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# $\eta^2$-1,3-Dimethyluracil Complexes of Pentaammineruthenium(II) and Pentaammineosmium(II)

SONGSHENG ZHANG and REX E. SHEPHERD*

*Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260 (U.S.A.)*

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## Abstract

$M(NH_3)_5(DMU)^{2+}$ complexes with $M^{II} = Ru^{II}$ and $Os^{II}$, DMU = 1,3-dimethyluracil have been prepared via Zn/Hg reduction of $(NH_3)_5RuCl_3$ and $(NH_3)_5Os(tfms)_3$ and characterized via $^1H$ NMR, $^{13}C$ NMR, cyclic voltammetry and differential pulse polarography. The upfield shifts of the C-5 and C-6 protons (1.2–2.0 ppm) or carbons (52 to 79 ppm) are similar to the shifts observed for olefin coordination to $(NH_3)_5M^{2+}$, $M^{II} = Ru^{II}$ or $Os^{II}$. The $E_{1/2}$ values for the III/II reduction potentials ($Ru^{II}$ complex, 0.98 V; $Os^{II}$ complex, 0.77 V) also indicate an olefinic $\eta^2$-coordination at the C-5–C-6 bond of DMU. Metallation of this bond produces a disruption of the aromaticity of the pyrimidine ring. This induces a steric interaction between $M(NH_3)_5^{2+}$ and the methylated nitrogen positions which is most important at N-3. The steric effect reduces the affinity of DMU relative to uridine binding at C-5–C-6. The equilibrium constant for binding DMU is only *c.* 8 $M^{-1}$ for the $Ru^{II}$ complex and 23 $M^{-1}$ for the $Os^{II}$ complex such that both the free and bound forms of these complexes are readily detected by $^1H$ NMR, $^{13}C$ NMR and electrochemical methods. Labilization of *trans*-$NH_3$ in the $(NH_3)_5Ru(DMU)^{2+}$ complex catalyzes formation of $(NH_3)_4Ru(H_2O)_2^{2+}$ and $(NH_3)_4(H_2O)Ru(DMU)^{2+}$, yielding *c.* 30% of the tetraammine products in 20 h.

## Introduction

Pentaammineruthenium(II) and pentaammineosmium(II) possess strong affinities for $\pi$-acceptor ligands including pyridines, pyrimidines, pyrazines, CO, $N_2$ and olefins [1–10]. Recent studies have been carried out with linear olefins including 1,3-butadiene [11] and the vinylic donor of styrene [12]. Harman and Taube have reported a series of studies of the coordination of $M(NH_3)_5^{2+}$ ($M^{II}$ = $Os^{II}$ or $Ru^{II}$) with arene donors [13–16]. $Ru(NH_3)_5^{2+}$ or $Os(NH_3)_5^{2+}$ has been shown to disrupt the aromaticity in arenes such as benzene and naphthalene [15, 16]. The $(NH_3)_5OsL^{2+}$ complexes (L = an arene) are found coordinated in an $\eta^2$ manner, consistent with strong $\pi$-backbonding to an olefinic unit in the altered aromatic ring. The coordination of $M(NH_3)_5^{2+}$ ($M^{II} = Ru^{II}$ or $Os^{II}$) to the exo vinylic donor of styrene shows that disruption of the aromaticity generally occurs only in the absence of suitable sites for $M(NH_3)_5^{2+}$ in the same molecule. The $(NH_3)_5Ru^{2+/3+}$ and $(NH_3)_5Os^{2+/3+}$ moieties are also of interest as potential heavy metal labelling units for DNA or RNA or as possible antitumor agents. These metal centers have been shown in the laboratories of Taube [17, 18] and of Clarke [19–23] to bind the purine and pyrimidine bases used in DNA and RNA polymers. No mention of a $\pi$-type or olefin-like binding has been made in these careful studies [17–23] or elsewhere [24]. All of the previous $Ru(NH_3)_5^{2+/3+}$ complexes with purines or pyrimidines exhibit coordination via one of the ring N donors or an exocyclic amino functionality [23]. DNA itself is labelled almost entirely at the N-7 of guanine residues [23b, 24b].

Studies in progress in our laboratory using $Ru^{II}(hedta)(H_2O)^-$ as a labelling metal ion center have suggested that an isomer mixture for the coordination of cytidine (C) or uridine (U) is produced [25]. One of these species has properties of an olefin-bound form, presumably at the C-5–C-6 bonds of C and U. In order to reduce the isomer complexity and to establish unequivocally whether the pyrimidine bases which are used in DNA or RNA can bind metals via the C-5–C-6 bonds of U or C, we have examined the $M(NH_3)_5^{2+}$ complexes ($M^{II} = Os^{II}$ and $Ru^{II}$) with 1,3-dimethyluracil (DMU) where both the N-1 and N-3 ring locations are hindered by methylation.

