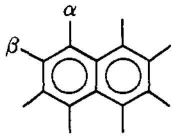
Several attempts have been made to fit the hyperfine coupling constants of alkali metal–organic radical anion systems by varying structural parameters of the metal complex.[12,19] The results obtained by Pedersen and Griffin[12] are given in Table VI along with observed values reported by Hirota.[11] The striking point is the greatly improved fit obtained for the hyperfine coupling constant of the β proton using the nonplanar structure of the carbanion as found in the structure of [LiTMEDA]$_2$ naphthalene. Ring carbon bond lengths are not nearly as important as evidenced by the results in column 1 which are very similar to those obtained by Pedersen and Griffin for the naphthalene (O) geometry. It is interesting that including the lithium atom in the position observed in the crystal structure algebraically increases the magnitudes of the hyperfine coupling constants of the α and β protons in the direction suggested by the observed data. The implications of the above to reported esr data for other radical anions are being investigated. It is also reassuring that structural data obtained in the solid state give reasonable results when applied to the interpretation of solution spectra. The bond lengths in the radical anion of naphthalene are probably intermediate between those of the naphthalene dianion and the naphthalene molecule. The angular distortion of the ring from planarity may, however, be similar in the radical and dianion since angular deformations are of lower energy. An additional complication should be mentioned here, namely, that the angular deformation of the carbanion in the contact ion pair may not be the same as in the solvent separated ion pair.

Table VI



	INDO hyperfine coupling constants				
	Calcd				
	Free anion		Complex		Obsd[a]
	b	c	c	d	
Li			0.19	0.22	0.1–0.4
α	−5.3	−5.8	−5.5	−5.3	(−)4.9
β	−0.88	1.60	1.72	−0.86	1.83

[a] N. Hirota, *J. Amer. Chem. Soc.*, **90**, 3603 (1968). [b] Assuming planar D_{2h} symmetry, with bond lengths as determined in the crystal structure of [LiTMEDA]$_2$ naphthalene and C–H distances of 1.08 Å. [c] Naphthalene geometry as observed in the crystal structure of [LiTMEDA]$_2$ naphthalene and C–H distances of 1.08 Å. [d] L. Pedersen and R. G. Griffin, *Chem. Phys. Lett.*, **5**, 373 (1970).

A calculation was carried out on the puckered naphthalene monoanion which suggests that the ^{13}C hyperfine coupling constants are much more sensitive to the position of the Li atom than the hydrogen atom hyperfine coupling constants. In the naphthalene monoanion, a coupling constant of 4.3 G was calculated for RC(5) and RC(5)′ while in the metal complex, $C_{10}H_8Li(NH_3)_2$, the corresponding hyperfine coupling constant is 0.26 G. It would appear that ^{13}C nmr and esr investigations may be a useful method of excluding certain structural possibilities in solution.

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Heat of Binding of Dinitrogen and Related Ligands to $[Ru(NH_3)_5H_2O]^{2+}$

G. D. Watt

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Abstract: The ΔH values for the reaction of $[Ru(NH_3)_5H_2O]^{2+}$ and $[Ru(NH_3)_5H_2O]^{3+}$ with ligands ranging from σ donors to π acceptors were measured by calorimetric techniques. The $[Ru(NH_3)_5H_2O]^{3+}$ ion binds more strongly to σ donor ligands while $[Ru(NH_3)_5H_2O]^{2+}$ forms more stable complexes with π-acceptor ligands. The replacement of one NH_3 by H_2O on each of the Ru atoms in $[Ru(NH_3)_5]_2N_2^{4+}$ decreases the ΔH of binding of the N_2 molecule by 6 kcal/mol. The reaction of $[Ru(NH_3)_5CO]^{2+}$ with a tenfold excess of Ce(IV) results in the oxidation of the bound CO to CO_2.

The $[Ru(NH_3)_5H_2O]^{2+}$ ion can coordinate a wide variety of ligands in place of the H_2O molecule. Stable and well-defined complexes range from ligands which are completely σ-donating (NH_3) to those ligands which are considered as weakly σ-donating and very likely strongly π-accepting (N_2, CO, etc.). The latter complexes have been studied recently[1] and, based primarily on the interpretation of infrared spectral data, the bonding to the unique ligand is thought to be best described as metal to ligand π-bonding, with perhaps a small degree of σ-bonding.

Although this explanation is reasonable, it appeared desirable to test these conclusions using an independent approach in which some property related to metal–ligand bonding is measured as the ligand char-

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acter is varied. The ΔH for the replacement of the H_2O molecule in $[Ru(NH_3)_5H_2O]^{2+}$ by various ligands is useful because bonding differences resulting from varying the ligand character is directly reflected in the ΔH for the ligand replacement reaction.

