the value of 10.1 from the potentiometric pH titrations (Table II; section 2), thus confirming that the alterations of the shifts are coupled with the formation of $Cd(ATP)(OH)^{3-}$.

The alterations of the chemical shifts produced by the coordination of Zn^{2+} to ATP are less pronounced than those obtained with Cd^{2+}; this agrees with earlier observations.[19] However, it is still evident that all the conclusions outlined above for Cd^{2+}/ATP are also valid for Zn^{2+}/ATP; especially, the release of N-7 from the coordination sphere of Zn^{2+} by the formation of $Zn(ATP)(OH)^{3-}$ is clearly seen. This release occurs at a pH that is about 1.3 log units lower than in the Cd^{2+}/ATP system, a result in excellent agreement with $pK^{H}_{Zn(ATP)(H_2O)} = 8.87$ (ref 41) and $pK^{H}_{Cd(ATP)(H_2O)} = 10.1$ (Table II).

Hence, the formation of the simple mixed-ligand complex $M(ATP)(OH)^{3-}$ is connected with the release of N-7 from the coordination sphere of the metal ion and therefore also with the opening of the macrochelate. Consequently, it seems possible that the formation of mixed-ligand complexes is usually always connected with the disappearance of the macrochelated isomer.

Conclusions

The results show that the coordinating properties of Cd^{2+} and Zn^{2+} with regard to nucleotides are similar and that ATP^{4-} is a very versatile ligand. The complex $M(ATP)^{2-}$ may exist at least in two isomeric forms: (i) the metal ion may only be coordinated to the phosphate chain or (ii) the metal ion may in addition interact with the base residue. This contrasts with the $M(CTP)^{2-}$ complexes, which exist only in the phosphate-coordinated form.

Considering that ATP participates in enzymic reactions usually in the form of $M(ATP)^{2-}$, these different structures may be of biological relevance. Important also in this connection is the indication, obtained from the present studies with Zn^{2+} and Cd^{2+}, that formation of mixed-ligand complexes leads to the release of N-7 from the coordination sphere of the metal ion, and hence a structural rearrangement is in this way initiated.

The described observations, together with the metal ion promoted self-association of ATP[19] and its ability to interact in an intramolecular fashion via hydrophobic and stacking interactions with the second ligand in mixed-ligand complexes,[35,51] show that ATP is a ligand suitable to satisfy many demands regarding specificity. CTP is in this respect a much less versatile ligand. Obviously, nature is making use of these differences, as well as of all the possibilities inherent in the ATP molecule.

Acknowledgment. We thank Professor R. Bruce Martin from the University of Virginia for stimulating discussions and helpful suggestions, Rita Baumbusch for the skillful performance of the potentiometric pH titrations, and K. Aegerter for recording the 90-MHz NMR spectra. The computers were made available by the Rechenzentrum der Universität Basel (Univac 1100/81). This support, research grants from the Swiss National Science Foundation (H.S.), support of the sabbatical leave of R.M.M. to the University of Basel through Boston University, and grants from the U.S. and Swiss National Science Foundations under the U.S.-Switzerland Cooperative Science Program are gratefully acknowledged.

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Contribution from the Chemistry Department,
University of Victoria, Victoria, B.C., Canada V8W 2Y2

Preparation, Characterization, and Outer-Sphere Electron-Transfer Reactions of Nickel Complexes of 1,4,7-Triazacyclononane

A. McAULEY,* P. R. NORMAN, and O. OLUBUYIDE[†]

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An unusually stable nickel(III) complex ion, $[Ni(1,4,7\text{-triazacyclononane})_2]^{3+}$, is described. Modification of an existing procedure leads to good yields of the ligand trihydrochloride. The nickel(III) complex has been prepared via oxidation of the nickel(II) analogue reported previously. The octahedral NiN_6 configuration is retained on electron transfer, and outer-sphere reactions have been studied. In the oxidation of iodide, under conditions of $[I^-]$ up to 80-fold in excess over oxidant, the rate law may be written as $R = k_6[Ni(III)][I^-]$ with $k_6 = 191\ M^{-1}\cdot s^{-1}$. A similar first-order dependence is observed in the oxidation of $Co(phen)_3^{2+}$ ($k_5 = 5.6 \times 10^5\ M^{-1}\cdot s^{-1}$). A self-exchange rate for the Ni(III/II) couple of $6.0 \times 10^3\ M^{-1}\cdot s^{-1}$ has been evaluated by using a Marcus correlation. The system represents one of the few examples where outer-sphere reaction pathways of Co^{3+} and $CoOH^{2+}$ may be assigned. The observed rate constant for the reaction of $Co^{3+} + Ni(nonaneN_3)_2^{2+}$ ($k_3 = 430\ M^{-1}\cdot s^{-1}$) is in good agreement with that predicted ($370\ M^{-1}\cdot s^{-1}\cdot$) by using recent data for the $Co^{3+/2+}$ exchange. Estimates are presented for the $CoOH^{2+/+}$ exchange rate.

Introduction

The oxidation of nickel(II) amine complexes in aqueous solution has been studied extensively over the past few years,[1,2] and the existence of this metal center in both the trivalent[3,4] and tetravalent[2,5] states has now been well documented. Since the nickel(III) complexes are conveniently generated by oxidation of the corresponding nickel(II) amines and because the higher valent ions are in aqueous media generally only kinetically stable to any extent only under acidic conditions ($[H^+] > 0.1$ M), studies have centered mainly on those compounds that are stable in acid. This criterion is well met by the tetraaza macrocyclic complexes of nickel(II).[6-8] In contrast, studies with ethylenediamine as ligand provide evidence for $Ni(en)_3^{3+}$ as having only transitory existence.[9] Only

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[†] Chemistry Department, University of Ife, Ile-Ife, Nigeria.

