δ bonding and ligand–ligand π-bonding, and is doubtless relatively weak, as judged by the tendency of $[\mathrm{NiL}]_2^{2+}$ to dissociate in solution. In formulating this simple bonding scheme each half-dimer has been treated as $[\mathrm{Ni^{II}L\cdot^{-}}(15\pi)]^{+}$.[3] The alternative possibility, $[\mathrm{Ni^{III}L^{2-}}(16\pi)]^{+}$ $[\mathrm{Ni^{I}L^{0}}(14\pi)]^{+}$, is inconsistent with the equivalence of each half-dimer. This arrangement would result in one antiaromatic 16π ligand with fixed double bonds (as observed for **5**[28]) and an aromatic 14π delocalized ligand, contrary to observation.

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Supplementary Material Available: The calculated hydrogen atom parameters (Table II), root-mean-square amplitudes of vibration (Table III), and the list of structure amplitudes (Table IV) (16 pages). Ordering information is given on any current masthead page.

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The Stabilization of α- and β-Diimines: Hexaammineruthenium(III), -osmium(III), and -platinum(IV) Condensed with α- and β-Diketones

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Abstract: Biacetyl condenses with $\mathrm{Ru(NH_3)_6^{3+}}$ in basic solution to yield the chelated diimine complex $\mathrm{[(NH_3)_4\,Ru(NH{=}C(CH_3)(CH_3)C{=}NH)]^{2+}}$ which oxidizes readily with $\mathrm{Br_2}$ (aq) to give the Ru(III) ion, $E = 0.56$ V. The condensation requires coordinated amide ions to capture the carbonyl groups followed by elimination of water. In basic solution the Ru(III) reduces to the Ru(II) ion in a reaction which apparently involves some intramolecular reduction by the ligand. Analogously $\mathrm{Os(NH_3)_6^{3+}}$ captures biacetyl to give the trans bis-diimine complex with approximately the same redox potential. Acetylacetone and trifluoroacetylacetone also condense with $\mathrm{Pt(NH_3)_6^{4+}}$ to stabilize a chelated diimine anion.

Several intramolecular reactions between carbonyl centers and coordinated amide ions leading to carbinolamine and imine chelates have been observed recently.[1-5] Although analogous chelated imines have been known for many years with labile metal ions, the route whereby the chelate formed has not been ascertained. Condensation of the imine could occur off or on the metal complex with such labile systems.

The present paper investigates the prospect of forming chelates using coordinated nucleophiles and reactive dicarbonyl systems in intermolecular reactions.[6] The investigation is part of a general program to develop rational syntheses of chelate complexes and organic molecules where the metal center activates, protects, and organizes the syntheses.

Experimental Section

^{1}H NMR spectra were obtained with a JEOL 100-MHz Minimar spectrometer at 30 °C using tetramethylsilane ($\mathrm{Me_4Si}$) as the internal reference. INDOR nitrogen spectra were obtained using a Varian HA-100 spectrometer. Electrochemical measurements were performed using a PAR Model 170 electrochemistry system in water/0.1 M $\mathrm{NaClO_4}$ vs. a saturated calomel electrode. A three-electrode iR compensated system with a platinum auxiliary electrode was used throughout. Both the ac polarography and cyclic voltammetry were performed at a Beckmann platinum disk stationary electrode with an area of ~0.27 cm^2 at a scan rate of 200 mV s^{-1}. Phase sensitive ac measurements were made at 80 Hz with a phase angle of 90° with respect to the charging current and with an ac perturbation of 5 mV peak-peak. Solutions were degassed with nitrogen before measurements were taken at 22 °C under a blanket of inert gas.

Spectrophotometric measurements were made with either a Cary 14 or a 118C spectrophotometer. Determinations of pH were made with a Radiometer Model pH meter using a $\mathrm{TTA_3}$ electrode assembly.

