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Notes

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Slow Solution Reaction of Dimeric Dimethylaminoborane with Lithium Hydride

Philip C. Keller

There are no literature reports on the interaction of an alkali metal hydride with $[(CH_3)_2NBH_2]_2$ under mild conditions. Burg and Randolph[1] showed that $[(CH_3)_2NBH_2]_2$ reacted with NaH (but not LiH) at elevated temperature in the absence of solvent according to

$$[(CH_3)_2NBH_2]_2 + NaH \rightarrow HB[N(CH_3)_2]_2 + NaBH_4 \qquad (1)$$
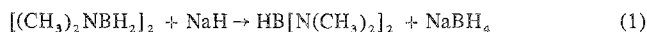
This reaction probably results from a thermally induced disproportionation of $[(CH_3)_2NBH_2]_2$

$$[(CH_3)_2NBH_2]_2 \rightarrow HB[N(CH_3)_2]_2 + \tfrac{1}{2}B_2H_6 \qquad (2)$$
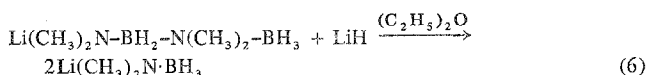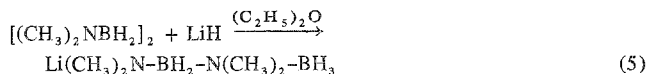
$$NaH + \tfrac{1}{2}B_2H_6 \rightarrow NaBH_4 \qquad (3)$$
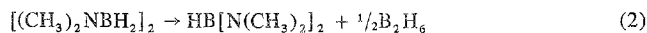
As part of another project, we have had the opportunity to observe the action of LiH on $[(CH_3)_2NBH_2]_2$ at room temperature in diethyl ether over periods of several months. We find that under these conditions the sole final product is $Li(CH_3)_2N\cdot BH_3$.

$$[(CH_3)_2NBH_2]_2 + 2LiH \xrightarrow[25°]{(C_2H_5)_2O} 2Li(CH_3)_2N\cdot BH_3 \qquad (4)$$
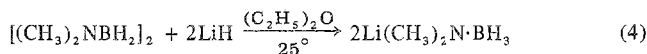
A typical reaction was 90% complete after 2 months at ambient temperature.

If the system is monitored periodically by boron-11 nmr, weak signals due to an intermediate product can be detected (Figure 1). The nmr parameters compare favorably with those of the ion $(CH_3)_2NBH_2N(CH_3)_2BH_3^-$ [2] (triplet −2.4 ppm, $J_{BH} = 92$ Hz; quartet 13.1 ppm, $J_{BH} = 81$ Hz; data for potassium salt in 1,2-dimethoxyethane). The presence of this ion strongly suggests that the main pathway for eq 4 involves ring opening by reaction of LiH with dimethylaminoborane *dimer* followed in a subsequent step by cleavage of the NBNB chain by LiH.

$$[(CH_3)_2NBH_2]_2 + LiH \xrightarrow{(C_2H_5)_2O}$$
$$Li(CH_3)_2N-BH_2-N(CH_3)_2-BH_3 \qquad (5)$$

$$Li(CH_3)_2N-BH_2-N(CH_3)_2-BH_3 + LiH \xrightarrow{(C_2H_5)_2O}$$
$$2Li(CH_3)_2N\cdot BH_3 \qquad (6)$$

The cleavage reaction (eq 6) has been demonstrated elsewhere.[2]

Experimental Section

Standard vacuum techniques were used in this work. Lithium hydride (Alfa Inorganics) was used without further purification; $[(CH_3)_2NBH_2]_2$ was prepared by the pyrolysis of $(CH_3)_2NH\cdot BH_3$ (Research Organic/Inorganic Chemical Corp.).[3] Diethyl ether was stored in an evacuated bulb over $LiAlH_4$ and when needed was
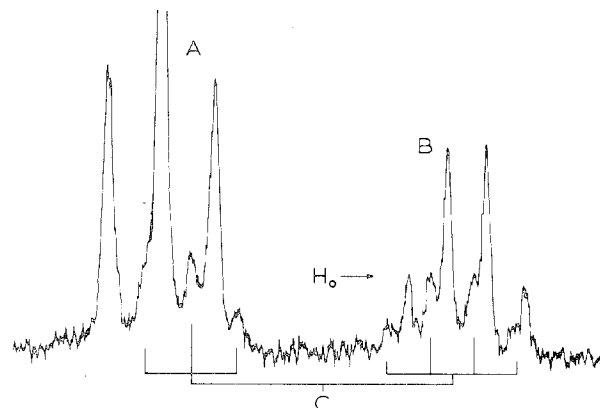