*Author to whom correspondence should be addressed.

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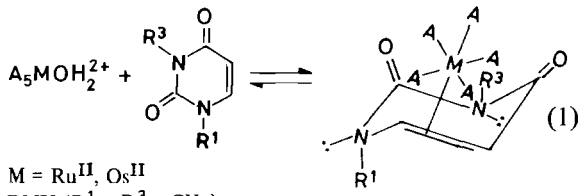
## Experimental

Solutions of $Ru(NH_3)_5(DMU)^{2+}$ and $Os(NH_3)_5(DMU)^{2+}$ were prepared by reduction of $[Ru(NH_3)_5Cl]Cl_2$ and $[Os(NH_3)_5(tfms)](tfms)_2$ over Zn/Hg under Ar in the presence of excess 1,3-dimethyluracil (DMU). DMU was obtained from Aldrich. The procedures are the same as those reported previously for linear olefin and styrene complexes from our laboratories [11, 12]. In a typical experiment 10 mg of the $Ru^{III}$ or $Os^{III}$ precursor were dissolved in 1.50 ml of $H_2O$ or $D_2O$ over Zn/Hg in a sealed 10 ml flask. Syringe methods were used to prevent air oxidation of the products. Ar was continuously passed while stirring was maintained by agitation due to the Ar flow or by magnetic stirring. The product solutions at *c.* 18 h were transferred to purged NMR tubes for $^1H$ NMR or $^{13}C$ NMR determinations. NMR spectra were obtained on Bruker AF300 or AF500 NMR spectrometers operating at magnetic fields of 70.46 and 117.44 kG, respectively. $^{13}C$ NMR spectra were obtained at a radio frequency of 125.767 MHz at the 117.44 kG field. $^{13}C$ spectra were decoupled using a 14H broadband decoupling power. All spectra were recorded in $D_2O$ as the solvent. HOD or a free ligand resonance served as an internal standard for the $^1H$ NMR spectra; dioxane was an internal standard for $^{13}C$ spectra. Electrochemical studies were performed on an IBM 225 electrochemical analyzer operating in the cyclic voltammetry (CV) mode at a sweep of 50 mV/s or for differential pulse polarograph (DPP) at 40 mV/s and a 50 mV stepping voltage. The working electrode was glassy carbon; the reference was a sodium chloride saturated calomel electrode (SSCE). Voltammograms were obtained in 0.10 M NaCl at 22 °C. The DMU complexes were not isolated as solids. Prior experience with the $Os(NH_3)_5(styrene)^{2+}$ complex, isolated as a $PF_6^-$ salt, has shown the $Os^{II}$ olefin complexes are not particularly stable as solids [12]. The $Ru(NH_3)_5(olefin)^{2+}$ complexes are also readily isolated as $PF_6^-$ salts as powders upon addition of $NH_4PF_6$ [11, 12]. However, crystalline products suitable for X-ray diffraction were not obtained. Recrystallization from polar solvents would surely lead to ligand dissociation since $K_f \cong 8\ M^{-1}$ (see the main text).

## Results and Discussion

We have observed that both the $Ru^{II}$ and $Os^{II}$ derivatives of U and DMU readily form when either $Ru(NH_3)_5Cl^{2+}$ or $Os(NH_3)_5(tfms)^{2+}$ are treated with DMU under Ar over Zn/Hg in water or $D_2O$ (eqn. (1))*.




(1)

M = $Ru^{II}$, $Os^{II}$
DMU ($R^1 = R^3 = CH_3$)
U ($R^1$ = deoxyribose, $R^3$ = H)