In this study are reported ΔH values for the binding of ligands, with varying donor acceptor properties, to $[Ru(NH_3)_5H_2O]^{2+}$ and, in some cases, $[Ru(NH_3)_5H_2O]^{3+}$. While these measurements were in progress, ΔH values of -25 ± 2 and -24.4 ± 2 kcal/mol were reported[2,3] for eq 1, and ΔH values of -13.2 and -9.1

$$2[\mathrm{Ru(NH_3)_5H_2O}]^{2+} + \mathrm{N_2(g)} = [\mathrm{Ru(NH_3)_5}]_2\mathrm{N_2}^{4+} + 2\mathrm{H_2O} \quad (1)$$

kcal/mol were reported[3] for eq 2, with L = N_2 and

$$[\mathrm{Ru(NH_3)_5H_2O}]^{2+} + \mathrm{L(g)} = [\mathrm{Ru(NH_3)_5L}]^{2+} + \mathrm{H_2O} \quad (2)$$

N_2O, respectively.

Experimental Section

Instruments. A Beckman 190-C flow-microcalorimeter of the type previously described[4] was used. The fluid delivery system was modified by using 2.5-ml Hamilton gas flush syringes to allow for evacuation and flushing of the entire calorimeter with oxygen-free gases prior to introducing air-sensitive compounds. Visible-uv and ir spectra were recorded on Cary 14 and Beckman IR-20A spectrophotometers, respectively. Gas evolution was measured manometrically and the gases were identified with a Finnigan 1015 mass spectrometer.

Materials and Solutions. $[Ru(NH_3)_5Cl]Cl_2$ was prepared by refluxing $[Ru(NH_3)_6]Cl_3$ (Matthey-Bishop, Malvern, Pa.) in 10 *M* HCl followed by recrystallization from dilute HCl. The *cis*-$[Ru(NH_3)_4OHCl]Cl$ was supplied by Alfa Inorganics (Beverly, Mass.). The CH_3NC was synthesized in this laboratory by published methods.[5] All other reagents were used as received from commercial sources.

Solutions of $[Ru(NH_3)_5H_2O]^{2+}$ and *cis*-$[Ru(NH_3)_4(H_2O)_2]^{2+}$ used both for synthesis and the calorimetric reactions discussed below were prepared from $[Ru(NH_3)_5Cl]Cl_2$ and *cis*-$[Ru(NH_3)_4OHCl]Cl$ either by (a) controlled-potential electrolysis at pH 6 or (b) Zn amalgam reduction in 0.05 *M* H_2SO_4. In method b, Zn^{2+} and excess H^+ were removed to prevent reaction with excess ligand during the calorimetric measurements by adjusting the pH of the solutions to 9–10 with NaOH, followed by filtration to remove the zinc hydroxide precipitate and readjustment of the pH to 6 with 1 *M* H_2SO_4.

Solutions of $[Ru(NH_3)_5X]^{2+}$ (X = NH_3,N_2,CH_3CN, pyridine, CO), $[Ru(NH_3)_5]_2N_2^{4+}$, and *cis*- $[Ru(NH_3)_4H_2O]_2N_2^{4+}$ were prepared and characterized by published procedures.[6-11] Solutions of $[Ru(NH_3)_5CH_3NC]^{2+}$ were prepared by the procedure[9] used in making $[Ru(NH_3)_5CH_3CN]^{2+}$ but using CH_3NC in place of CH_3CN.

Direct Calorimetric Measurements. The heat of reaction of a 0.01 *M* solution of $[Ru(NH_3)_5H_2O]^{2+}$ with aqueous (~0.1 *M*) NH_3, pyridine, CH_3CN, CH_3NC, and $[Ru(NH_3)_5N_2]^{2+}$ to form the respective 1:1 adducts was determined directly in the microcalorimeter. The excess ligand not only ensured complete conversion to the desired products but also increased the rate of reaction, making the calorimetric measurements more precise.

Heat of dilution corrections were made by mixing the $[Ru(NH_3)_5H_2O]^{2+}$ solution with argon-saturated water and the ligand solutions with either H_2O or 0.05 *M* H_2SO_4 solutions adjusted to pH 6.0. The heat of dilution of $[Ru(NH_3)_5H_2O]^{2+}$ and $[Ru(NH_3)_5N_2]^{2+}$ was endothermic and represented about 1% of the total heat while that for the other solutions was negligible.