Figure 1. Boron-11 nmr spectrum of the partially complete reaction of $[(CH_3)_2NBH_2]_2$ with LiH after 2.5 weeks: A, triplet, $[(CH_3)_2NBH_2]_2$, −5.1 ppm, $J = 113$ Hz; B, quartet, $(CH_3)_2NBH_3^-$, 15.0 ppm, $J = 83$ Hz; C, $(CH_3)_2N-BH_2-N(CH_3)_2-BH_3^-$, triplet, −2.7 ppm, $J = 100$ Hz; quartet, 14.1 ppm, $J = 88$ Hz. Chemical shifts are relative to $(C_2H_5)_2O\cdot BF_3$.

condensed directly into the reaction vessel. Boron-11 nmr spectra were obtained with a Varian HA-100 spectrometer operating at 32.1 MHz. Chemical shifts and coupling constants were measured by the substitution side band method.

In a typical experiment an all-Pyrex nmr reaction vessel was charged with 8–10 mmol of LiH, 1–2 mmol of $[(CH_3)_2NBH_2]_2$ and 1 ml of diethyl ether were condensed in, and the vessel was sealed. The mixture was allowed to stand at room temperature for 2–3 months with occasional shaking and periodic monitoring by nmr. Products were identified by their nmr parameters.

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Reactions of Coordinated Nickel(II) Complexes Containing Imine and Amine Groups[1]

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Nickel(II) complexes (I, II) containing a Schiff base ligand derived from pyrrole-2-carboxaldehyde and dipropylenetriamine (bis(2-pyrrolyl)-2,6,10-triaza-1,10-undecadiene

(H$_2$BPTU)), having the general formula Ni(HBPTU)Br, were prepared.[2a] Physical measurements of Ni(HBPTU)Br in the solid state suggested that this diamagnetic complex is square planar and that the HBPTU acts as a tetradentate ligand containing a dangling pyrrole group (I). However, in solution
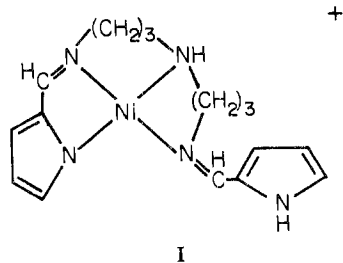
I

the terminal imine is displaced by the solvent, and the HBPTU functions as a tridentate ligand containing a dangling un-coordinated imine and protonated pyrrole group (II).
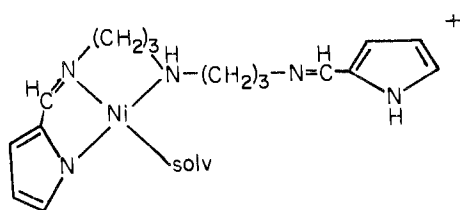
II

It was hoped that the dangling imine in solution could be hydrolyzed to an amine group. The resulting ligand could function as either a tetradentate ligand analogous to I or a tridentate with a dangling amine analogous to II. Complexes which contain measurable amounts of dangling amine in solution should function as an active intermediate for a variety of ligand reactions.

Experimental Section

General Information. The chemicals and the physical methods employed in this study have been reported.[2a]

Preparation of Metal Complexes. C$_{11}$H$_{18}$N$_4$NiBr (Ni(PTD)Br). Sodium (0.16 g, 7.1 g-atom) was added to 50 ml of absolute methanol. To this solution of sodium methoxide was added 0.48 g of pyrrole-2-carboxaldehyde (5.1 mmol) and 0.75 ml of dipropylene-triamine (5.7 mmol). The resulting solution was refluxed for 5 min. Upon addition of ((C$_2$H$_5$)$_4$N)$_2$NiBr$_4$[2b] (3.2 g, 5.1 mmol) the solution turned red-brown. The solution was refluxed for 5 min, allowed to cool at room temperature, and then filtered to remove a small amount of residue. The filtrate was slowly evaporated (to a volume of 3–5 ml) at room temperature. The resulting orange crystals were filtered and washed with ethanol and acetone. The product weighed 1.40 g for a 79.% yield. A 0.5000-g sample of the crude product was recrystallized from 17 ml of absolute methanol; yield 0.23 g. *Anal.* Calcd for C$_{11}$H$_{18}$N$_4$NiBr: C, 38.31; H, 5.26; N, 16.24. Found: C, 38.40; H, 5.52; N, 16.13.