Kinetics (25 °C). (a) The formation of I from $\mathrm{Ru(NH_3)_6Cl_3}$ was followed spectrophotometrically at 465 nm ($\lambda_{\max}$ for I) at constant pH using 0.05 M collidine buffer (pH 7.36, $\mu = 1.0$ M NaCl). The

$Ru(NH_3)_6Cl_3$ and biacetyl solutions in collidine buffer were equilibrated to 25 °C and mixed, and the absorbance change was recorded in 1-cm cells. After the reaction, the final pH of the solution was measured. For the kinetics in the absence of buffer, the pH was maintained automatically in the spectrophotometer cell using a Radiometer pH-stat with a TTA_3 electrode assembly in conjunction with Radiometer Auto Burette Type ABU12 (base), ABU1b (acid) and Titrator Type TTT11b.

(b) Reduction of $[Ru(NH_3)_4(Me_2diim)](ClO_4)_3$ in basic media was followed using a stopped-flow apparatus to achieve rapid mixing of the NaOH solution or buffer with a slightly acidic (pH 5) solution of the complex. The base was 2 M in either $NaClO_4$ (OH^- as base) or NaCl (collidine buffer) to maintain the final ionic strength of the solution at $\mu = 1.0$.

Hexaammineruthenium(III) Chloride. $Ru(NH_3)_6Cl_2$, prepared from $RuCl_3 \cdot 3H_2O$ by the method of Lever and Powell,[7] was dissolved in water acidified with HCl (pH 4). Excess, finely powdered AgCl was added, together with some glass beads. The mixture was shaken gently for a few minutes and filtered through filter aid. The filtrate was evaporated to dryness under vacuum and the crude $Ru(NH_3)_6Cl_3$ recrystallized from slightly acidified water by the addition of concentrated HCl. The yield of the crude Ru(III) complex was quantitative (based on $Ru(NH_3)_6Cl_2$).

Tetraammine-2,3-butanediimineruthenium(II) Perchlorate. $Ru(NH_3)_6Cl_3$ (0.2 g) was dissolved in the minimum quantity of water (~5 ml) and biacetyl (0.3 g) added. NaOH (1 M, ~4 ml) was added to the solution with shaking. An intense red-brown color immediately developed. The solution was filtered and treated with solid $NaClO_4$. Yellow crystals formed immediately. These were collected, washed with ethanol (2 × 10 ml) and ether (2 × 10 ml), and dried under vacuum over P_2O_5, yield 0.19 g (65%). The complex was recrystallized from water by the addition of $NaClO_4$. Anal. Calcd for $RuC_4H_{20}N_6Cl_2O_8$: C, 10.62; H, 4.46; N, 18.59; Cl, 15.68. Found: C, 10.9; H, 4.6; N, 18.0; Cl, 15.7.

Tetraammine-2,3-butanediimineruthenium(III) Perchlorate. Saturated bromine water (1.7 ml) was added dropwise to a stirred suspension of I (0.1 g) in water (~2 ml). The Ru(II) complex dissolved to yield a clear yellow-brown solution. The solution was filtered and solid $NaClO_4$ added. A yellow precipitate formed and after ~10 min of cooling in ice, it was collected, washed with ethanol (2 × 5 ml) and ether (2 × 5 ml), and dried under vacuum over P_2O_5, yield 0.07 g (57%). *This complex is explosive.* Anal. Calcd for $RuC_4N_6H_{20}Cl_3O_{12}$: C, 8.71; H, 3.65; N, 15.24; Cl, 19.28. Found: C, 8.7; H, 3.7; N, 15.3; Cl, 19.4.

Tetraammine-1,2-cyclohexanediimineruthenium(II) Perchlorate. This complex was prepared in an analogous manner to the dimethyldiimine using $Ru(NH_3)_6Cl_3$ (0.2 g) and 1,2-cyclohexanedione (0.35 g). It was isolated as an orange-brown perchlorate salt and dried over P_2O_5, yield 0.21 g (68%). It was recrystallized from water with $NaClO_4$. Anal. Calcd for $RuC_6H_{22}N_6Cl_2O_8$: C, 15.07; H, 4.64; N, 17.58; Cl, 14.83. Found: C, 15.5; H, 5.0; N, 17.8; Cl, 14.8.