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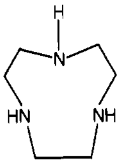
in the cases of deprotonated amino acids, where Margerum[10,11] has shown the stability of Ni(III) species to be considerable under basic conditions, and for Ni(III) species incorporating polypyridine ligands[12,13] have such noncyclic amine complexes been well characterized. Part of the difficulty inherent in this situation may be attributed to the high kinetic lability of the nickel(II) amine complexes. Although tetraaza macrocyclic complexes of Ni(III) are sufficiently stable to enable kinetic studies to be undertaken,[14,15] there is the disadvantage that the oxidation to the higher state is accompanied by a geometry change from square planar to distorted octahedral.[1,16] This results in significant contributions to the reorganizational terms in the energetics of electron transfer. Also, subtle electronic effects are possible in reactions of $Ni(bpy)_3^{3+}$ as a result of the low-lying π orbitals present in the unsaturated ligand. These difficulties are avoided in the formation of the title complex, a species of pseudomacrocyclic stability. The nickel(II) complex may be prepared by reaction of $Ni(ClO_4)_2$ with 1,4,7-triazacyclononane (L) in methanol.[17] The $(nonaneN_3)_2$ species, NiL_2^{2+}, is stable in 1.0 M acid for several hours.[18] The crystal structure[19] shows evidence for trigonal distortion. Oxidation of NiL_2^{2+} in a variety of solvents produces a stable Ni(III) ion that retains the original inner coordination sphere and is much more stable with respect to decomposition than many other Ni(III) ions ($t_{1/2} > 24$ h at pH ~3). We report here details of studies of electron-transfer reactions involving the $NiL_2^{2+/3+}$ couple. Attempts have also been made to measure the rate of self-exchange via ^{61}Ni-labeling experiments.



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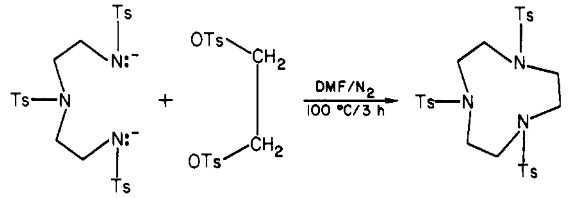
Experimental Section

All materials used were of reagent grade except where indicated. Dimethylformamide, used in ligand syntheses, was dried (distillation under reduced pressure over Type 4A molecular sieves) and stored over sieves. ^{61}Ni (86.4% ^{61}Ni) was obtained as the metal (Oak Ridge National Laboratory), and $^{61}Ni(ClO_4)_2$ was prepared by dissolution of the metal in 3 M $HClO_4$ and crystallization of the product. Solutions containing ~0.04 M $Co(ClO_4)_3$ were prepared as described previously[20] and stored at -5 °C. $LiClO_4$, formed on reaction of Li_2CO_3 with ~3 M $HClO_4$, was recrystallized three times from distilled water. Solutions were shown to be sulfate free by using Ba^{2+} ions. A similar procedure was used in preparing lithium *p*-toluenesulfonate solutions. $Co(phen)_3(ClO_4)_2$ was prepared as described previously.[21] The ligand, 1,4,7-triazacyclononane, was synthesized by a modification of the method described by Atkins,[22,23] which utilizes the high degree of cyclization achieved by the reaction of the disodium salt of *N,N′,N″*-tritosyldiethylenetriamine with the ditosyl derivative of 1,2-ethanediol (tosyl = Ts = *p*-toluenesulfonyl):



All ligand synthesis reactions were carried out under a stream of dry N_2.

***N,N′,N″*-Tritosyldiethylenetriamine** was prepared as described.[24] Synthesis of the disodium salt was achieved by dissolving 5.0 g of sodium metal in 200 mL of absolute ethanol under dry N_2 to generate NaOEt. The resulting solution was added rapidly to a suspension of 57 g of tritosyldiethylenetriamine in 250 mL of absolute ethanol. The slurry was brought to the boil, whereupon most of the solid dissolved. After decantation of undissolved material, the solution was kept (moisture excluded) at 0 °C overnight. The resulting white crystalline precipitate was filtered under dry N_2, washed with ice-cold absolute ethanol and diethyl ether, and dried in vacuo; yield of the disodium salt 57 g (90%).

Ditosylate of 1,2-Ethanediol. A 6.2-g sample of 1,2-ethanediol (0.1 mol) was dissolved in 500 mL of dry CH_2Cl_2 in a three-necked flask. The solution was cooled to 0 °C in a stream of dry N_2 and 50 mL of triethylamine added. With the temperature maintained at 0 °C, a solution of 38 g of *p*-toluenesulfonyl chloride (0.2 mol) in 250 mL of dry CH_2Cl_2 was added over a period of 45 min. The mixture was stirred under these conditions for 12 h after which the Et_3NHCl formed was filtered off. The filtrate was washed with 250 mL of 2 M HCl, and the CH_2Cl_2 layer was removed and subsequently washed with two 250-mL portions of distilled water followed by two similar portions of saturated Na_2CO_3 solution. The organic layer was dried over anhydrous Na_2SO_4. Removal of solvent and recrystallization ($EtOH/H_2O$ mixture) gave the white product: yield 30 g (90%); mp 120–122 °C. NMR: aromatics (8 H), δ 7.55; CH_2 (4 H), δ 4.18; CH_3 (6 H), δ 2.42.

1,4,7-Tritosyl-1,4,7-triazacyclononane (L-Ts_3). A 53-g amount of disodium diethylenetriaminate (0.086 mol) was dissolved in 350 mL of dry DMF under a stream of dry N_2 in a flask (three neck) equipped with a mechanical stirrer. The solution was heated to 90 °C, and a solution of 32 g of 1,2-ethanediol ditosylate in 180 mL of DMF was added over a 45-min period. Initially the solution turned turbid, but on further heating at 105 °C (4 h) the contents of the flask turned a clear golden yellow when heating was stopped and the flask allowed to cool to room temperature. The product was precipitated as a white powder by *slow* addition of the DMF solution to 2 L of rapidly stirred water. After filtration and washing with 500 mL of H_2O, the product was dried in a vacuum oven at 80 °C (recrystallization if necessary may be accomplished by using a $EtOH/H_2O$ mixture): yield 38 g (74%); mp 220–223 °C. NMR: aromatics (12 H), δ 7.50; CH_2 (12 H), δ 3.40; CH_3, δ 3.40.