C$_{11}$H$_{18}$N$_4$NiPF$_6$ (Ni(PTD)PF$_6$). A 50-mg (0.145-mmol) sample of Ni(PTD)Br was dissolved in 15 ml of H$_2$O. A solution containing 0.300 g of KPF$_6$ (1.77 mmol) was added dropwise until no more precipitate was formed. The mixture was filtered, and the crystals were washed with ethanol; 40 mg was recovered for a 66.9% yield. *Anal.* Calcd for C$_{11}$H$_{18}$N$_4$NiPF$_6$: C, 32.22; H, 4.64; N, 13.67. Found: C, 31.62; H, 4.81; N, 13.98.

C$_{35}$H$_{39}$N$_4$NiB (Ni(PTD)B(C$_6$H$_5$)$_4$). A 50-mg sample of purified Ni(PTD)Br (0.145 mmol) was dissolved in 13 ml of water. A solution containing 50 mg of sodium tetraphenylboron in 10 ml of water was added dropwise until no more precipitate was formed. The mixture was filtered and the pale orange powder was washed with ethanol; 60.5 mg was recovered for a 71.3% yield. *Anal.* Calcd for C$_{35}$H$_{39}$N$_4$NiB: C, 71.82; H, 6.72; N, 9.57. Found: C, 72.16; H, 6.70; N, 9.35.

C$_{12}$H$_{18}$N$_5$SNiBr (Ni(PTD)SCN). A solution containing 200 mg of sodium thiocyanate in water was added slowly to 50 mg (0.145

mmol) of Ni(PTD)Br dissolved in 15 ml of water until no more precipitate formed. The yellow creamy precipitate was filtered, washed with water, and dried; it weighed 3 mg for a 64% yield. *Anal.* Calcd for C$_{12}$H$_{18}$N$_5$SNiBr: C, 44.62; H, 5.89; N, 21.69. Found: C, 44.67; H, 5.43; N, 21.77.

C$_{12}$H$_{19}$N$_5$SeNi (Ni(PTD)SeCN). A 50-mg sample of Ni(PTD)Br (0.145 mmol) was dissolved in 15 ml of water. A solution containing 0.200 g of KSeCN (14.0 mmol) in 20 ml of water was added dropwise until no more precipitate formed. The mixture was filtered and the brown powder was washed with water and dried. Forty-four milligrams was recovered for an 82% yield. *Anal.* Calcd for C$_{12}$H$_{19}$N$_5$SeN: C, 38.90; H, 5.13; N, 19.90. Found: C, 38.86; H, 4.86; N, 18.76.

C$_{18}$H$_{31}$N$_4$NiBr (Ni(PTD-Hep)Br). To 40 ml of 95% ethanol 0.200 g (0.00058 mol) of Ni(PTD)Br and 0.096 g (0.113 ml, 0.0084 mol) of heptanal were added. The mole ratio of Ni(PTD)Br to heptanal was 1:1.5. The mixture was refluxed for 24 hr and cooled to room temperature, and the solvent was stripped off in a rotary evaporator. The resultant mixture of light orange crystals and oil was filtered to separate the crystals which were washed with absolute ether. The product was a light yellow powder weighing 0.1965 g for a 77% yield. The heptanal derivative was recrystallized from acetone by refluxing 0.1884 g of (Ni(PTD-Hep)Br with 5 ml of acetone for 5 min. The hot solution was filtered immediately and upon standing yielded 0.013 g. *Anal.* Calcd for C$_{18}$H$_{31}$N$_4$NiBr: C, 49.02; H, 6.81; N, 12.26. Found: C, 48.43; H, 6.59; N, 12.20.

Hydrolysis of Ni(PTD-Hep)Br. The heptanal derivative was hydrolyzed completely to Ni(PTD)Br by dissolving 0.100 g in hot water and heating for 0.5 hr. Upon evaporation of water, 0.057 g of Ni(PTD)Br was obtained. Ni(PTD)Br was identified by infrared spectrum.

Hydrolysis of Ni(HBPTU)Br. A 0.10-g sample of Ni(HBPT-U)Br[2a] (0.24 mmol) and 0.15 ml of a 0.345 M NaOH solution (0.50 mmol) were refluxed in 20 ml of a 1:1 water–ethanol solution for 2 hr. The reaction mixture was allowed to cool to room temperature and was then filtered. About 0.030 g of gray-white residue was obtained (probably pyrrole-2-carboxaldehyde). The residue's spectrum could not be identified. The filtrate was evaporated to dryness using a rotary evaporator. About 0.050 g of material from the flask was recovered. Ni(PTD)Br was identified by infrared spectrum.