Indirect Calorimetric Measurements. Solutions 0.01 *M* in $[Ru(NH_3)_5H_2O]^{2+}$, $[Ru(NH_3)_5N_2]^{2+}$, $[Ru(NH_3)_5]_2N_2^{4+}$, $[Ru(NH_3)_4(H_2O)_2]^{2+}$, or $[Ru(NH_3)_4H_2O]_2N_2^{4+}$ were oxidized in the microcalorimeter with a standard 0.01 *M* Ce(IV) solution. The Ce(IV) solution was just limiting in all cases so that the ΔH could be calculated on the amount of Ce(IV) reduced. When the gas adduct compounds were oxidized, the solutions were saturated with N_2 so that liberated gas could be referred thermodynamically to the gaseous state. A small endothermic correction of 1–2% of the total heat resulting from water evaporation into the liberated gas was applied. In the case of $[Ru(NH_3)_5N_2^{4+}$, the $[Ru(NH_3)_5]_2N_2^{4+}$/Ce(IV) ratio was varied from 0.5 to 50 so that at low ratios the oxidation produced $2[Ru(NH_3)_5H_2O]^{3+}$ and $N_2(g)$ while at higher ratios the oxidation selectively formed $[Ru(NH_3)N_2]^{2+}$ and $[Ru(NH_3)_5H_2O]^{3+}$.

In the preparation of both $[Ru(NH_3)_5N_2]^{2+}$ and $[Ru(NH_3)_5]_2N_2^{4+}$ 5–10% contamination by the other complex was routinely observed from quantitative measurements at 221 and 262 nm.[6] Small corrections to the measured ΔH values were made for this contamination by means of an iterative cycle assuming initially that the ΔH of oxidation of $[Ru(NH_3)_5]_2N_2^{4+}$ was correct. The $[Ru(NH_3)_4H_2O]_2N_2^{4+}$ solutions were found[11] to be essentially free of contaminating $[Ru(NH_3)_4H_2O]N_2^{2+}$.

Although $[Ru(NH_3)_5HSO_4]^{2+}$ was the observed species[11,12] (λ 308 nm) after oxidation of the ruthenium(II) compounds and not $[Ru(NH_3)_5H_2O]^{3+}$, all data are referred to the latter species using a ΔH value of -0.8 kcal/mol for the reaction $[Ru(NH_3)_5HSO_4]^{2+} + H_2O = Ru(NH_3)_5H_2O^{3+} + HSO_4^-$ as discussed later.

From the above Ce(IV) oxidation reactions, thermochemical cycles can be devised to give ΔH values for the reactions which form the various nitrogen adduct complexes. This procedure is outlined for the reaction forming $[Ru(NH_3)_5N_2]^{2+}$ (eq 3-5).

$$[\mathrm{Ru(NH_3)_5H_2O}]^{2+} + \mathrm{Ce(IV)} = [\mathrm{Ru(NH_3)_5H_2O}]^{3+} + \mathrm{Ce(III)} \quad \Delta H_3 \quad (3)$$

$$[\mathrm{Ru(NH_3)_5H_2O}]^{3+} + \mathrm{N_2(g)} + \mathrm{Ce(III)} = [\mathrm{Ru(NH_3)_5N_2}]^{2+} + \mathrm{Ce(IV)} \quad \Delta H_4 \quad (4)$$

$$[\mathrm{Ru(NH_3)_5H_2O}]^{2+} + \mathrm{N_2(g)} = [\mathrm{Ru(NH_3)_5N_2}]^{2+} \quad (5)$$

$$\Delta H_5 = \Delta H_3 + \Delta H_4$$

Attempts to determine ΔH for the formation of $[Ru(NH_3)_5CO]^{2+}$ using an approach similar to that previously outlined for $[Ru(NH_3)_5N_2]^{2+}$ resulted in the unexpected utilization of $3Ce(IV)/Ru(NH_3)_5CO]^{2+}$ and the production of CO_2. The presence and amount of CO_2 was measured by mass spectrometry, quantitative gas evolution, and also by the decrease in titer of a $Ba(OH)_2$ solution and the formation of $BaCO_3$. The $Ce(IV)/[Ru(NH_3)_5CO]^{2+}$ was determined by reacting a known amount of $[Ru(NH_3)_5CO]^{2+}$ with a tenfold excess of Ce(IV) and then determining the excess Ce(IV). These observations and measurements lead to the conclusion that reaction 6 describes the reaction occurring when $[Ru(NH_3)_5CO]^{2+}$ reacts with a tenfold excess of Ce(IV).

It should be emphasized that the above reactions involving $[Ru(NH_3)_5CO]^{2+}$, including the calorimetry, were run with a tenfold excess of Ce(IV) because at lower ratios (1:1 to 3:1) there occurs a dark brown intermediate which as yet remains uncharacterized.