1,4,7-Triazacyclononane Trihydrochloride. Twenty-five grams of the crude tritosyl derivative was dissolved in 120 mL of concentrated H_2SO_4, and the mixture was heated with stirring at 130 °C for 48 h. After cooling, the solution was neutralized by slow addition to 300 g of NaOH dissolved in 600 mL of H_2O. The resulting solution was allowed to cool at 0 °C overnight to allow Na_2SO_4 to crystallize out. The supernatant was decanted into a continuous-extraction apparatus and extracted with 400 mL of $CHCl_3$ over a 3-day period. The solid sodium sulfate was washed with 200 mL of $CHCl_3$, the slurry formed being filtered through Whatman phase-separation paper to remove the excess inorganic solid. The chloroform fractions were combined and taken to dryness on a rotary evaporator. Following dissolution in 25 mL of ethanol and filtration, the ligand trihydrochloride was precipitated by addition of 10 mL of concentrated HCl. The product was filtered, washed with ethanol and diethyl ether, and air-dried; yield 9.0 g. NMR: no aromatics, singlet δ 4.00 in D_2O. The material was used without further purification in the synthesis of the nickel(II) complex.

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$NiL_2(ClO_4)_2$. A solution of 960 mg of the ligand trihydrochloride (4 mmol) dissolved in 12 mL of 1 M NaOH (0.012 mol) was warmed on a steam bath. To this solution was added 0.73 g (2 mmol) of $Ni(ClO_4)_2 \cdot 6H_2O$ dissolved in 15 mL of methanol. The solution pH was adjusted to 10.5, and after 5 min of warming the color changed to light pink. The pH was further lowered to 5 (1 M $HClO_4$), and the solution on cooling at 0 °C (1 h) yielded light lilac crystals in almost quantitative yield. These were recrystallized from $MeOH/H_2O$, washed with propan-2-ol and then diethyl ether, and dried under vacuum (12 h). Anal. Calcd for $C_{12}H_{30}N_6Cl_2O_8Ni$ (M_r = 516.03): C, 27.93; H, 5.86; N, 16.29; Cl, 13.74. Found: C, 27.98; H, 5.73; N, 16.01; Cl, 13.61. UV [λ, nm (ϵ, $L \cdot mol^{-1} \cdot cm^{-1}$)]: 322 (11), 504 (11), 799 (16) (for the nitrate salt corresponding literature[17] values are 505 (5), 800 (7)). IR (cm^{-1}): ν_{NH} 3230, 3305; δ_{NH} 1620; ClO_4^- 1050–1100 unsplit indicative of ionic perchlorate.

Note! Metal perchlorate complexes are hazardous and should be treated with caution.

$NiL_2(ClO_4)_3$. The nickel(III) complex was formed by oxidation of 25 mg of the nickel(II) species in ~1 M $HClO_4$ using a slight excess of aquocobalt(III). the brown/green complex that crystallized readily was recrystallized from 10^{-3} M $HClO_4$ in ~70% yield. λ_{max} = 312 nm, ϵ = 10100 ± 200 $L \cdot mol^{-1} \cdot cm^{-1}$. Anal. Calcd for $C_{21}H_{30}N_6Cl_3O_{12}Ni$ (M_r = 615.0): C, 23.41; H, 4.91; N, 13.65; Cl, 17.28. Found: C, 23.55; H, 4.95; N, 13.57; Cl, 17.44. In distilled water Λ_m = 440, as expected for a 3:1 electrolyte. Analyses were performed by the Canadian Microanalytical Services, Vancouver.

Infrared spectra were obtained from KBr disks on a Perkin-Elmer 283 grating spectrometer. UV/visible measurements were made on a Beckman DU-8 instrument and ^1H NMR spectra in $CDCl_3$ on a 90-MHz Perkin-Elmer R32 instrument with Me_4Si as internal standard. The stopped-flow apparatus has been described previously.[25] Pseudo-first-order conditions (excess reductant in the case of Ni(III) reactions) were employed, and reactions were monitored at 350 nm. Absorbance data derived from the photomultiplier output were collected with use of a PCM-12 minicomputer. Plots of ln ($A_\infty - A_t$) against time were linear for greater than 3 half-lives. ESR spectra were obtained at 77 K with a Varian E-6S instrument. DPPH was used as a reference standard.

Results

(a) Formation and Geometry of NiL_2^{3+}. The nickel(II) complex may be readily oxidized to the nickel(III) species under a variety of conditions. The oxidation may be accomplished by $NOPF_6$ in CH_3CN or CH_3NO_2 or in aqueous media with hexaaquocobalt(III). In all cases the product is an intensely green ion that shows an ESR spectrum characteristic of a low-spin d^7 complex (Figure 1). Anisotropic spectra are obtained in both aqueous and nonaqueous solutions, $g_\perp \sim 2.14$ and $g_\parallel = 2.02$. There is some evidence for hyperfine interaction ($A_\parallel \sim 23.7$ G) in the $g_\parallel$ feature, involving both axial nitrogen atoms with the appearance of a quintet. In this regard, the spectra are very similar to those of the only other NiN_6^{3+} systems so far characterized, which involved bipyridines as ligands. The $A_\parallel$ values for the latter complexes are in the range of 25 G, close to that derived in the present study. The difference $g_\perp - g_\parallel \sim 0.12$ for the $(nonaneN_3)_2$ complex ion is smaller than that (~0.19) for the tetraaza macrocycles, e.g. $Ni(cyclam)(CH_3CN)_2^{3+}$, resulting probably from a greater symmetry of the octahedral field in the present case. There is thus good evidence that the primary coordination sphere remains intact on oxidation. This is confirmed by the isolation of solid NiL_2^{3+} as the perchlorate salt from aqueous media. Addition of high concentrations of coordinating anions in different solvents (2 M LiCl in aqueous solutions, 1 M *t*-BuNCl in CH_3CN or CH_3NO_2) shows no tendency for the anion to enter the first coordination sphere. There is no evidence in ESR spectra of any hyperfine interaction with Cl^- as is seen in the case of the tetraaza macrocycles, where the coordinated solvent is readily displaced.