Conversion of Ni(PTD)Br to Ni(HBPTU)Br. A mixture of Ni(PTD)Br (0.20 g, 0.58 mmol) and pyrrole-2-carboxaldehyde (0.11 g, 1.16 mmol) in 25 ml of 95% EtOH was refluxed for 5.5 hr. The solution was allowed to cool to room temperature. A few crystals of Ni(PTD)Br were filtered off. The filtrate was allowed to evaporate slowly at room temperature. A first crop of crystals was filtered resulting in 0.050 g of mostly Ni(PTD)Br. A second crop of crystals 0.060 g, was recovered after evaporation of all the solvent. These crystals were identified by infrared analysis to be essentially Ni(HBPTU)Br.

Results and Discussion

Previous research has established that Ni(HBPTU)Br dissolved in a polar solvent contains one imine group within a chelate ring and one noncoordinating dangling imine group.[2a] A noncoordinating exocyclic imine is more susceptible to hydrolysis than an imine group that is within a chelate ring or within a multiple fused ring system.[3] Therefore, it was possible to accomplish the hydrolysis of only the noncoordinating imine and to form a new complex, Ni(PTD)Br. This reaction does not go readily but in the presence of a base the conversion of Ni(HBPTU)Br to Ni(PTD)Br was accomplished. The function of the metal ion is to mask the imine linkage within the chelate ring from hydrolysis, but not the exocyclic imine group. The net result is a selective hydrolysis.

Ni(PTD)Br was also prepared by the reaction of pyrrole-2-carboxaldehyde with dipropylenetriamine in a 1:1 ratio in the presence of the NiBr$_4^{2-}$ anion. Both procedures gave products with identical infrared and electronic spectra. In a water solution the bromide anion in Ni(PTD)Br was replaced by B(C$_6$H$_5$)$_4^-$, PF$_6^-$, SCN$^-$, and SeCN$^-$ thereby producing the complexes Ni(PTD)X, where X is B(C$_6$H$_5$)$_4$, PF$_6$, SCN, or SeCN. All these compounds are red-orange

Table I. Ultraviolet–Visible Spectra of Ni(PTD)X Complexes

| Complex	Solvent	Wavelength, nm ($\epsilon \times 10^{-3}$)
Ni(PTD)Br	CHCl$_3$	475 sh^a (0.285), 397 (5.7), 337 (9.3), 296 (11.1)
	CH$_3$CN	475 sh^a (0.253), 379 (3.29), 330 (7.4), 300 (6.4)
	CH$_3$NO$_2$	475 sh^a (0.248), 385 (10.7)
	H$_2$O	475 sh^a (0.110), 386 (1.84), 324 (8.4), 294 (12.4)
	Solid^b	460 sh,^{a} 388
	Solid^c	475 sh^a
Ni(PTD)(C$_6$H$_5$)$_4$B	CHCl$_3$	398 (5.0), 384 sh^a (4.75), 331 (7.95), 296 (9.36)
	CH$_3$CN	475 sh^a (0.227), 370 (2.87), 325 (5.2), 299 (6.4)
	CH$_3$NO$_2$	475 sh^a (0.123), 385 (5.34)
	Solid^b	480 sh,^{a} 395
	Solid^c	475 sh^a
Ni(PTD)PF$_6$	CHCl$_3$	475 sh^a (0.117), 388 (2.42), 333 (3.4), 298 (3.1)
	CH$_3$CN	475 sh^a (0.193), 375 (2.89), 325 (5.3), 299 (5.8)
	CH$_3$NO$_2$	475 sh^a (0.137), 385 (6.16)
	Solid^c	470 sh^a
Ni(PTD)SCN	CHCl$_3$	475 sh^a (0.269), 400 (3.55), 331 (8.4), 302 (7.8)

^{a} All shoulders were difficult to assign. ^{b} Refectance spectra.
^{c} Diffuse-transmittance spectra.

**Table II.** Magnetic Data for Ni(PTD)X Complexes

Complex	Temp, °K	Magnetic moment μ_{eff}, BM
Ni(PTD)Br	303	0.53
Ni(PTD)B(B$_6$H$_5$)$_4$	297	0.80
Ni(PTD)PF$_6$	300	0.67
Ni(PTD)SCN	300	3.3

except Ni(PTD)SCN which is light brown and Ni(PTD)SeCN which is brown. Also all four of the above complexes have limited solubility in organic solvents such as CHCl$_3$, alcohol, and nitromethane but are insoluble in water except Ni(PTD)Br which has slight solubility in water.