Hexaammineplatinum(IV) Chloride Monohydrate. A more convenient synthesis was developed as the procedure involving $[Pt(CH_3NH_2)_4Cl_2]Cl_2$ gave only 32% yield from K_2PtCl_4 or 16% from K_2PtCl_6.[8] K_2PtCl_6 (4 g) was dissolved in liquid ammonia (100 ml) and K_2PtCl_4 (0.1 g) added as a catalyst. The solution was stirred for 5 days, with addition of liquid ammonia at regular intervals to keep the volume at ~100 ml. The liquid ammonia was removed rapidly on the rotary evaporator. Chlorine water (~3 ml) was added and slurried with the reaction mixture to oxidize any Pt(II) up to Pt(IV). Water (~5 ml) was added and the slurry strongly acidified with HCl. The gray-white solid was collected. It was redissolved in water, pH adjusted to ~9.0, and the slight undissolved impurity filtered off. $Pt(NH_3)_6Cl_4 \cdot H_2O$ was precipitated with concentrated HCl, collected, washed with ethanol and ether, and dried under vacuum over P_2O_5 (yield 0.13 g, 40%). Recycling the residues improves the yield to ~60%. Anal. Calcd for $PtN_6H_{18}Cl_4 \cdot 2H_2O$: N, 17.69; H, 4.67; Cl, 29.85. Found: N, 17.5; H, 4.8; Cl, 29.9.

Tetraammine-2,4-pentanediiminatoplatinum(IV) Perchlorate. A solution of 2,4-pentanedione (0.48 g) in NaOH (1 M, 2.8 ml) was added to $Pt(NH_3)_6Cl_4 \cdot H_2O$ (0.25 g) in a solution in water (10 ml). The solution was warmed to ~60 °C for a few minutes, cooled, and filtered. Treatment of the filtrate with excess $NaClO_4$ gave the bright yellow salt which was collected, washed with ethanol (2 × 5 ml) and ether (2 × 5 ml), and dried under vacuum over P_2O_5 (yield 0.21 g, 60%). The complex was recrystallized from water by the addition of $NaClO_4$. Anal. Calcd for $PtC_5N_6H_{21}Cl_3O_{12}$: C, 9.12; H, 3.21; N, 12.76; Cl, 16.15; Pt, 29.62. Found: C, 9.2; H, 3.5; N, 12.5; Cl, 16.0; Pt, 30.6.

Tetraammine-1,1,1-trifluoro-2,4-pentanediiminatoplatinum(IV) Perchlorate was synthesized as described for the acetylacetone reaction above except that 1,1,1-trifluoroacetylacetone (0.74 g) was used. After the addition of $NaClO_4$, and evaporation of the filtrate, the large crystals of $NaClO_4$ which formed were carefully removed, and the product was washed with EtOH (2 × 5 ml) and Et_2O (2 × 5 ml) and dried in vacuo over P_2O_5, yield 0.12 g (31%). Anal. Calcd for $PtC_5H_{18}F_3N_6Cl_3O_{12}$: C, 8.42; H, 2.53; N, 11.78; Cl, 14.94. Found: C, 8.5; H, 2.5; N, 11.5; Cl, 14.9.