The formation constants at 25 °C based on $^1H$ NMR integration are only 8 $M^{-1}$** for $Ru(NH_3)_5^{2+}$ and 23 $M^{-1}$ for $Os(NH_3)_5^{2+}$ with DMU. The respective solutions were prepared under Ar over Zn/Hg. Under these conditions the initial $[(NH_3)_5Ru^{II}]_{tot}$ = 0.108 M and $[DMU]_{tot} = 8.90 \times 10^{-2}$ M. In the $Os^{II}$ case $[(NH_3)_5Os^{II}]_{tot} = 9.12 \times 10^{-2}$ M and $[DMU]_{tot} = 8.17 \times 10^{-2}$ M. The concentrations of free DMU ligand and the coordinated complexes were determined from the integration of the free ligand and coordinated DMU and $[DMU]_{tot}$. The amount of the free $(NH_3)_5MOH_2^{2+}$ species at equilibrium was calculated from $[(NH_3)_5M^{II}]_{tot}$ by difference with the concentration of the DMU complex. The solutions for NMR were transferred from Zn/Hg contact into carefully purged NMR tubes for immediate analysis. Absence of any electron-transfer catalyzed exchange of the $(NH_3)_5M(DMU)^{2+}$ species was indicated by the sharpness of the $^1H$ NMR resonance lines. Since neither $(NH_3)_5RuOH_2^{3+}$ or $(NH_3)_5OsOH_2^{3+}$ are sufficiently oxidizing to cause a rapid, catalytic oxidation of their respective $(NH_3)_5M(DMU)^{2+}$ species, the integration ratio of the free ligand and bound ligand represents its equilibrium value in the presence of Zn/Hg. Oxidation of $(NH_3)_5OsH_2O^{2+}$ by $H_2O$ represents the greatest potential problem. However, dissociation of the DMU from even the $Os^{III}$ complex is

*A kind referee has mentioned that space-filling models in his hands favored an alternative structure than the one implied in eqn. (1). We assume he means a structure with both $CH_3$ groups directed below the plane and the $(NH_3)_5M^{2+}$ moiety above in the sense depicted in the structured equation. The problem with this orientation is a strong interaction between the $CH_3$ units. This is avoided, together with a $CH_3 \cdots (NH_3)_5M^{2+}$ repulsion if one $CH_3$ group is below the plane and the other at N-3 is turned into an equatorial position. We cannot prove this structure from our data. However, recent work with the deoxyribose pyrimidine nucleosides blocked at N-3 by methylation reveal four isomers as detectable by $^1H$ and $^{13}C$ NMR. In these latter cases several permutations of the $R^1$ and $R^3$ moieties relative to the $(NH_3)_5M^{2+}$ site are possible. They are not all of equivalent intensity with two dominant structures. These results have been described in detail elsewhere [25].

**Amplitudes of differential pulse peaks at a $[Ru^{II}]$:[L] ratio of 24.4 give an estimated $K_f$ value of 7.4 $M^{-1}$ in agreement with the NMR data.

adventitiously slow as shown in electrochemical studies reported below. Dissociation from the $Os^{II}$ species is certain to be even slower due to the back-bonding from $Os^{II}$ to the olefinic bond. Thus, the $^1H$ NMR ratio will give the equivalent of a quenched kinetic ratio at the time of equilibration. The values reported here are perhaps more interesting in regard to the greater $K_f$ of $Ru^{II}(hedta)(DMU)^-$. The $Ru^{II}$-(hedta)$^-$ moiety exhibits a much higher affinity for the C-5–C-6 olefin bond of DMU ($K_f = 1.99 \pm 0.07 \times 10^3$ $M^{-1}$, $\mu = 0.10$, T = 25 °C) [25, 26]. Since the $M(NH_3)_5^{2+}$ unit is physically smaller than $Ru^{II}$-(hedta)$^-$, this suggests that electronic factors in forming the $Ru^{II}$–olefin or $Os^{II}$–olefin bond are more important than steric effects. However, the less hindered uridine ($R^3$ = H) is much more completely bound with $(NH_3)_5M^{2+}$ complexes. The amount of free ligand U at equilibrium in a (1:1) $M^{II}(NH_3)_5^{2+}$:L was too small for a reliable estimate of $K_f$. However, the presence of a steric effect provided by a methyl substituent at N-3 clearly implies a buckling of the DMU ring upon coordination of