The colors and electronic spectral and magnetic properties of solid Ni(PTD)Br, Ni(PTD)PF$_6$, and Ni(PTD)B(C$_6$H$_5$)$_4$ are similar. The position of only one shoulder in the vicinity of 475 mμ (Table I) for all these diamagnetic (Table II) complexes suggests that the complexes are square planar and have the same donor groups positioned around the coordination sphere of the nickel(II). Since B(C$_6$H$_5$)$_4^-$ and PF$_6^-$ are not as likely to coordinate to the nickel(II) as the Br$^-$, the similarity of the spectra of Ni(PTD)Br with the spectra of Ni(PTD)-B(C$_6$H$_5$)$_4$ and Ni(PTD)PF$_6$ suggests that the bromide ion is not coordinated in the solid state. Therefore, the ligand PTD must be functioning as a tetradentate ligand (III).

III
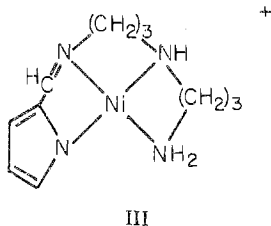
Unlike the above complexes Ni(PTD)SCN is paramagnetic (μ = 3.3 BM) and the Nujol electronic spectrum of Ni(P-TD)SCN contains a shoulder at 553 mμ as well as at 475 mμ (Table I). However, this spectrum is not consistent with known spectra for four-, five-, and six-coordinate nickel(II) complexes.

The N–H stretching bands for Ni(PTD)Br are broader and
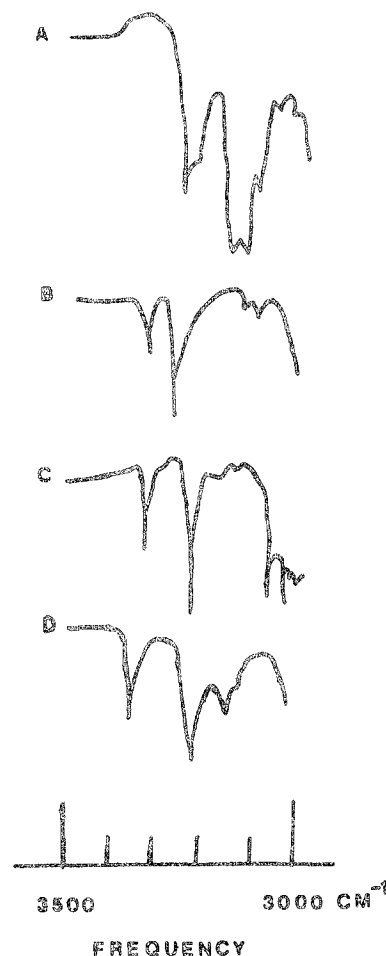
Figure 1. Infrared spectra in Nujol mull: A, Ni(PTD)Br; B, Ni-(PTD)SCN; C, Ni(PTD)B(C$_6$H$_5$)$_4$; D, Ni(PTD)PF$_6$.

are shifted to a lower energy compared to Ni(PTD)PF$_6$, Ni(PTD)B(C$_6$H$_5$)$_4$, Ni(PTD)SCN, and Ni(PTD)SeCN (Figure 1). Unlike the B(C$_6$H$_5$)$_4^-$ and PF$_6^-$, the uncoordinated bromide anion is able to hydrogen bond to the amine hydrogens thereby producing a broadening of the peaks and a shift to a lower energy. The N–H regions in the infrared spectra for Ni(PTD)SCN and Ni(PTD)SeCN are very similar to those for Ni(PTD)B(C$_6$H$_5$)$_4$ and Ni(PTD)PF$_6$ (Table III). Such data along with the spectral and magnetic data suggest that the SCN$^-$ and the SeCN$^-$ are not functioning as anions but are coordinated to the nickel(II) and hence cannot effectively hydrogen bond to the amine hydrogens. The C–N stretch for Ni(PTD)SCN occurs at 2080 cm^{-1}, and it occurs at 2090 cm^{-1} for Ni(PTD)SeCN. Both these C–N stretches are within the region indicative of coordination through nitrogen.[4,5]

The solution spectra of Ni(PTD)X (X = Br, B(C$_6$H$_5$)$_4$, PF$_6$) in CHCl$_3$, CH$_3$CN, and CH$_3$NO$_2$ look similar to the solid spectra. Therefore it is likely that the geometry around the nickel(II) atom in the solid state is similar to that in solution. In a strongly coordinating solvent such as pyridine only small changes are observed in the 1600–350 mμ range. Conductometric measurements of all Ni(PTD)X compounds reveal a complex solution chemistry (Table IV). The molar conductances in acetonitrile and nitromethane are indicative of a 1:1 electrolyte. However the Onsager slopes are much higher than expected for a 2:1 electrolyte.[6–8] It appears from these conductometric measurements that Ni(PTD)X complexes cannot exist as a simple monomer in solution.