Hexaammineosmium(III) Iodide. The published synthesis by Bottomly[9] was irreproducible and the method of Hogarth and Dwyer[10] was modified to give a more convenient synthesis. $(NH_4)_2OsBr_6$ (5 g) was placed in a small wide-necked tube. This tube was placed carefully on top of a tube of narrower bore containing solid ammonia (~30 g) in a high pressure vessel (Baskerville and Lindsay, Manchester; capacity ~200 ml). The vessel was rapidly sealed with a high pressure head, connected to a pressure gauge and thermocouple. The vessel was heated to 160 °C (above the critical temperature of ammonia gas) and the pressure rose to ~150 atm ($\sim 150 \times 10^5$ Nm^{-2}). This was maintained for 16 h, after which the vessel was cooled, the pressure released, and the vessel opened. The reacted material was white-green in color and was extracted into ~150 ml of water. KI was added to the filtered solution and the yellow hexaammine salt was filtered, washed with EtOH and Et_2O, and dried under vacuum over P_2O_5, yield 2.6 g (55%). Anal. Calcd for $OsN_6H_{18}I_3$: N, 12.49; H, 2.69; I, 56.56. Found: N, 12.5; H, 2.9; I, 59.9.

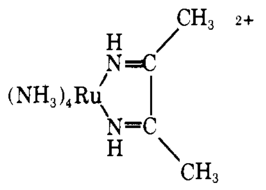
Diamminebis(2,3-butanediimine)osmium(II) Perchlorate. $Os(NH_3)_6I_3$ (0.5 g) was slurried in water (~5 ml) and biacetyl (0.3 g) added. Aqueous NaOH (1 M, ~10 ml) was added dropwise until no further deepening of the red-brown color was observed and the hexaammine salt had dissolved. After filtration, solid $NaClO_4$ was added and the solution chilled in ice and scratched with a glass rod. The brown-black crystals which separated were collected, washed with cold ethanol (1 × 10 ml) and ether (2 × 5 ml), and dried under vacuum over P_2O_5. The complex was recrystallized from water by the addition of sodium perchlorate. Anal. Calcd for $OsC_8H_{24}N_6Cl_2O_9$: C, 15.77; H, 3.97; N, 13.79; Cl, 11.64. Found: C, 15.6; H, 3.9; N, 13.7; Cl, 11.9.

Results and Discussion

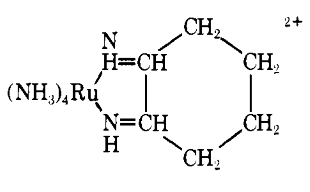
The heavy metal hexaammines were chosen as starting materials for the intermolecular condensation reactions for several reasons. Firstly, the hexaammines of Ru(III), Os(III), and Pt(IV) are kinetically robust so that the coordinated NH_2^- ion can be used as the nucleophile in the reaction. Secondly, the ease with which the complex ammines are deprotonated is significant. A reasonable concentration of the coordinated amide ion is desirable to attack the electrophilic carbonyl center and the pK_a values of $Ru(NH_3)_6{}^{3+}$ and $Pt(NH_3)_6{}^{4+}$ are 12.4[11,12] and 7.9,[13] respectively. There are no data available for the pK_a of $Os(NH_3)_6{}^{3+}$ but the rate constant for proton exchange in 0.1 M C_2H_3COOD/CH_3COO^- buffer at 25 °C is 6×10^6 M^{-1} s^{-1} compared with 6×10^8 M^{-1} s^{-1} for $Ru(NH_3)_6{}^{3+}$.[14] It seems likely then that $Os(NH_3)_6{}^{3+}$ is somewhat less acidic than the Ru(III) complex. However, all three complexes would supply reasonable concentrations of the coordinated nucleophile in basic media.

Ruthenium. If the pK_a of $Ru(NH_3)_6{}^{3+}$ is 12.4,[11] at least one proton should be removed in 1 M OH^-. However, under these conditions appreciable decomposition occurs with changes in the electronic spectrum within 1 min.[11] Addition of the organic reagent to a solution of the hexaammine before addition of base helps to minimize the effect of this decomposition. With biacetyl or 1,2-cyclohexanedione the imines I and II were isolated, as their perchlorate salts, and it should be noted that all the Ru immine complexes are potentially explosive.