The ΔH value for the formation of $[Ru(NH_3)_5CO]^{2+}$ from $[Ru(NH_3)_5H_2O]^{2+}$ and CO(g) was determined by the thermochemical cycle of eq 6–10.

$$[\mathrm{Ru(NH_3)_5CO}]^{2+} + \mathrm{H_2O} + 3\mathrm{Ce(IV)} = [\mathrm{Ru(NH_3)_5H_2O}]^{3+} + 3\mathrm{Ce(III)} + \mathrm{CO_2(g)} + 2\mathrm{H^+} \quad \Delta H_6 \quad (6)$$

$$[\mathrm{Ru(NH_3)_5H_2O}]^{3+} + \mathrm{Ce(III)} = [\mathrm{Ru(NH_3)_5H_2O}]^{2+} + \mathrm{Ce(IV)} \quad \Delta H_7 \quad (7)$$

$$\mathrm{CO_2(g)} + 2\mathrm{H^+} = \mathrm{H_2O} + \mathrm{CO(g)} \quad \Delta H_8 \quad (8)$$

$$2\mathrm{Ce(III)} = 2\mathrm{Ce(IV)} \quad \Delta H_9 \quad (9)$$

$$[\mathrm{Ru(NH_3)_5CO}]^{2+} = [\mathrm{Ru(NH_3)_5H_2O}]^{2+} + \mathrm{CO(g)} \quad (10)$$

$$\Delta H_{10} = \Sigma \Delta H_{6-9}$$

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Table I. Observed Enthalpy Changes

Calorimetric reaction	ΔH, kcal/mol	Designation
$[Ru(NH_3)_5H_2O]^{2+} + Ce(IV) = [Ru(NH_3)_5H_2O]^{3+} + Ce(III)$	-29.7 ± 0.5	a
$[Ru(NH_3)_4(H_2O)_2]^{2+} + Ce(IV) = [Ru(NH_3)_4(H_2O)_2]^{3+} + Ce(III)$	-24.4 ± 0.5	b
$[Ru(NH_3)_5NH_3]^{2+} + Ce(IV) = [Ru(NH_3)_5NH_3]^{3+} + Ce(III)$	-33.1 ± 0.4	c
$[Ru(NH_3)_5CH_3CN]^{2+} + Ce(IV) = [Ru(NH_3)_5CH_3CN]^{3+} + Ce(III)$	-17.9 ± 0.4	d
$[Ru(NH_3)_5CH_3NC]^{2+} + Ce(IV) = [Ru(NH_3)_5CH_3NC]^{3+} + Ce(III)$	-13.5 ± 0.5	e
$[Ru(NH_3)_5N_2]^{2+} + Ce(IV) = [Ru(NH_3)_5H_2O]^{3+} + N_2(g) + Ce(III)$	-11.4 ± 0.4	f
$\{[Ru(NH_3)_5]_2N_2\}^{4+} + 2Ce(IV) = 2[Ru(NH_3)_5H_2O]^{3+} + N_2(g) + 2Ce(III)$	-33.8 ± 0.4	g
$\{[Ru(NH_3)_4H_2O)_2]N_2\}^{4+} + 2Ce(IV) = 2[Ru(NH_3)_4(H_2O)_2]^{2+} + N_2(g) + 2Ce(III)$	-29.4 ± 0.5	h
$[Ru(NH_3)_5H_2O]^{2+} + CH_3NC = [Ru(NH_3)_5CH_3NC]^{2+} + H_2O$	-17.5 ± 0.9	i
$[Ru(NH_3)_5H_2O]^{2+} + CH_3CN = [Ru(NH_3)_5CH_3CN]^{2+} + H_2O$	-4.8 ± 0.5	j
$[Ru(NH_3)_5H_2O]^{2+} + NH_3 = [Ru(NH_3)_5NH_3]^{2+} + H_2O$	-1.21 ± 0.11	k
$[Ru(NH_3)_5H_2O]^{2+} + Py = [Ru(NH_3)_5Py]^{2+} + H_2O$	-3.86 ± 0.40	l
$[Ru(NH_3)_5H_2O]^{2+} + [Ru(NH_3)_5N_2]^{2+} = [Ru(NH_3)_5]_2N_2{}^{4+} + H_2O$	-6.7 ± 0.7	m
$\{[[Ru(NH_3)_5]_2N_2\}^{4+} + Ce(IV) = [Ru(NH_3)_5N_2]^{2+} + [Ru(NH_3)_5H_2O]^{3+} + Ce(III)$	-24.0 ± 1.0	n
$[Ru(NH_3)_5CO]^{2+} + 3Ce(IV) + H_2O = [Ru(NH_3)_5H_2O]^{3+} + 3Ce(III) + CO_2(g) + 2H^+$	-84.5 ± 0.5	o
$Fe(CN)_6{}^{4-} + Ce(IV) = Fe(CN)_6{}^{3-} + Ce(III)$	-18.3 ± 0.3	p
$CO_2(g) + 2H^+ = H_2O + CO(g)$	$+0.70$ (ref 16)	q
$2Ce(IV) = 2Ce(III)$	-90.2 ± 0.6	r

The ΔH value for reaction 9 was obtained by measuring ΔH for reaction 11 and combining it with the known[13] ΔH value of -26.7

$$Ce(IV) + Fe(CN)_6{}^{4-} = Ce(III) + Fe(CN)_6{}^{3-} \qquad \Delta H_{11} \quad (11)$$

$$Fe(CN)_6{}^{3-} + {}^1/_2H_2 = Fe(CN)_6{}^{4-} + H^+ \qquad \Delta H_{12} = -26.7 \quad (12)$$

$$Ce(IV) + {}^1/_2H_2 = Ce(III) + H^+ \qquad \Delta H_{13} = \Delta H_{11} - 26.7 \quad (13)$$

for reaction 12. By definition the $\Delta H°$ for ${}^1/_2H_2 = H^+ + e$ is zero, giving a $\Delta H_{13} = \Delta H_{11} - 26.7$ for the reaction, $Ce(IV) = Ce(III)$.