The solution data can be more easily understood if a polar solvent displaces the terminal amine group from the coor-

Table III. Important Infrared Spectral Band Assignments for Ni(PTD)X Complexes (cm^{-1})

						ν_{CH}(out-of-plane band)	
Complex	ν_{NH}	ν_{ND}	ν_{CH} (aromatic)	$\nu_{C=N}$	$\nu_{(CH_2)n}$ (rock)	Pyrrole	Phenyl
Ni(PTD)Br	3242 m 3229 sh 3146 m 3101 m 3075 sh			1594 s	754 m	739 m	
Ni(PTD)Br, deuterated		2413 m 2321 m 2292 m		1595 s	754 w	739 s	
Ni(PTD)B(C$_6$H$_5$)$_4$	3332 m 3236 m 3166 w, br		3061 m 3035 m 3018 sh 3004 sh	1590 s	750 m	734 s	721 sh 714 sh 706 s
Ni(PTD)PF$_6$	3331 m 3195 m 3131 m 3111 sh			1600 s	771 m	741 w	
Ni(PTD)SCN	3311 m 3241			1609 s	772 w	747 s	
Ni(PTD)SeCN	3332 m 3270 m 3085 w			1605 s	772 w	749 s	
Ni(PTD-Hep)Br	3020 m			1670 s 1589 s		744 s	

Table IV. Conductivities^a for Ni(PTD)X Complexes

Complex	Solvent	Molar conductance,^{b,c} ohm^{-1} cm^{-2} mol^{-1}	Λ_0	Onsager slope^d
Ni(PTD)Br	CH$_3$NO$_2$	42	66	730
	CH$_3$CN	90	170	2400
	H$_2$O	225		
Ni(PTD)B(C$_6$H$_5$)$_4$	CH$_3$NO$_2$	76	92	770
	CH$_3$CN	112	141	880
Ni(PTD)PF$_6$	CH$_3$NO$_2$	109	130	660
	CH$_3$CN	155	174	610
Ni(PTD)SCN	CH$_3$NO$_2$	72	102	1000
	CH$_3$CN	111	168	1850
Ni(PTD-Hep)Br	CH$_3$NO$_2$	65	90	770
	CH$_3$CN	144	189	1500

^{a} Temperature 25° for all Ni(PTD)X complexes. ^{b} Obtained at 1×10^{-3} *M*. ^{c} Molar conductances reported for 1:1 and 2:1 electrolytes in nitromethane, acetonitrile, and water are 70–95, 160–190; 135–160, 250–310; and 85–100, 220–250, respectively. ^{d} Onsager slopes reported for 1:1 and 2:1 electrolytes in nitromethane and acetonitrile are 200, 450; and 350, 900, respectively.

dination sphere leaving a dangling amine group available for intermolecular association. The deviation from linearity upon plotting Λ *vs.* $c e^{1/2}$ at high dilution is additional evidence of some type of equilibrium in solution. Possible explanations for the curved conductivity plots include the solvent partially displacing the PTD from the nickel(II) or the solvent aiding in the breaking up solute–solute interaction. Support for these explanations is the observation that the pH of an aqueous solution of Ni(PTD)Br slowly increases with time. The pH data suggest that PTD is being sequentially unwrapped from the nickel(II) or there is decreasing molecular association *via* the dangling amine group, thereby making the lone-pair electrons on the amine more available for hydrolysis.

Should several polymers exist in solution, held together by either hydrogen bonds or a bridging ligand, it would be expected that the degree of intermolecular association should vary with the concentration of solute and the nature of the solvent. Unfortunately, the low solubility of Ni(PTD)Br prevented confirmation of intermolecular association by the infrared or nmr techniques.

The conductivity in water, the pH of Ni(PTD)Br solutions, and spectra in coordinating solvents suggest the presence of a dangling primary amine. The molar conductance in water
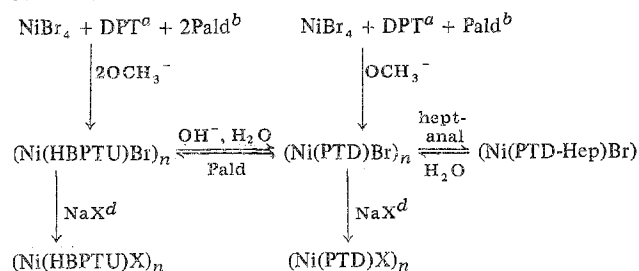
of Ni(PTD)Br is indicative of a 2:1 electrolyte (Table IV). An aqueous solution of Ni(PTD)Br is also basic with a pH of 9.66 at a concentration of 0.0003 *M*. For a water solution of Ni(PTD)Br, the K_b, based on the equilibrium B + H$_2$O $\rightleftharpoons$ BH$^+$ + OH$^-$, where B represents Ni(PTD)Br, is approximately 4×10^{-6}. This equilibrium constant is somewhat less than found for ethylenediamine, 1.8×10^{-5}.[9] The value of the K_b indicates that the uncoordinated primary amine probably exists in equilibrium with a coordinated primary amine in solution. The fact that the pyridine does not coordinate to the nickel(II) in solution but the weaker ligand SCN$^-$ does coordinate to the nickel(II) in the solid state (as evidenced by spectral and magnetic data), suggests that either the dangling primary amine in solution sterically inhibits the expansion of the coordination number or the dangling amine weakly coordinates to the axial position of another solute molecule.