The ^1H NMR spectrum of I in Me_2SO-d_6 showed resonances at δ −11.83, −3.28, −2.38, and −1.67 ppm (relative to Me_4Si) integrating for 1:3:3:3 protons, respectively. The



I



II

signals at δ −3.28 and −1.67 disappeared in D_2O indicating ammine protons. Decoupling nitrogen (Ξ 7 223 233 ± 50 Hz for the ammine protons at δ −1.67; Ξ 7 223 332 ± 50 Hz for the ammine protons at δ −3.28; 7 225 417 ± 100 Hz for the imine protons) sharpened the ammine and imine proton resonances which confirms the assignment. Exchange of the cis and trans ammine protons was rapid, even in 10^{-3} M DCl ($t_{1/2} \sim$ 3 min and 15 min), and at this pH the imine protons exchanged too rapidly to be observed. The methyl protons, however, did not exchange even in 1 M OH^-. The cyclohexane diimine complex II had an essentially similar spectrum with imine proton signals again at very low field δ −11.27 ppm.

Since the Ru(II) complex was isolated, a reduction from Ru(III) to Ru(II) occurred during the reaction. The electrochemical behavior of the complex was then investigated in an attempt to gain some insight into the reduction step. An ac polarogram showed the potential of the reaction

$$e^- + [Ru(NH_3)_4(Me_2diim)]^{3+} \rightharpoondown [Ru(NH_3)_4(Me_2diim)]^{2+}$$

to be 0.54 V in water relative to the hydrogen electrode (SCE 0.25 V). Cyclic voltammetry indicated a reversible redox process with a ratio of reverse to forward currents of 1.09. This was also supported by a peak separation of 62 mV. Since the potential of the reaction

$$^{1}/_{2}O_2 + 2H^+ + 2e^- \rightharpoondown H_2O \text{ is } 0.42 \text{ V}$$

in 1 M OH^-, water could act as a reductant under these conditions. It would also be expected that Br_2 would oxidize the Ru(II) diimine quantitatively to the Ru(III) diimine ion and the latter was isolated as the perchlorate in this manner. As expected, the Ru(III) ion was reduced in 1 M base but it was also reduced by pyridine, collidine, and carbonate buffers at much lower pH values and clearly a route to reduction other than reduction by H_2O is required.

The yield of the Ru(II) complex from the synthesis was >50% so that disproportionation of Ru(III) into Ru(II) and Ru(IV) products can be eliminated as the sole route to Ru(II). Prospects for the reduction are discussed more fully in the sections on kinetics where the rates of the reduction step were followed.

The visible spectrum of I showed an intense absorption at 465 nm (ε 7.2×10^3 M^{-1} cm^{-1} in 10^{-3} M $HClO_4$) characteristic for Ru(II) bonded to an unsaturated N-center.[15] This absorption was unchanged in the pH range 1-14 which probably requires the pK_a of both the ammine and imine protons to be greater than 14. These absorptions are described as d → π^* charge transfer bands in which spin-orbit coupling plays a dominant role.[16]

The large stabilization derived from delocalization of the t_{2g} electrons into the ligand orbital system can be judged by comparing the potential of 0.54 V found for $[Ru(NH_3)_4(Me_2diim)]^{2+/3+}$ with that for the $Ru(NH_3)_6{}^{2+/3+}$ couple, 0.10 V.[17] Further evidence for this extensive back-donation of charge has been advanced[18,19] from the comparison of the pK_a values of $(pyrazineH)^+$, $[Ru^{III}(NH_3)_5pyrazineH]^{4+}$, and $[Ru^{II}(NH_3)_5pyrazineH]^{3+}$ 0.6, ∼−0.8, and 2.5 ± 0.1 respectively. The increase in basicity of the uncoordinated N atom of pyrazine when the ligand is attached to the Ru(II) moiety over that of the free ligand appears to be the best evidence to date for extensive metal to ligand π donation of charge.