Heat of dilution corrections for the above Ce(IV) oxidation reactions were measured separately by mixing the Ce(IV) solutions with 0.05 M H_2SO_4 and by mixing the appropriate solutions containing the ruthenium complexes with a solution free of Ce(IV) but otherwise identical with the solutions used in oxidation. The heat of dilution of the Ce(IV) solution was exothermic and represented 6% of the total measured heat while that for the ruthenium complexes was endothermic and represented 1-2% of the total heat.

After oxidation by Ce(IV) in the presence of sulfate, the ruthenium-containing species was found to be $[Ru(NH_3)_5HSO_4]^{2+}$ by its absorbance[11,12] at 308 nm. In order to avoid referring the thermal data to this species, the ΔH for the replacement of $HSO_4{}^-$ by H_2O was determined by utilizing $[Ru(NH_3)_5H_2O]^{2+}$-catalyzed substitution reactions[14] of pentaammineruthenium(III) complexes. Solutions of $[Ru(NH_3)_5Cl]^{2+}$ in water were treated with $[Ru(NH_3)_5H_2O]^{2+}$ solutions in water or in 0.10 M Na_2SO_4 (pH 6.0) resulting in the substitution of H_2O and $HSO_4{}^-$, respectively, for the Cl^-. From the respective ΔH values of -1.8 and -1.0 for these two reactions was derived the ΔH of -0.8 kcal/mol for the substitution of $HSO_4{}^-$ by H_2O.

Using other thermochemical cycles, ΔH values were determined for the replacement of H_2O in $[Ru(NH_3)_5H_2O]^{3+}$ by NH_3, CH_3CN, and CH_3NC. This procedure is outlined for the replacement of H_2O by CH_3CN.

$$[Ru(NH_3)_5H_2O]^{2+} + CH_3CN(g) = [Ru(NH_3)_5CH_3CN]^{2+} + H_2O \qquad \Delta H_{14} \quad (14)$$

$$[Ru(NH_3)_5CH_3CN]^{2+} + Ce(IV) = [Ru(NH_3)_5CH_3CN]^{3+} + Ce(III) \qquad \Delta H_{15} \quad (15)$$

$$[Ru(NH_3)_5H_2O]^{3+} + Ce(III) = [Ru(NH_3)_5H_2O]^{2+} + Ce(IV) \qquad \Delta H_{16} \quad (16)$$

$$[Ru(NH_3)_5H_2O]^{3+} + CH_3CN(g) = [Ru(NH_3)_5CH_3CN]^{3+} \qquad \Delta H_{17} = \Sigma\Delta H_{14-16} \quad (17)$$

To obtain reliable ΔH values using Hess' law sums, it is an absolute requirement that each species type in every reaction of a thermochemical cycle be referred to the same thermodynamic state. If this condition is met, then thermal effects due to species on different sides of equations will cancel. In the calorimetric reactions reported in this study great care was taken to fully characterize the conditions and solutions both before and after reaction in the calorimeter so that measured heats were unequivocally assigned to specific reactions and also so that thermodynamic states were clearly established.

Results and Discussion

Table I contains the observed ΔH values for the various reactions discussed above. Derived ΔH values using the data in Table I together with the methods of derivation are given in Table II. Where possible, the data in Table II are referred to reactions in which the ligands are in the gaseous state by using available heat of vaporization data.[15,16] This simplifies the comparison of ΔH values of ligand binding to $[Ru(NH_3)_5H_2O]^{2+}$ by eliminating the heats of solution of the various and diverse types of ligands.

There are several internal checks on the data reported here. For example, reaction 13 in Table II gives a derived ΔH value of -7.3 ± 1.3 kcal/mol for the formation of $[Ru(NH_3)_5]_2N_2{}^{4+}$ from $[Ru(NH_3)_5H_2O]^{2+}$ and $[Ru(NH_3)_5N_2]^{2+}$ in agreement with the value of -6.7 ± 0.7 kcal/mol (reaction m in Table I) measured directly. Also, selective oxidation of $[Ru(NH_3)_5]_2N_2{}^{4+}$ with Ce(IV) to form $[Ru(NH_3)_5N_2]^{2+}$ and $[Ru(NH_3)_5H_2O]^{3+}$ gives a ΔH value of -24.0 ± 1.0 kcal/mol (reaction n in Table I) in agreement with a value of -22.4 ± 0.8 kcal/mol for reaction 14 in Table II.