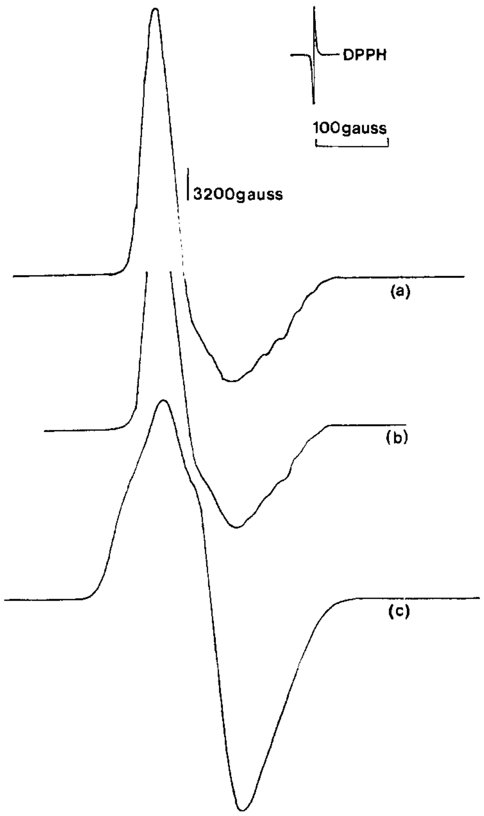

Figure 1. ESR spectra of frozen solutions of $Ni(nonaneN_3)_2^{3+}$: (a) $^{58}Ni(nonaneN_3)_2^{3+}$ in 2 M Li_2SO_4(aq); (b) $^{58}Ni(nonaneN_3)_2^{3+}$ in CH_3CN + 1 M *tert*-butylammonium chloride; (c) $^{61}Ni(nonaneN_3)_2^{3+}$, $[Ni(III)]_t \sim 6.4 \times 10^{-5}$ M, 1.0 M $HClO_4$.

The nickel(III) complexes formed show greater stability than any others so far prepared in this laboratory. The solid complex is unchanged in air at room temperature over several weeks, and in anhydrous nonaqueous media the solutions appear indefinitely stable with respect to redox decomposition. In aqueous solution there is no apparent decomposition at pH ~3 over a 24-h period. The kinetic stability was measured at λ_{max} = 312 nm where the extinction coefficient is ~10^4 $M^{-1} \cdot cm^{-1}$, similar to that for other Ni(III) amine complexes. In contrast to the macrocyclic systems, however, no d–d transition is apparent. This may be expected in a molecule of high symmetry where a very low extinction coefficient may be masked by the large absorbance at 312 nm. In view of the kinetic stability of the ion and of the retention of configuration in redox systems, it is considered that the system will be very useful as an outer-sphere reagent. There are relatively few such couples available at present for Ni(II/III) exchanges.

(b) Oxidation by Aqueous Co(III). The kinetics of the oxidation of NiL_2^{2+} by aqueous Co(III) were investigated spectrophotometrically at λ = 342 nm (appearance of NiL_2^{3+}). Spectrophotometric titration revealed a one-electron transfer in accord with the overall reaction

$$NiL_2^{2+} + Co(III) \rightarrow NiL_2^{3+} + Co(II) \qquad (1)$$

Reactions were monitored over the range T = 15.9–30 °C, and in all cases pseudo-first-order conditions were maintained with $[NiL_2^{2+}]$ (3–200 × 10^{-4} M) in excess over [Co(III)] (~2 × 10^{-5} M). The results are summarized in Table I. The first-order dependence on [Ni(II)] is maintained over a wide concentration range consistent with the rate law

$$d[Ni^{III}L_2^{3+}]/dt = k_2[Ni^{II}L_2^{2+}][Co(III)] \qquad (2)$$

A significant increase of the rate constant, k_2, was observed on decreasing the hydrogen ion concentration. Since there are

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Table I. Rate Data and Thermodynamic Parameters for the Reaction of $[NiL_2](ClO_4)_2$ with $Co^{3+}(aq)$ ($I = 1.00$ M ($LiClO_4$); $[Co(III)]_t \approx 2 \times 10^{-5}$ M)

Dependence on [Ni(II)][a]

$10^4[Ni(II)]/M$	2.45	4.90	7.30	9.85	12.05
$10k_{obsd}/s^{-1}$	1.50 ± 0.05	3.05 ± 0.05	4.70	6.00 ± 0.1	7.72
$k_2/M^{-1}\cdot s^{-1}$ [b]	612	622	643	609	632

Dependence of Rate Constants on [H⁺][c]

$[Ni(II)] = 4.6_2 \times 10^{-4}$ M; $T = 15.9$ °C

$[H^+]/M$	0.20	0.60	1.00
$10k_{obsd}/s^{-1}$	4.80 (± 0.2)	2.37 (± 0.10)	1.93 (± 0.10)

mean $k_4K_h/s^{-1} = 159 \pm 18$; intercept $k_3 = 255\ M^{-1}\cdot s^{-1}$

$[Ni(II)] = 4.59 \times 10^{-4}$ M; $T = 20.9$ °C

$[H^+]/M$	0.25	0.33	0.60	1.00
$10k_{obsd}/s^{-1}$	4.99	4.08 ± 0.1	3.21 ± 0.1	2.46

mean $k_4K_h/s^{-1} = 172 \pm 10$; intercept $k_3 = 389\ M^{-1}\cdot s^{-1}$

$[Ni(II)] = 4.5_3 \times 10^{-4}$ M; $T = 25$ °C

$[H^+]/M$	0.20	0.40	0.60	0.80	1.00[d]
$10k_{obsd}/s^{-1}$	8.00 ± 0.05	5.05	3.88 ± 0.05	3.45 ± 0.05	

mean $k_4K_h/s^{-1} = 268 \pm 10$; intercept $k_3 = 432\ M^{-1}\cdot s^{-1}$

$[Ni(II)] = 4.62 \times 10^{-4}$ M; $T = 30.0$ °C

$[H^+]/M$	0.20	0.60	1.00
$10k_{obsd}/s^{-1}$	15.40 (± 0.2)	7.07 (± 0.1)	4.76

mean $k_4K_h/s^{-1} = 563 \pm 17$; intercept $k_3 = 546\ M^{-1}\cdot s^{-1}$

[a] $[H^+] = 1.00$ M ($HClO_4$); $T = 25$ °C. [b] Mean = 623 ± 20 $M^{-1}\cdot s^{-1}$. [c] Composite rate constants, k_4K_h, yield $\Delta H^\ddagger = 8.7 \pm 1.2$ kcal·mol⁻¹ and $\Delta S^\ddagger = -17.2 \pm 4.3$ cal·mol⁻¹·K⁻¹. [d] See [Ni(II)] dependence.