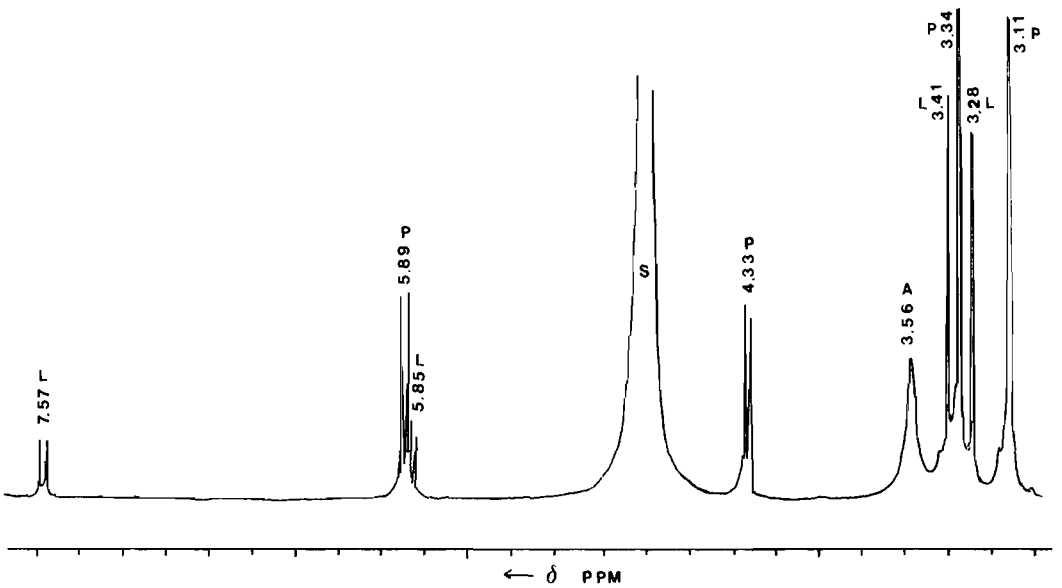



Fig. 1. 300 MHz $^1H$ NMR spectrum of $(ND_3)_5Os(DMU)^{2+}$. L = free ligand, DMU; P = $(ND_3)_5Os(DMU)^{2+}$. A = trace of unexchanged amine; S = HOD solvent resonance; shifts are assigned in Table 1.

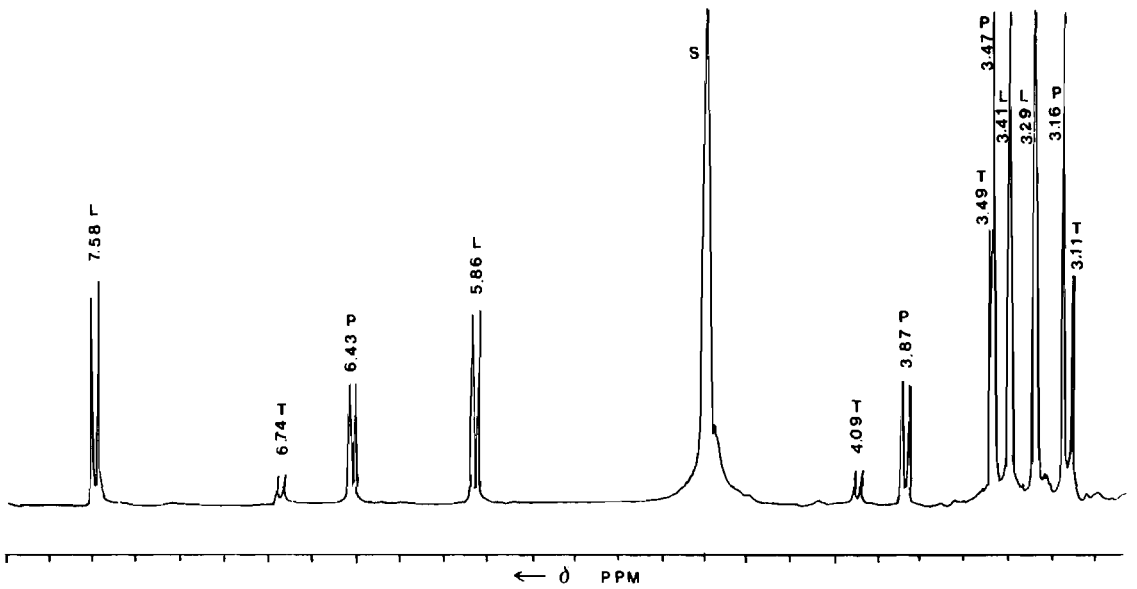



Fig. 2. 300 MHz $^1H$ NMR spectrum of $(ND_3)_5Ru(DMU)^{2+}$ and $(ND_3)_4(D_2O)Ru(DMU)^{2+}$. L = free ligand, DMU; P = $(ND_3)_5Ru$-$(DMU)^{2+}$; T = $(ND_3)_4(D_2O)Ru(DMU)^{2+}$; S = HOD solvent resonance; shifts are assigned in Table 1.