The ΔH values of -25 ± 2 and -24.4 ± 2 kcal/mol reported previously[2,3] for reaction 1 are in good agreement with the value of -25.6 ± 1.5 kcal/mol measured in this study. However, the ΔH values of -18.3 ± 0.9 and -6.7 ± 0.7 kcal/mol for reaction 1 in Table II and reaction m in Table I, respectively, are in poor agreement with the values of -13.2 ± 1.4 and -11.2 ± 1.4 kcal/mol reported by Armor and Taube[3] for these same reactions. Since the ΔH values reported in this study were obtained by two independent methods, it seems that the method of plotting log K against $1/T$ used by Armor and Taube[3] to calculate ΔH

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Table II. Derived Enthalpy Changes

	Reaction	How derived[a]	ΔH, kcal/mol
1.	$[Ru(NH_3)_5H_2O]^{2+} + N_2(g) = [Ru(NH_3)_5N_2]^{2+} + H_2O$	a − f	−18.3 ± 0.9
2.	$2[Ru(NH_3)_5H_2O]^{2+} + N_2(g) = \{[Ru(NH_3)_5]_2N_2\}^{4+} + 2H_2O$	2a − g	−25.6 ± 1.5
3.	$2[Ru(NH_3)_4(H_2O)_2]^{2+} + N_2(g) = \{[Ru(NH_3)_4H_2O)_2]_2N_2\}^{4+} + 2H_2O$	2b − h	−19.4 ± 1.5
4.	$[Ru(NH_3)_5H_2O]^{2+} + Py(g) = [Ru(NH_3)_5Py]^{2+} + H_2O$	1 − 6.36	−10.2 ± 0.4
5.	$[Ru(NH_3)_5H_2O]^{2+} + NH_3(g) = [Ru(NH_3)_5NH_3]^{2+} + H_2O$	k − 8.28	−9.49 ± 0.11
6.	$[Ru(NH_3)_5H_2O]^{3+} + NH_3(g) = [Ru(NH_3)_5NH_3]^{3+} + H_2O$	k + c − a − 8.30	−12.9 ± 1.0
7.	$[Ru(NH_3)_5H_2O]^{2+} + CH_3CN(g) = [Ru(NH_3)_5CH_3CN]^{2+} + H_2O$	j − 8.80	−13.6 ± 0.5
8.	$[Ru(NH_3)_5H_2O]^{3+} + CH_3CN(g) = [Ru(NH_3)_5CH_3CN]^{3+} + H_2O$	j + d − a − 8.80	−2.8 ± 1.4
9.	$[Ru(NH_3)_5H_2O]^{2+} + CH_3NC(g) = [Ru(NH_3)_5CH_3NC]^{2+} + H_2O$	i − 8.30	−25.8 ± 0.9
10.	$[Ru[NH_3]_5H_2O]^{3+} + CH_3NC(g) = [Ru(NH_3)_5CH_3NC]^{3+} + H_2O$	i + e − a − 8.30	−9.6 ± 1.9
11.	$[Ru(NH_3)_5H_2O]^{2+} + CO(g) = [Ru(NH_3)_5CO]^{2+} + H_2O$	a − o − q + r	−36.1 ± 1.6
12.	$[Ru(NH_3)_5H_2O]^{2+} + N_2O(g) = [Ru(NH_3)_5N_2O]^{2+} + H_2O$	Ref 3	−9.1
13.	$[Ru(NH_3)_5H_2O]^{2+} + [Ru(NH_3)_5N_2]^{2+} = \{[Ru(NH_3)_5]_2N_2\}^{4+} + H_2O$	a + f − g	−7.3 ± 1.3
14.	$\{[Ru(NH_3)_5]_2N_2\}^{4+} + Ce(IV) = [Ru(NH_3)_5N_2]^{2+} + [Ru(NH_3)_5H_2O]^{3+} + Ce(III)$	g − f	−22.4 ± 0.8

[a] The numerical values are sums of the enthalpy of solution and the enthalpy of vaporization of the ligands taken from ref 15 and 16.

is subject to large uncertainty. The calorimetric ΔH data show conclusively that the bound N_2 in $[Ru(NH_3)_5N_2]^{2+}$ is a poorer ligand toward $[Ru(NH_3)_5H_2O]^{2+}$ than is the free N_2 molecule.

Several features of interest are seen in the data of Table II. The $[Ru(NH_3)_5H_2O]^{2+}$ ion has an affinity (ΔH is negative) for both σ-donor and π-acceptor ligands but prefers the latter. This preference is seen as an increase in $-\Delta H$ as the π-accepting ability of the ligands increases. A similar trend is also seen in the ir spectra[1,17] of these triple bonded adducts where the change in stretching frequency ($\Delta\nu = \nu_{\text{free}} - \nu_{\text{bound}}$) of the triple bond increases as the π-accepting ability of the ligand increases. Attempts have been made to correlate the measured ΔH with known $\Delta\nu$ values, but no simple relationship exists. This lack of correlation is not surprising because populating the π-accepting orbitals of these various ligands with electrons from $[Ru(NH_3)_5]^{2+}$ will destabilize the triple bond to varying degrees due to the varying contributions[18,19] of the atomic orbitals comprising the triple bond molecular orbitals. It is likely that a better correlation would result from the ΔH values and the metal–ligand stretching frequency, but at this time too few unambiguous metal–ligand stretching frequencies have been reported to permit an analysis.