Table II. Reaction of $Co(phen)_3^{2+}$ with NiL_2^{3+} in Nitrate Media ($I = 1.0$ M; $[H^+] = 0.5$ M;[a] $[NiL_3^{3+}] \sim 5 \times 10^{-6}$ M; $\lambda = 335$ nm)

$T/°C$	$10^5[Co(II)]/M$	k_{obsd}/s^{-1}	$10^{-5}k_5/M^{-1}\cdot s^{-1}$ [b]
9.3	7.50	29.0 ± 0.4	3.87 ± 0.05
	10.0	38.7	
13.1	7.5	31.2 ± 1.2	4.2 ± 0.2
	10.0	40.9	
18.1	5.55	29.5 ± 0.9	5.0 ± 0.3
	7.50	35.5	
25.0	4.4	24.8 ± 1.5	
	5.5	30.6 ± 1.0	5.6 ± 0.1
	6.6	37.7 ± 0.5	
	7.5	40.8 ± 0.9	
	8.8	48.8 ± 0.7	

[a] No [H⁺] dependence observed in the range 0.1–1.0 M. [b] $\Delta H^\ddagger = 3.3 \pm 0.2$ kcal·mol⁻¹; $\Delta S^\ddagger = -21 \pm 1$ cal·mol⁻¹·K⁻¹.

Table III. Rate Data and Thermodynamic Parameters for the Reduction of NiL_2^{3+} by Iodide [$I = 1.00$ M (ClO_4^-)]

Dependence on [I⁻][a]

$10^4[I^-]/M$	4.19	5.06	6.22	7.98	8.22	11.70
$10^2k_{obsd}/s^{-1}$	7.31	9.98	11.03	15.99	16.9	22.4
$(k_{obsd}/[I^-])/M^{-1}\cdot s^{-1}$ (k_6)[c]	174	199	177	194	212	191

Hydrogen Ion Dependence[b]

$[H^+]/M$	0.05	0.10	0.30	0.50	0.70	1.00
$k_6/M^{-1}\cdot s^{-1}$	170	180	166	199	187	212

Temperature Dependence

$T/°C$	15.2	20.8	25.0	29.3
$k_6/M^{-1}\cdot s^{-1}$	63.5	148	191	250

$-\Delta H^\ddagger = 16.0 \pm 2.6$ kcal·mol⁻¹; $\Delta S^\ddagger = 5.5 \pm 8$ cal·mol⁻¹·K⁻¹

[a] $[Ni(III)] = 1 \times 10^{-5}$ M; $T = 25$ °C; $I = 1.0$ M ($LiClO_4$); $[H^+] = 0.1$ M. [b] $[Ni(III)] = 1 \times 10^{-5}$ M; $T = 25$ °C. [c] Mean $k_6 = 191 \pm 11\ M^{-1}\cdot s^{-1}$.

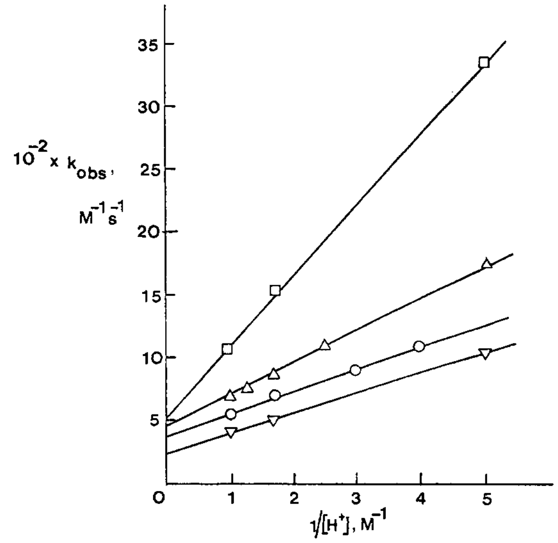

Figure 2. Hydrogen ion dependence of observed second-order rate constants in the oxidation of $Ni(nonaneN_3)_2^{2+}$ by $Co(III)_{aq}$ ($I = 1.0$ M): □, 30.5 °C; △, 25.0 °C; ○, 20.9 °C; ▽, 15.9 °C.

no proton-related equilibria associated with the reductant, the mechanisms may be expressed as

$$K_h = [CoOH^{2+}][H^+]/[Co^{3+}]$$

$$NiL_2^{2+} + Co^{3+}(aq) \xrightarrow{k_3} NiL_2^{3+} + Co^{2+} \qquad (3)$$

$$NiL_2^{3+} + CoOH^{2+} \xrightarrow{k_4} NiL_2^{3+} + Co(II) \qquad (4)$$

The overall second-order rate constant, k_{obsd}, may be written in the form

$$k_{obsd} = k_3 + k_4K_h/[H^+] \qquad (5)$$

and plots of k_{obsd} against $[H^+]^{-1}$ should be linear with intercept k_3 and slope k_4K_h. Such behavior is observed (Figure 2) at all temperatures studied. Since the reactions are unambiguously outer sphere, the present system provides data for an analysis of both reactions 3 and 4 (vide infra). At 25 °C, $k_3 = 430 \pm 30\ M^{-1}\cdot s^{-1}$, somewhat higher than the rate constant obtained from the oxidation of $Ni^{II}cyclam^{2+}$ ($88 \pm 40\ M^{-1}\cdot s^{-1}$).[20,15] On the basis of $K_h = 2 \times 10^{-3}$ M,[26] $k_4 = (1.34 \pm 0.1) \times 10^5\ M^{-1}\cdot s^{-1}$ and lies in the range 10^5–$10^6\ M^{-1}\cdot s^{-1}$ derived for other reactions of this type.[20]