$M(NH_3)_5^{2+}$ at the C-5–C-6 bond, in concert with disruption of resonance in the parent planar ring structure. Evidence for coordination of $M(NH_3)_5^{2+}$ ($M^{II}$ = $Ru^{II}$ and $Os^{II}$) is readily obtained from the $^1H$ NMR spectra of the complexes. The $^1H$ NMR spectrum for the $(NH_3)_5Os(DMU)^{2+}$ complex is shown in Fig. 1. A lesser species with four ammonias and one water is also observed for the $Ru(NH_3)_5$-$(DMU)^{2+}$ system (Fig. 2). Presence of the tetra-ammine complex is confirmed electrochemically. Both the C-5H and C-6H positions are strongly shifted upfield from the free ligand values ($\Delta\delta$). The shifts for the dominant isomers of the complexes are as follows: $(Ru(NH_3)_5(DMU)^{2+}$: ($\delta$, $\Delta\delta$) C-5H 3.87, 1.98; C-6H 6.42, 1.16); $Os(NH_3)_5$-$(DMU)^{2+}$: C-5H 4.32, 1.53; C-6H 5.89, 1.69). These shifts are similar to the influence of these metal donors on the olefinic protons of ethylene or 1,3-butadiene [11, 12]. Complete chemical shift data for $^1H$ and $^{13}C$ NMR spectra are given in Tables 1 and 2. Furthermore, the cyclic voltammograms and differential pulse polarograms of the $M(NH_3)_5$-$(DMU)^{2+}$ species gives III/II $E_{1/2}$ reduction potentials of 0.98 V for the $Ru^{II}$ complex and 0.77 V for the $Os^{II}$ complex. These are above the $E_{1/2}$ values of the simple olefins such as ethylene (0.95 for $(NH_3)_5$-$Ru(C_2H_4)^{2+}$ and 0.40 V for $(NH_3)_5Os(C_2H_4)^{2+}$) [11–16], but characteristic of $(NH_3)_5Ru^{2+}$ or $(NH_3)_5Os^{2+}$ coordination to strong $\pi$ acceptors such as olefins. The cyclic voltammogram and differential pulse polarogram for the $(NH_3)_5RuOH_2^{2+}$/DMU system at a metal ion to ligand ratio of 24.4 are shown in Fig. 3 at 20 h after mixing. Waves are clearly observed for the $(NH_3)_5RuOH_2^{2+}$ and $(NH_3)_5$-$Ru(DMU)^{2+}$ complexes at 0.04 and 0.98 V versus NHE, respectively. It has been shown in careful studies of the electrochemical behavior of the styrene complexes of $(NH_3)_5Ru^{2+}$ and $(NH_3)_5Os^{2+}$ that the III/II couples are pseudo-reversible waves [12]. The $Os^{III/II}$ couples are *c.* 79 mV peak-to-peak in their CV waves and 90 mV wide at half-height in the DPP wave when the CV and DPP are obtained in 50 mV/s and 40 mV/s, respectively. This shows that the $Os^{III/II}$–styrene complex is nearly reversible at these scan rates. However, the $Ru^{II}$ analog shows only the oxidation wave and an equivalent DPP of the same integration per mole. This shows that the $Ru^{III}$–olefin complexes are very unstable and undergo rapid aquation. When more rapid CV scanning rates (100 to 2000 mV/s) are utilized, the $Os^{III/II}$–olefin waves become increasingly irreversible and the oxidation wave-to-reduction wave separation becomes increasingly large (90 to 300 mV); similarly the $Ru^{III/II}$ oxidation wave shifts in the same manner as the $Os^{III/II}$ oxidation wave. The absence of the $Ru^{III/II}$ reduction wave due to the

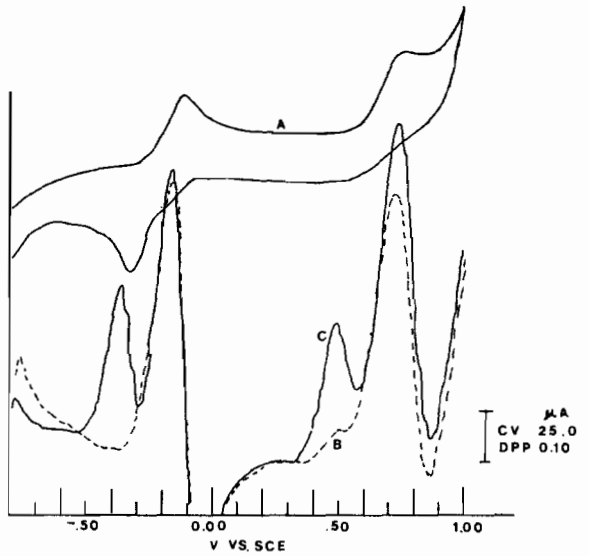



Fig. 3. Cyclic voltammogram and differential pulse polarograms of the $(NH_3)_5Ru(DMU)^{2+}$ system. $[Ru^{II}]_{tot}$ = 5.64 × $10^{-3}$ M; [DMU]:$[Ru^{II}]$ = 24.4 in A; 34.6 in B and C; (A) CV at 20 min; (B) DPP at 1 h; (C) DPP at 20 h.