Measurements of the rates of dissociation of polyamine nickel(II) complexes indicate that the terminal amine groups are more labile than the central amine groups.[10] The strain imposed by the arrangement and two consecutive six membered rings can be partially relieved by the dissociation of the weakest terminal donor–metal bond. In the case of these complexes the terminal amine coordinated to the nickel(II) is partially displaced by solvent.

A dangling primary amine should interact with aldehydes to form Schiff bases. It is believed that strongly coordinated primary amines will not undergo Schiff base condensation.[11] Ni(PTD)Br was converted to Ni(HBPTU)Br by allowing Ni(PTD)Br to react with pyrrole-2-carboxaldehyde in refluxing alcohol. Also the dangling amine on Ni(PTD)Br was condensed with heptanal to form the yellow-orange complex Ni(PTD-Hep)Br (Scheme I).

The Ni(PTD-Hep)Br has solubility, Onsager slopes, and solid and solution properties similar to Ni(HBPTU)Br.[2a] The Ni(PTD-Hep)Br can be easily reconverted to Ni(PTD)Br by refluxing in hot water (Scheme I). The Ni(PTD-Hep)Br is far more susceptible to hydrolysis than Ni(HBPTU)Br.

It has been suggested that uncoordinated amines can function as intermediates in metal-controlled condensation with ketones or aldehydes.[12,13] We have demonstrated that a dangling amine can be reactive to various aldehydes. Currently we are preparing novel ligands by the reaction of pyridine-2-carboxaldehyde and salicylaldehyde with a terminal amine group in Ni(PTD)Br. It has also been demonstrated that the metal ion can mask or protect certain reactive groups (imines)

Scheme I[c]

NiBr$_4$ + DPT[a] + 2Pald[b]   NiBr$_4$ + DPT[a] + Pald[b]

        | 2OCH$_3$$^-$ | OCH$_3$$^-$

        | | hept-
                          OH$^-$, H$_2$O   anal
(Ni(HBPTU)Br)$_n$ ⇌⇌⇌⇌⇌ (Ni(PTD)Br)$_n$ ⇌⇌⇌⇌ (Ni(PTD-Hep)Br)
                          Pald   H$_2$O

        | NaX[d] | NaX[d]

        ↓   ↓
(Ni(HBPTU)X)$_n$ (Ni(PTD)X)$_n$

[a] DPT = dipropylenetriamine. [b] Pald = pyrrole-2-carboxaldehyde.
[c] All other symbols are defined in the text of this paper. [d] X =
B(C$_6$H$_5$)$_4$, PF$_6$, SeCN, SCN.

from ligand reaction while allowing other functional groups to become more susceptible to a ligand reaction.

Registry No. Ni(PTD)Br, 53293-21-3; Ni(PTD)(C$_6$H$_5$)$_4$B, 53293-23-5; Ni(PTD)PF$_6$, 53293-24-6; Ni(PTD)SCN, 53293-25-7; Ni(PTD)SeCN, 53293-26-8; Ni(PTD-Hep)Br, 53293-27-9; pyrrole-2-carboxaldehyde, 1003-29-8; dipropylenetriamine, 56-18-8; ((C$_2$H$_5$)$_4$N)$_2$NiBr$_4$, 1185-60-0; heptanal, 111-71-7.

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**Reactivity of Coordinated Nitrosyls. IV.
One-Electron Reduction of Ruthenium
Nitrosylpentaammine(3+) Ion in Aqueous Solution[1,2]**

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The reduction of Ru(NH$_3$)$_5$NO^{3+} by metal ion reducing agents, such as Cr^{2+}, proceeds *via* multiple-electron-transfer pathways[3] and implies the existence of Ru(NH$_3$)$_5$NO^{2+} as an important reactive intermediate.[4] Because of further reaction of this one-electron-reduced species with the reductant to produce ultimately Ru(NH$_3$)$_6$$^{2+}$, characterization has not been possible.[3] This species is of particular interest because of the ability of the coordinated NO to show properties ranging from those of NO$^-$ to those of NO$^+$.[5-8] We have used cyclic voltammetric and pulse radiolytic techniques to effect the one-electron reduction and to permit the characterization of the reduced species.