(c) Reaction of NiL_2^{3+} with $Co(phen)_3^{2+}$. Kinetic studies were made in nitrate media under conditions of excess reductant, the disappearance of Ni(III) being followed at 335 nm. Spectrophotometric data are consistent (to ±2%) with a one-electron transfer

$$NiL_2^{3+} + Co(phen)_3^{2+} \rightarrow NiL_2^{2+} + Co(phen)_3^{3+} \qquad (6)$$

Rate data are given in Table II. The rate law may be described adequately by the expression

$$\text{rate} = k_5[NiL_2^{3+}][Co(phen)_3^{2+}] \qquad (7)$$

with no observed dependence on [H⁺]. The rate constant ($T = 25$ °C), $k_5 = 5.6 \times 10^5\ M^{-1}\cdot s^{-1}$, is consistent with an outer-sphere process.

(d) Oxidation of Iodide by NiL_3^{3+}. A facile oxidation of I⁻ is observed on addition of NiL_2^{3+}:

$$NiL_2^{3+} + I^- \rightarrow NiL_2^{2+} + I\cdot\ (\rightarrow I_3^-) \qquad (8)$$

Kinetic studies were carried out in acidic media (0.1–0.7 M H⁺) with no associated hydrogen ion dependence on the rate. Reactions were monitored by using the disappearance of Ni(III) ($\lambda = 342$ nm), and the data are given in Table III. As is seen, up to an iodide excess of ~80-fold over the $Ni^{III}L_2^{3+}$, a first-order dependence on reductant is observed, consistent with the rate law

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$$R = k_6[\mathrm{NiL_2}^{3+}][\mathrm{I}^-] \qquad (9)$$

When $[\mathrm{I}^-]$ is increased above this ratio, however, there is a deviation from the rate law (9) with evidence for an $[\mathrm{I}^-]^2$ term, as has been observed in other outer-sphere reactions involving this ion.[27,28] Unfortunately at higher iodide concentrations the absorbance of $\mathrm{I_3}^-$ interfered with the monitoring reaction, leading to less accurate rate constants. Rate data are reported for only reaction 8.

(e) Self-Exchange of the $\mathrm{NiL_2}^{3+/2+}$ Couple. In a previous study[29] we measured the rate of self-exchange of a Ni(II/III) tetraaza macrocycle using the hyperfine interaction associated with $^{61}\mathrm{Ni}$ ($I = {}^3/_2$). We have attempted a similar experiment in the present reaction. As is seen in Figure 1, line broadening is observed for the $^{61}\mathrm{NiL_3}^{3+}$ ion when compared under similar conditions to that for the $^{58}\mathrm{NiL_2}^{3+}$ species, although there is not the same elaboration of the spectrum (leading to the expected four resonances) as is observed in the case of $\mathrm{Ni^{III}(cyclam)(H_2O)_2}^{3+}$. The change at 3420 G relative to the $g_\parallel$ peak (which remains at a constant value for any Ni(III) concentration) was used to monitor the rate of reaction of $^{58}\mathrm{Ni^{II}L_2}^{2+}$ (6.4×10^{-4} M) with $^{61}\mathrm{NiL_2}^{3+}$ (6.4×10^{-5} M) at −4 °C, $[\mathrm{H}^+] = 0.2$ M, $I = 1.0$ M. Mixed solutions were allowed to stand for predetermined times at the reaction temperature and were then quenched by immersion in liquid $\mathrm{N_2}$. Systematic variations in ESR spectra were recorded, and an approximate value of k_{11} for the $\mathrm{NiL_2}^{3+/2+}$ exchange is $30 \pm 15\ \mathrm{M^{-1}{\cdot}s^{-1}}$ at this temperature. (Under reaction conditions used the time taken to reach infinity was ~3 min.) At 25 °C, however, the reaction was too rapid to permit rate measurements to be made.

Discussion

From the variety of reactions studied, the data are consistent with $\mathrm{NiL_2}^{3+}$ acting as an outer-sphere redox reagent. The nickel(II) and nickel(III) complexes are stable in acidic media, and in the case of the reactions involving aquocobalt(III), at 1.0 M H^+ the extent of decomposition of the $\mathrm{Ni^{II}L_2}^{2+}$ complex is <1% during the total time for oxidation to the $\mathrm{Ni^{III}L_2}^{3+}$ ion. We are therefore confident that there is no pH-dependent decomposition of $\mathrm{Ni(nonaneN_3)_2}^{2+}$ contributing to the observed relaxations even under the most acidic conditions employed.

The lack of any hydrogen ion dependence on the iodide and $\mathrm{Co(phen)_3}^{2+}$ reductions is consistent with no related proton equilibria for the Ni(III/II) couple. This is significant in view of the designation of the $[\mathrm{H}^+]^{-1}$-dependent pathway in the cobalt(III) oxidation. To further substantiate this point, the reaction of $\mathrm{NiL_2}^{2+}$ with $\mathrm{Fe(bpy)_3}^{3+}$ was examined. Again, no $[\mathrm{H}^+]$ effects were observed, the second-order rate constant (T = 25 °C) being $2.7 \times 10^6\ \mathrm{M^{-1}{\cdot}s^{-1}}$. Attribution of the inverse acid dependence in the cobalt(III) reactions to a pathway involving CoOH^{2+} is in accord with no proton dissociation of the Ni(II) ion. Cyclic voltammetry studies on the $\mathrm{NiL_2}^{2+}$ ion show good reversibility ($[\mathrm{H}^+] = 0.1$ M, peak to peak separation 70 mV), resulting in a reduction potential for the $\mathrm{NiL_2}^{3+/2+}$ couple of 940 mV (vs. NHE). Self-exchange rates may be estimated from reaction data and the overall free energy change by using the Marcus cross-correlation[30,31]