TABLE 1. $^1H$ NMR data for $M^{II}(NH_3)_5(DMU)^{2+}$ complexes[a]

| | 6H | 5H | $CH_3(1)$ | $CH_3(3)$ |
|---|---|---|---|---|
| Free ligand | 7.58 (7.8) | 5.85 (7.7) | 3.40 | 3.29 |
| $Ru^{II}$ complex $\delta$ | 6.42 (7.26) | 3.87 (7.20) | 3.48 | 3.16 |
| $Ru^{II}$ complex $\Delta\delta$ | 1.16 | 1.98 | −0.08[b] | 0.13 |
| $Os^{II}$ complex $\delta$ | 5.89 (7.25) | 4.32 (7.22) | 3.35 | 3.11 |
| $Os^{II}$ complex $\Delta\delta$ | 1.69 | 1.53 | 0.05 | 0.18 |

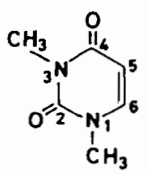
[a]Numbering scheme  *J* values in parentheses. [b]A negative shift is a downfield shift relative to the free ligand.

TABLE 2. $^{13}C$ NMR data for $M^{II}(NH_3)_5(DMU)^{2+}$ complexes[a]

| | C-2 | C-4 | C-5 | C-6 | C-1 | C-3 |
|---|---|---|---|---|---|---|
| Free ligand | 168.8 | 155.7 | 102.9 | 148.4 | 39.7 | 30.3 |
| $Ru^{II}$ complex $\delta$ | 155.3 | 179.2 | 50.8 | 94.5 | 40.2 | 29.9 |
| $Ru^{II}$ complex $\Delta\delta$ | 13.5 | −23.5 | 52.1 | 53.9 | −0.5 | 0.4 |
| $Ru^{II}$ minor complex $\delta$ | | | 52.5 | 97.2 | 40.0 | 29.8 |
| $Os^{II}$ complex $\delta$ | 155.7 | 183.1 | 102.9 | 148.4 | 39.7 | 29.7 |
| $Os^{II}$ complex $\Delta\delta$ | 13.1 | −27.4 | 63.1 | 78.7 | 4.1 | 0.6 |

[a]The numbering scheme is the same as defined in Table 1; a negative shift is a downfield shift relative to the free ligand.

EC electrochemical process precludes assignment of its position, but the related behavior to its $Os^{III/II}$ analog and the 90 mV width of the DPP wave at half-height under a 40 mV/s scan rate is the best evidence that the reported $E_{1/2}$ values herein represent the most reliable estimate of what the true $E_{1/2}$ would be in the absence of the rapid aquation of $(NH_3)_5Ru^{III}(olefin)^{3+}$ moieties. For the DMU complexes of this paper the same general chemical behavior was observed: the $Ru^{III/II}$ complex exhibits a chemically irreversible, but electrochemically quasi-reversible wave due to the EC sequence. More rapid scan rates up to 2000 mV/s did not intercept the $(NH_3)_5Ru^{III}(DMU)^{3+}$ species electrochemically. The $Os^{III/II}$ analog exhibits more reversible character although it is not as reversible as the $(NH_3)_5$-$Os(styrene)^{3+/2+}$ couple; its width at half-height of the DPP wave is 100 mV rather than the theoretical 90 mV even at a sweep of 40 mV/s. Additional DPP waves are also seen at −0.13 and 0.74 V for the $(NH_3)_4Ru(OH_2)_2^{2+}$ and $(NH_3)_4(H_2O)Ru(DMU)^{2+}$ complexes. The waves at −0.13 and 0.74 V grow in with a time dependence and are not originally present at about 1 h reaction time. Under similar conditions the 3-cyclohexene-1,1-dimethanol complex (CHDM), which shares similar steric factors with DMU upon coordination, also exhibits the catalysis of tetraammineruthenium(II) formation with waves at −0.13 V for $(NH_3)_4Ru(OH_2)_2^{2+}$ and 0.74 V for $(NH_3)_4(H_2O)Ru(CHDM)^{2+}$ [12].