Experimental Section

Ru(NH$_3$)$_5$NO^{3+} was prepared either by the direct addition of NO(aq) to [Ru(NH$_3$)$_6$]Cl$_3$ in acidic medium[9] or by the addition of (NH$_4$)$_2$S$_2$O$_8$ to [Ru(NH$_3$)$_5$Cl]Cl$_2$.[10] The nitrosyl complex was then recrystallized twice as the Cl$^-$, Br$^-$, ClO$_4$$^-$, or TFMS$^-$ (trifluoromethylsulfonate) salts.[3] Trifluoromethylsulfonic acid (3M Corp.) was distilled under vacuum at 10 Torr and 62°. The pure acid was diluted immediately to a concentration of 3 M and stored in a polyethylene bottle.

Cyclic voltammetry and dme polarography equipment at Stanford University and the California Institute of Technology was used for these experiments. Similar electrochemical devices have been described in the literature.[11] Cyclic voltammograms of the substitution-inert Ru(NH$_3$)$_5$NO^{3+} were recorded on an X-Y recorder at a sweep rate of 0.1 V/sec. In order to obtain more symmetrical anodic and cathodic waves, higher sweep rates (0.4–40 V/sec) were employed with the use of a storage oscilloscope. A hanging mercury drop (area 0.032 cm^2) was used as the working electrode. In the experiments involving dme polarography, h = 90 cm, drop time = 5.3 sec, m = 1.35 mg/sec. Potentials were measured with respect to a calomel electrode saturated with NaCl; such an electrode has a potential 5 mV more negative than sce. The values given in this paper correspond to the formal potentials converted to the nhe scale.

Controlled-potential coulometry[12] was performed on Ru(NH$_3$)$_5$NO^{3+} in 0.1 M NaCl at pH ~3 or in 0.1 M NaClO$_4$ at pH ~7.

Solutions of Ru(NH$_3$)$_5$NO^{3+} (as the Cl$^-$ or TFMS$^-$ salt) were subjected to 30-nsec pulses of 2.3-MeV electrons using the Febetron 705 pulse radiolysis system at the U. S. Army Natick Laboratories. Transient spectra and the decay behavior of intermediates were examined by kinetic spectrophotometry using a 2-cm optical path length as has been described in the past.[13] All rates were measured at 23°.

Results and Discussion

Cyclic voltammograms of deoxygenated solutions of Ru(NH$_3$)$_5$NO^{3+} in 0.1 M NaCl (pH 3-7) or NaTFMS yielded a reversible, one-electron wave (Figure 1). At fast scan rates, the anodic and cathodic peak heights at the maxima were similar to those observed for the same number of moles of Ru(NH$_3$)$_6$$^{3+}$ [11] in the same medium, thereby establishing the one-electron change, a fact that was further confirmed by conventional dme polarography and controlled-potential coulometry. At a scan rate of 1.0–10 V/sec (between 0.0 and –0.45 V *vs.* sce), the potentials of the anodic and cathodic peaks were separated by approximately 70 ± 10 mV indicative of a reversible, one-electron process (theoretical separation 57 mV). This fact argues strongly that the coordination shell of the one-electron-reduced species maintains its integrity and does not undergo rapid aquation. However, at a slower scan rate (0.1 V/sec between 0.0 and –0.45 V *vs.* sce), the intensity of the anodic wave was diminished and broadened showing that the stability of the one-electron reduction product, designated as Ru(NH$_3$)$_5$NO^{2+}, perhaps toward aquation, is limited.

From the average of the anodic and cathodic peak potentials at the fast scan rates, an estimate of the standard reduction potential of Ru(NH$_3$)$_5$NO^{3+} can be made: $E°$ = –0.12 V at 23°. In comparison, $E°$ for Ru(NH$_3$)$_6$$^{3+}$ is +0.05 V.[11] It is interesting to note that despite the fact that Ru(NH$_3$)$_5$NO^{3+} contains a reducible ligand, this complex is harder to reduce than is Ru(NH$_3$)$_6$$^{3+}$.

The electrochemical results indicate that Ru(NH$_3$)$_5$NO^{3+} can be reduced in a one-electron step and that the product is moderately stable. By using the pulse radiolysis technique, specific reducing radicals can be generated in the submicrosecond time range from aqueous solutions containing se-