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}W_{12} \qquad (10)$$

where k_{11} and k_{22} are the rate constants for the individual self-exchange reactions, k_{12} is the cross-reaction constant, and K_{12} is the overall equilibrium constant, with

$$\ln f_{12} = \frac{[\ln K_{12} + (w_{12} - w_{21})/RT]^2}{4\left[\ln\left(\dfrac{k_{11}k_{22}}{A_{11}A_{22}}\right) + \left(\dfrac{w_{11} + w_{22}}{RT}\right)\right]} \qquad (11)$$

$$W_{12} = \exp[-(w_{12} + w_{21} - w_{11} - w_{22})/2RT] \qquad (12)$$

$$A_{ii} = \left[\frac{4\pi N\sigma^2 v_n \delta r}{1000}\right]_{ii} \qquad (13)$$

In the above expressions, w_{12} and w_{21} represent the work required to bring the reactants and the products, respectively, to a separation distance r (the sum of the ionic radii); w_{11} and w_{22} have similar meanings for the self-exchange processes. A value of A/σ^2 of $\sim 3 \times 10^{10}\ \mathrm{M^{-1}{\cdot}\AA^{-2}{\cdot}s^{-1}}$ was used in the calculations.

For the reaction of $\mathrm{Co(phen)_3}^{2+}$, the self-exchange rate of $8\ \mathrm{M^{-1}{\cdot}s^{-1}}$[21] for the cobalt couple may be used to derive a value of $k_{11} \sim 6 \times 10^3\ \mathrm{M^{-1}{\cdot}s^{-1}}$ for the $\mathrm{NiL_2}^{3+/2+}$ exchange. This rate is similar to that for other Ni(II/III) systems. There are, however, very few data relating to octahedral Ni(II)/Ni(III) reagents. A recent estimate of $2 \times 10^3\ \mathrm{M^{-1}{\cdot}s^{-1}}$ has been made[31] for the $\mathrm{Ni(bpy)_3}^{3+/2+}$ exchange, and in the system where a hexadentate oxime ligand system is used, the $\mathrm{NiL}^{3+/2+}$ exchange rate has been found to be $(1\text{–}2) \times 10^3\ \mathrm{M^{-1}{\cdot}s^{-1}}$ in two separate studies.[5,33] In all cases there is a need for structural data and spectroscopic analysis prior to a discussion of these values, but in most examples of this type a bond extension of ~0.1 Å (Δd(Ni–N)) has been assumed.[32,33]

Typical of data for the outer-sphere oxidations of iodide are those involving metal(III) polypyridine complexes.[27,28] From such data, the $E°(\mathrm{I}\cdot/\mathrm{I}^-)$ has been estimated to be 1.38 V,[28] with the corresponding self-exchange rate of $\sim 10^7\ \mathrm{M^{-1}{\cdot}s^{-1}}$. In these reaction sequences, there is evidence not only for a first-order term in $[\mathrm{I}^-]$ but also one in $[\mathrm{I}^-]^2$. The present system $(\mathrm{Ni(nonaneN_3)_2})^{3+}/\mathrm{I}^-$ shows many similarities to this pattern although we have restricted our investigations to the concentration range of ~20–60-fold excess of reductant where rate law 9 represents the data. By the use of the Marcus cross-correlation together with the self-exchange rate of $\sim 6 \times 10^3\ \mathrm{M^{-1}{\cdot}s^{-1}}$ (vide supra), the calculated value of the second-order rate constant k_6 is $11.4\ \mathrm{M^{-1}{\cdot}s^{-1}}$, compared with the observed value of $191\ \mathrm{M^{-1}{\cdot}s^{-1}}$. There will undoubtedly be some ion pairing in this system that may affect the rate. The agreement is, however, considered satisfactory.

A feature of the present study is that it provides further measurements of the reactions involving aquocobalt(III), in addition to the relatively few available. From the data (Figure 2) it is evident that both $\mathrm{Co^{3+}(aq)}$ and CoOH^{2+} are reactive species in the oxidation of $\mathrm{Ni(nonaneN_3)_2}^{2+}$. Endicott[15] has recently discussed the redox reactions of $\mathrm{Co^{3+}(aq)}$, suggesting that for cross-reactions an outer-sphere process may be envisaged but that the self-exchange $\mathrm{Co}^{3+/2+}$ proceeds via a bridged mechanism. On the basis of the calculated value proposed for the outer-sphere exchange ($k_{\mathrm{aa}} = 10^{-12}\ \mathrm{M^{-1}{\cdot}s^{-1}}$) for the $\mathrm{Co}^{3+/2+}$ couple, the predicted value for the second-order rate constant is $k_3 = 370\ \mathrm{M^{-1}{\cdot}s^{-1}}$, in excellent agreement with an observed value of $432 \pm 30\ \mathrm{M^{-1}{\cdot}s^{-1}}$. The outer-sphere nature of these reactions thus allows us to comment on the CoOH^{2+} pathway. In many instances for reactions involving this ion, an inner-sphere route is indicated. The outer-sphere reaction with $\mathrm{Ni(nonaneN_3)_2}^{2+}$ may be used to provide a possible estimate of the $\mathrm{CoOH}^{2+/+}$ self-exchange rate. By the use of $K_\mathrm{h} = 2 \times 10^{-3}$ M for $\mathrm{Co^{3+}(aq)}$ and $10^{-9}\text{–}10^{-10}$ M for $\mathrm{Co^{2+}(aq)}$,[34] the $E°$ for the $\mathrm{CoOH}^{2+/+}$ couple may be evaluated