A referee has noted that loss of $NH_3$ from the Ru(II) center opens the possibility for formation of polymeric species as precipitates. No evidence of precipitates was observed in solutions of the $(NH_3)_5Ru(DMU)^{2+}$ or $(NH_3)_5Os(DMU)^{2+}$ complexes as a function of time. However, upon oxidation of several of the related pyrimidine bases coordinated with $Ru^{II}(hedta)^-$ we have observed electrode coating as a function of time. In these cases, multiple coordination sites for bridging via N-3 and olefin binding sites do exist. This situation is precluded here by the stereochemical blocking provided by methylation in the DMU ligand. The $(NH_3)_5Os$-$(DMU)^{2+}$ system was studied by both CV and DPP as shown in Fig. 4. In the case of the $(NH_3)_5Os$-

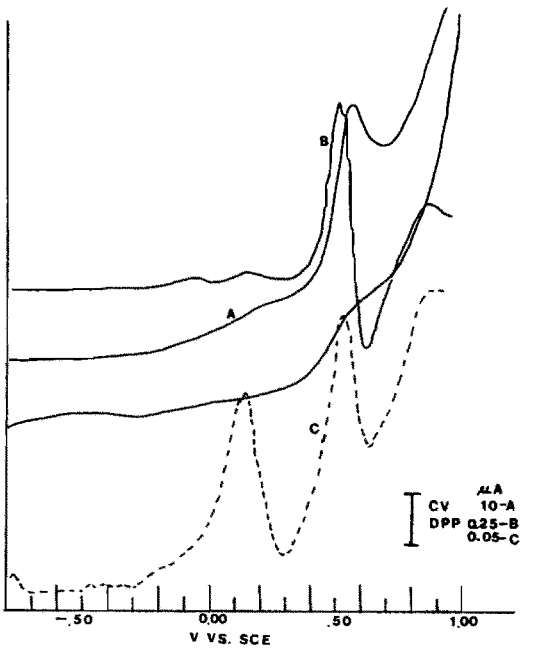
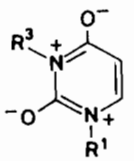



Fig. 4. Cyclic voltammogram and differential pulse polarograms of the $(NH_3)_5Os(DMU)^{2+}$ system. $[Os^{II}]_{tot} = 4.91 \times 10^{-3}$ M; $[DMU]:[Os^{II}] = 30.1$; (A) CV at 20 h; (B) DPP at 20 h; (C) DPP at 45 min.

$(DMU)^{2+}$ complex two species are readily detectable by the CV and DPP procedures after 45 min. After an additional 12 h of reaction, only the species exhibiting large upfield shifts for the $^1H$ and $^{13}C$ NMR spectra for the C-5 and C-6 positions are observed. This is indicative of the olefinic coordination mode after 12 h. The competitor species which forms in parallel to the olefin-bound form appears to be an $Os^{II}$ complex of the keto carbonyl, similar to the $(NH_3)_5Os((CH_3)_2CO)^{2+}$ complex [12]. The competitor species exhibits its $E_{1/2}$ value at 0.38 V which is similar to the 0.30 V value for the acetone complex [14]. Migration to the more basic olefin binding site would account for the loss of this species and growth of the other. The $E_{1/2}$ values of $(NH_3)_5$-$RuL^{3+/2+}$ complexes for N-bound *N*-heterocycles pyridine, pyrimidine, and pyrazine are 0.305, 0.40

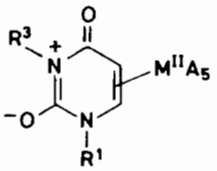
0.49 V, respectively [27]. The reduction potential for $(NH_3)_5Ru(cytidine)^{2+}$ is much less positive (0.09 V); this has been attributed to coordination via the exo amino functionality of cytidine [20]. Coordination of $Ru(NH_3)_5^{2+}$ to cytidine (C) or uridine (U) or DMU at N-3 or the exo $-4NH_2$ should not produce a complex with an $E_{1/2}$ value as positive as 0.98 V. Parallel studies with $Ru^{II/III}(hedta)L^{-/0}$ complexes of C, U, uracil, cytosine, and 2-pyridone have shown that heterocycles with an *ortho* electron releasing substituent ($-NH_2$ for C and $-OH$ for U and 2-pyridone) give $E_{1/2}$ values for binding at N-3 of C or U (N-1 of 2-pyridone) as follows: cytidine, +0.07 V; cytosine, +0.05 V; uridine, −0.078 V; uracil, −0.06 V; 2-pyridone, 0.01 V [25]. Since the $Ru^{II/III}(hedta)L^{-/0}$ complexes have $E_{1/2}$ values very nearly 0.23 V more negative than their $(NH_3)_5RuL^{2+/3+}$ analogs, one predicts $E_{1/2}$ values for the N-3 bound forms of cytidine or cytosine to be about +0.30 V and uridine or uracil about 0.16 V versus NHE for the $(NH_3)_5RuL^{3+/2+}$ couples. Therefore, coordination via one of the ring nitrogen positions is clearly incompatible with the 0.98 V potential of $(NH_3)_5Ru(DMU)^{2+}$ and only consistent with olefinic coordination.

