, which would have to break up for the hydroxylamine group to be oxidized further. In short, these bound hydroxylamine groups do not show any of the reducing capability displayed by the parent NH_2OH molecule toward reduction of the Co(III) ion. This presumably arises from the absence of protons on the coordinated hydroxylamine N sites and the consequent inability of the molecule to generate an electron pair on an atom adjacent to the metal ion that would promote such reductions.

These hydroxylamine complexes are one of the few ways available so far to derivatize the cage N sites in a multiple manner. The derivatization leads, via deprotonation of the hydroxyl groups, to 0, +1, and +2 as well as the +3 charged ions. These charge changes have a substantial effect on the redox potentials of the couples, and they may also affect the self-exchange rates although the latter effect has not yet been probed.

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Registry No. (II)Cl_3, 109636-97-7; (III)Cl_3, 109636-96-6; III^{2+}, 109636-98-8; (A-2NOH)Cl_3, 109669-07-0; (A-2NOH)(CF_3SO_3)(Cl), 109636-91-1; (B-3NOH)($ZnCl_4$)(Cl), 109636-93-3; (C-3NOH)Cl_3, 109636-95-5; dinosar, 87655-55-8; dichlosar, 109614-00-8; [Co(dinosar)]Cl_3, 71935-78-9; [Co(dinosar)]$(CH_3COO)_3$, 91192-19-7; [Co(dichlosar)]Cl_3, 91002-83-4; [Co(dichlosar)]$(ClO_4)_3$, 109636-94-4; H_2O_2, 7722-84-1; V^{2+}, 15121-26-3.

Supplementary Material Available: Non-hydrogen atom thermal parameters (Table SUP-1), hydrogen atom parameters (Table SUP-2), and ligand and anion geometries (Table SUP-3) (4 pages); a listing of structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

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