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as $\sim$1.44 V. Marcus cross-correlations from the present data then predict a self-exchange rate of $\sim$50 $M^{-1}\cdot s^{-1}$ for the hydroxo couple. Few other data are available where the outer-sphere pathway of $CoOH^{2+}$ may be assigned. In the reaction with the Ni(II) oxime ligand complex (L = 3,14-dimethyl-4,7,10,13-tetraazahexadeca-3,13-diene-2,15-dione dioxime) where the NiN_6 configuration is maintained on oxidation,[33] the calculated self-exchange rate for $CoOH^{2+/+}$ is $\sim$2 $M^{-1}\cdot s^{-1}$, which compares reasonably with that from the present study. More data on the spin states of the $CoOH^{2+}$ ion are required before substantive discussion may be made of these results. It is of interest, however, that from the value of $k(CoOH^{2+/+})$ = 50 $M^{-1}\cdot s^{-1}$, the predicted rate for the reaction of $CoOH^{2+}$ with $Ni^{II}(cyclam)^{2+}$ is 4.1×10^5 $M^{-1}\cdot s^{-1}$, compared with an observed rate constant of 4.4×10^5 $M^{-1}\cdot s^{-1}$. The reaction may thus involve an outer-sphere pathway. The corresponding calculation for the $Ni[Me_6[14]\text{-}4,11\text{-diene}]^{2+}$ complex predicts a value of $\sim 1.1 \times 10^2$ $M^{-1}\cdot s^{-1}$, about 4 orders of magnitude lower than that observed (2.55×10^5 $M^{-1}\cdot s^{-1}$). We are currently attempting to prepare other Ni(II/III) couples involving NiN_6 chromophores that will provide further details on these reactions.

Although this discussion has centered round the possible self-exchange rate of the $CoOH^{2+/+}$ couple, the origin of the pH dependence could derive from an intramolecular NiL_2–Co hydrogen-bonding interaction or from a proton transfer coupled to the electron-transfer step. Davies[35] has analyzed the variations in rate constants for outer-sphere reactions of $CoOH^{2+}$ in terms of outer-sphere precursor formation and the attainment of a species in which the distribution of OH^- in the inner sphere of the cobalt(III) is optimal for hydroxide-mediated electron transfer within the precursor complex. Specific interactions between the H atoms of the secondary amine and the $CoOH^{2+}$ cannot be ruled out at this stage.

The preparation of a very stable $Ni^{III}N_6{}^{2+/3+}$ couple has enabled us to gain further insights into the redox behavior of these d^7/d^8 systems and in addition has provided support for the outer-sphere character of reactions of aquocobalt(III). Details of the crystal structure of the $Ni^{III}(nonaneN_3)_2{}^{3+}$ ion will enable us to identify intrinsic contributions to the activation energy attributable to first-coordination-sphere reorganization. Such effects are considered to be much smaller for Ni than for similar systems involving other metal ions (e.g. Co) and may account for the generally higher self-exchange rates.

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Registry No. L·3HCl, 58966-93-1; L-Ts_3, 52667-89-7; Co^{3+}(aq), 15275-05-5; $CoOH^{2+}$, 68842-90-0; $Co(phen)_3(ClO_4)_2$, 15317-76-7; $NiL_2(ClO_4)_2$, 60296-44-8; $NiL_2(ClO_4)_3$, 86709-82-2; I^-, 20461-54-5; $NOPF_6$, 16921-91-8; *N*,*N*′,*N*″-tritosyldiethylenetriamine, disodium salt, 52601-80-6; 1,2-ethanediol ditosylate, 6315-52-2; *N*,*N*′,*N*″-tritosyldiethylenetriamine, 56187-04-3.

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Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305,
and Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, 91904 Jerusalem, Israel

Reactivity of Haloruthenocene(IV) Complexes

TERRANCE P. SMITH,[1] KEH SHIN KWAN,[1] HENRY TAUBE,*[1] AVI BINO,[2] and SHMUEL COHEN[2]

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The ruthenium(IV)-containing compounds $[Ru(cp)_2Br]PF_6$ and $[Ru(cp)_2Cl]PF_6$ react with H_2O, yielding ruthenocene and ring-oxidation products, Ru(cp)(cpO)Br and Ru(cp)(cpO)Cl, respectively. The structure of the oxidized bromo compound has been determined from 564 unique x-ray reflections. The compound crystallizes in the orthorhombic space group *Pnma* with unit cell dimensions a = 13.588 (2) Å, b = 8.876 (1) Å, c = 7.495 (1) Å, V = 904 (1) $Å^3$, and Z = 4. The discrepancy indices are R_1 = 3.05% and R_2 = 3.51%. A mirror plane, containing the ruthenium and bromine atoms, bisects the cyclopentadienyl and cyclopentadienone (cpO) rings. The rings are in a staggered conformation and are bent away from the halide.

Introduction

The chemical and electrochemical oxidations of the iron-group metallocenes have been extensively examined.[3-10] When ferrocene or osmacene is oxidized electrochemically, a one-electron change is observed. Surprisingly, when ruthenocene is electrochemically oxidized, a two-electron change is realized. Whereas ferrocene is oxidized to the ferrocenium cation by the halogens, both osmacene and ruthenocene form complexes of the general form $M(cp)_2X^+$ in which the metal is in the oxidation state 4+ and can be considered to be seven-coordinated. Gray et al.[3] have determined the structure of the triiodide salt of $Ru(cp)_2I^+$ by X-ray diffraction methods. The chemistry of these high-oxidation-state organometallic complexes has not been previously explored. In this paper we report the reaction of the Ru(IV) complexes with H_2O and the structure of one of the products of this kind of reaction.

Experimental Section

Materials. Ruthenocene was purchased from Strem Chemical, Inc.

$[Ru(cp)_2X]X_3$. The compounds with X = Br or I were prepared as described in the literature.[5] That with X = Cl has not heretofore been prepared, but it is readily formed following the procedure used for the other two complexes. Anal. Calcd for $C_{10}H_{10}RuCl_4$: C, 32.19; H, 2.70; Cl, 38.01; Ru, 27.09 Found: C, 31.68; H, 2.47; Cl, 37.02; Ru, 26.80. Satisfactory carbon, hydrogen, and halogen analyses were obtained for all other new compounds.

$[Ru(cp)_2Cl][PF_6]$. A 0.50-g sample of $Ru(cp)_2$ was dissolved in 50 mL of benzene and the resultant mixture added to 25 mL of 4 M

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