Data for the $^{13}C$ NMR spectrum of the $(NH_3)_5Os(DMU)^{2+}$ complex are given in Table 2. All six carbon resonances have been identified. A quartet between 118.39 and 125.96 ppm was identified for the presence of $tfms^-$ ($CF_3SO_3^-$). For the $(NH_3)_5Os^{2+}$ coordinated DMU C-5 and C-6 are shifted 63.1 and 78.7 ppm upfield of the free ligand values. The carbonyl carbons are less intense, due to the absence of a proton on these positions. C-4, being closer to the $(NH_3)_5Os^{2+}$ cation, is shifted downfield ($\Delta\delta = -27.4$ ppm). This position presumably also experiences a larger change in effective hybridization upon coordination of $(NH_3)_5Os^{2+}$. Coordination of $(NH_3)_5Os^{2+}$ to the C-5–C-6 bond disfavors this ionic resonance form of DMU by



$R^1 = R^3 = CH_3$

placing cationic charge of the $Os^{II}$ center near the charges on the ring nitrogens. Thus, stabilization of the following metallated species could account for a greater shift downfield experienced by C-4 compared to C-2. The C-2 carbon is shifted upfield by 13.12 ppm. This is not as great as the 215 ppm upfield shift when $(NH_3)_5Os^{2+}$ is directly $\eta^2$-coordinated to a keto functional as found by Harman *et al.* for the acetone complex [14c]. Both methyl groups experience small upfield shifts C-1 (4.11 ppm) and C-3 (0.64 ppm), consistent with an influence of $(NH_3)_5Os^{2+}$ at two and three bonds away, respectively. The assignment of the C-3H methyl shift has been made on the basis of the $\delta$ value and shift on coordination for the 3-methyluridine $(NH_3)_5Os^{2+}$ complex ($\delta = 3.15$; $\Delta\delta = 0.17$). The combination of the $^1H$ NMR spectra of $(NH_3)_5M(DMU)^{2+}$ ($M^{II} = Ru^{II}$ and $Os^{II}$) and the $^{13}C$ NMR spectrum of the $Os^{II}$ complex clearly indicates that the C–5H, C–6H and C-5, C-6 pairs are most influenced by coordination; smaller adjustments in the $^1H$ and $^{13}C$ shifts of the remaining components of DMU also support coordination to the C-5–C-6 olefinic region of DMU. As shown by the data in Tables 1 and 2, all positions are shifted in the same sense for the $Ru^{II}$ derivative of $M(NH_3)_5(DMU)^{2+}$ as its $Os^{II}$ derivative but to a slightly smaller amount. The sole exception to this trend is for the C-1 methyl group where the $Ru^{II}$ complex exhibits downfield shifts for C-1 or $CH_3$–1H. The magnitude of the shift is small for either of these resonances and may reflect slight differences in the favored conformational isomers of the $Ru^{II}$ and $Os^{II}$ complexes.



## Conclusions

The coordination of $M(NH_3)_5^{2+}$, $M^{II} = Ru^{II}$ and $Os^{II}$ occurs via the C-5–C-6 olefin bond of 1,3-dimethyluracil. Changes in the $^1H$ and $^{13}C$ shifts of the ring components and the III/II reduction potentials of these complexes indicate a localization of $\pi$ density in the C-5–C-6 region of coordinated DMU. This is in concert with prior studies of Harman and Taube on the ability of $(NH_3)_5Os^{2+}$ to alter aromaticity of arenes [15, 16]. The observation of C-5–C-6 coordination by $Ru^{II}$ and $Os^{II}$ reagents to DMU supports the possibility of soft metal donors to bind at the C-5–C-6 bond of biopolymers containing C and U nucleosides. Further work to exploit this advance is under study in our laboratories.

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