A comparison of ΔH values for adducts of the same ligand in both the +2 and +3 oxidation states of ruthenium gives some insight into the bonding in these compounds. For example, in the formation of the ammonia adducts from $[Ru(NH_3)_5H_2O]^{2+}$ and $[Ru(NH_3)_5H_2O]^{3+}$, $-\Delta H$ is larger for the +3 state than for the +2 state. Since ammonia only has the capability of σ donation, the greater charge of the +3 complex has a greater affinity for the electron pair than does the +2 state resulting in a larger $-\Delta H$. On the other hand, both CH_3CN and CH_3NC favor $[Ru(NH_3)_5]^{2+}$ and form less stable adducts with $[Ru(NH_3)_5]^{3+}$. This contrast in behavior of these two ligand types toward the +2 and +3 states of ruthenium is consistent with the explanation[1] that $[Ru(NH_3)_5]^{2+}$ is able to donate electrons to a suitable π acceptor, whereas when oxidation to $[Ru(NH_3)_5]^{3+}$ occurs the π-donating ability of ruthenium is drastically reduced. The stability of $[Ru(NH_3)_5CH_3CN]^{3+}$ and $[Ru(NH_3)_5CH_3NC]^{3+}$ is probably due to the residual σ-donating ability of these ligands. This loss of π-donating ability of the +3 state is also evident in the N_2 adducts where σ donation by the N_2 and π donation by $[Ru(NH_3)_5]^{3+}$ are both so low that there is in effect no metal–ligand bonding and the N_2 is released.

A decrease of 6 kcal/mol in the ΔH of binding of N_2 to $2[Ru(NH_3)_4(H_2O)_2]^{2+}$ compared with that for $2[Ru(NH_3)_5H_2O]^{2+}$ to form the respective binuclear ions shows that the strength of binding of the N_2 molecule is dependent on the ammonia ligands and decreases by about 3 kcal per NH_3 replaced. A value of 3–4 kcal per NH_3 replaced is also found when the ΔH values for Ce(IV) oxidation of $[Ru(NH_3)_6]^{2+}$, $[Ru(NH_3)_5H_2O]^{2+}$, and $[Ru(NH_3)_4(H_2O)_2]^{2+}$ are compared. These comparisons show an almost 1:1 relationship between the ease of removal of electrons from the ruthenium atom in these complexes and the stability of the corresponding nitrogen-bridged dimers and indicate that an increase in electron density at the ruthenium atom, provided by the better σ-donating NH_3 molecules, can be passed on directly to a suitable acceptor molecule.

The presently accepted mode of bonding[1] in $[Ru(NH_3)_5N_2]^{2+}$ and $[Ru(NH_3)_5CO]^{2+}$, for example, involves charge transfer from the filled t_{2g} orbitals on ruthenium to the $1\pi_g$ and 2π orbitals on N_2 and CO, respectively. Since $[Ru(NH_3)_5]^{2+}$ is common to both $[Ru(NH_3)_5N_2]^{2+}$ and $[Ru(NH_3)_5CO]^{2+}$, the difference in ΔH ($\Delta H[Ru(NH_3)_5CO]^{2+} - \Delta H[Ru(NH_3)_5N_2]^{2+}$) for the formation of these complexes must reflect the difference in electronic properties of CO and N_2. The difference in the measured ΔH values of -19.5 ± 2.5 kcal/mol compares well with a value[20] of −23 kcal/mol relating the energy separation of the $1\pi_g$ orbital on N_2 and the 2π orbital on CO. The calorimetry thus supports the explanation that the antibonding orbitals on N_2 and CO are involved in bonding to $[Ru(NH_3)_5]^{2+}$ and indicates that only a very small amount of σ-bonding is possible.

In aqueous solution or even in solutions of excess Ce(IV), free CO shows no indication of reaction, even though the following reactions indicate clearly the thermodynamic tendency of CO to be oxidized.[16] However, when bound in $[Ru(NH_3)_5CO]^{2+}$, the CO is readily oxidized to CO_2 by excess Ce(IV). This oxidation of bound CO to CO_2 is quite novel when compared

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$$CO(g) + H_2O = CO_2(g) + 2H^+ \qquad \Delta G^\circ = -5.8 \text{ kcal/mol}$$

$$CO(g) + H_2O + 2Ce(IV) = CO_2(g) + 2Ce(III) + 2H^+ \qquad \Delta G^\circ = -40.3 \text{ kcal/mol}$$

to the oxidation of other pentaammineruthenium(II) adducts in which the metal becomes oxidized and the adduct ligands are either released or remain attached to the oxidized metal. The activation of CO toward oxidation must certainly be a result of its being bound to $[Ru(NH_3)_5]^{2+}$, although excess Ce(IV) might also play an important role since a dark brown, stable intermediate was formed when the Ce(IV)/$Ru(NH_3)_5$-$CO]^{2+}$ ratio was less than about 3. The details of this reaction are certainly of interest because understanding this reaction may lead to methods for activating related molecules, *e.g.*, N_2, toward oxidation.

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Facile Promotion of Oxidative Dehydrogenation by Iron Ions and the Synthesis of New Complexes of Iron with Highly Unsaturated Tetraaza Macrocycles

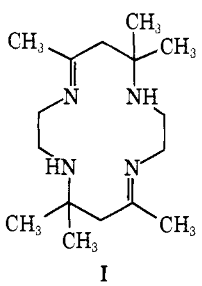
Virgil L. Goedken and Daryle H. Busch*

Contribution from the Evans Chemical Laboratory, The Ohio State University, Columbus, Ohio 43210. *Received January 18, 1972*

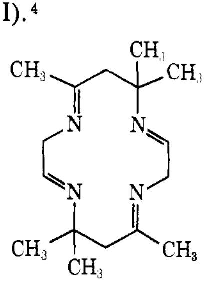
Abstract: We have discovered an extreme facility on the part of the ions of iron to promote the oxidative dehydrogenation of secondary amine groups bound to the iron as part of a macrocyclic ligand. The product complexes contain newly formed, coordinated azomethine functions. Atmospheric oxygen readily performs the oxidation under the influence of Fe(III), while stronger oxidizing agents are generally required in the case of nickel or copper complexes, and cobalt has failed to give the reaction. As a result of these and related studies, it is becoming possible to synthesize macrocyclic complexes having any desired degree of unsaturation. The reaction has been applied to synthesize important new macrocyclic complexes of iron, wherein the degree of unsaturation exceeds that previously built into such synthetic iron derivatives. Beginning with $Fe(Me_6[14]4,11\text{-dieneN}_4)(CH_3CN)_2{}^{2+}$ oxidative dehydrogenation produces a triimine complex $Fe(Me_6[14]1,4,11\text{-trieneN}_4)(CH_3CN)_2{}^{2+}$ and, under appropriate conditions, a tetraimine complex $Fe(Me_6[14]1,4,8,11\text{-tetraeneN}_4)(CH_3CN)_2{}^{2+}$. The presence of more double bonds in the ligand structure enhances the stability of iron(II). Several derivatives of the new complexes have been synthesized and all have been characterized by physical methods. In the presence of weak axial ligands, such as halide ions, only one of the axial sites is occupied and the resultant complexes are high spin, five coordinate with a square-pyramidal geometry. The ligand field strength is surprisingly low suggesting that the Fe^{2+} ion has been extruded from the plane of the four nitrogen donors. These complexes are stereochemical and electronic analogs of deoxyhemoglobin and deoxymyoglobin. Relatively strong axial ligands bind in pairs, producing low-spin, six-coordinate structures. The ligand field strength of the macrocycle in these complexes exceeds that of less highly unsaturated macrocyclic ligands of the same ring size, as expected. $Fe(Me_6[14]4,14\text{-dieneN}_4)(CH_3CN)_2{}^{2+}$ has also been oxidatively dehydrogenated to produce the complex of a tetraimine which contains a conjugated α-diimine linkage, $Fe(Me_4[14]1,3,7,11\text{-tetraeneN}_4)(CH_3CN)_2{}^{2+}$. The tetraimine, $Me_6[14]1,4,8,11\text{-tetraeneN}_4$, has been removed from the iron(II) complex, characterized in the free state (where it exists as a tautomer), and coordinated to cobalt(III). This shows how the facile promotion of oxidative dehydrogenation exhibited by iron can be used to obtain materials not available *via* other synthetic routes.

Under the proper conditions and in the presence of suitable reagents, complexes in which the metal has an unusual oxidation number, particularly the higher unstable states such as Ni(III),[1-3] can undergo intramolecular redox reactions which generate complexes with oxidized forms of the ligands.

The first example of this type of reaction involving a macrocyclic ligand was reported by Curtis who observed that the nickel(II) complex of 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene (abbreviated $[14]4,11\text{-dieneN}_4$ or more simply $[14]\text{dieneN}_4$) (I) reacts with concentrated nitric acid to yield a complex containing the new macrocyclic ligand, 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1,4,8,11-tetraene (abbreviated $[14]1,4,8,11\text{-tetraeneN}_4$ or $[14]\text{tetraeneN}_4$) (II).[4]



I



II

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