Table I. The Kinetics of Reduction of $[Ru(NH_3)_4(Me_2diim)](ClO_4)_3$ (25 °C and $\mu = 1.0$)

Base	$[Ru(NH_3)_4Me_2diim](ClO_4)_3$	10^2k (s^{-1})
OH^- 0.01 M[a]	10^{-4} M	1.9
OH^- 0.1 M[a]	10^{-4} M	2.4
OH^- 1.0 M[a]	10^{-4} M	2.7
Collidine 0.05[b]	6.6×10^{-5}	2.2
Collidine 0.05[b]	1.0×10^{-4}	1.1[c]

[a] $\mu = 1.0$ ($NaClO_4$). [b] $\mu = 1.0$ (NaCl) pH 7.43. [c] Biacetyl 0.48 M.

Upon oxidation of I the intense absorption band at 465 nm vanishes and the Ru(III) species has maxima at 438 (ε 932), 416 (ε 1340), 378 (ε 1360), and 289 (ε 3360) nm. All these absorptions are more intense than expected for ligand field bands but the charge transfer content has been sharply reduced relative to the Ru(II) system.

Kinetics of Reduction of $[Ru^{III}(NH_3)_4(Me_2diim)]^{3+}$. The reduction step was studied in NaOH solutions (μ = 1 with $NaClO_4$) and in 0.05 M collidine buffers (μ = 1 NaCl) at 25 °C. The reduction studies in collidine buffers were conducted both in the presence and absence of biacetyl, the former being necessary to correlate with the formation kinetics to be discussed later.

The reduction was followed by the increase of absorbance at 465 nm and plots of log $(A_\infty - A)$ against time were linear for at least three half-lives. The results for several conditions are given in Table I.

The reduction rate does not seem to vary greatly except when biacetyl is present. However, the stoichiometry is not clear. At least seven minor fractions were detected by chromatography of the reaction mixture using Sephadex SP-25 ion exchange resin. The major product was the Ru(II) diimine ∼70% although the yield varied somewhat with the conditions. For example, the yields from pyridine and collidine buffers were 73 and 69%, respectively, but the yields from carbonate buffers were consistently lower ∼54%. Reduction with Sn^{2+} or $S_2O_3{}^{2-}$ in 0.005 M HCl gave 60 and 56% of the diimine, respectively.

Addition of biacetyl to the Ru(III) diimine, before reduction, increases the yield significantly which is consistent with the yield from the synthetic reaction ∼85% (determined spectrophotometrically after chromatography).

Kinetics of Formation of $[Ru(NH_3)_4(Me_2diim)]^{2+}$. The formation of the Ru(II) diimine from $[Ru(NH_3)_6]Cl_3$ and excess biacetyl was followed for a variety of conditions at 465 nm. Plots of log $(A_\infty - A)$ against time were linear for at least three half-lives for most of the conditions studied. The pseudo-first-order rate constants for the formation kinetics in collidine buffer at pH 7.36 are given in Table IIa and the pseudo-first-order rate constants at constant biacetyl and varying pH are given in Table IIb. Plots of the sets of data show essentially a first-order dependence of the rate on biacetyl and OH^- concentrations. Also the buffer data and the pH-stat data equated to the same pH values agree which indicates little, if any, buffer dependence of the reaction.

The rate law takes the form

$$d[Ru^{II}(Me_2diim)]/dt = k_F[Ru(NH_3)_6{}^{3+}][OH^-][biacetyl]$$

and the derived third-order rate constant k_F from the best fit of the data has the value 1.5×10^4 M^{-2} s^{-1} from the data for varying biacetyl and 1.6×10^4 M^{-2} s^{-1} from the data where the pH varies (pK_{H_2O} = 13.77). There was an indication of a

Table II. Formation of $[Ru^{II}(NH_3)_4(Me_2diim)]^{2+}$ from $[Ru(NH_3)_6]^{3+}$ and Biacetyl at 25 °C, μ = 1.0

pH	10^2[Biacetyl] (M)	$10^4[Ru(NH_3)_6]^{3+}$ (M)	$10^4 k_{obsd}$ (s^{-1})
(a) Collidine buffer 0.05 M, μ = 1.0 M (NaCl)			
7.36	11	1.5	6.8
	3.2	1.3	2.6
	4.5	1.7	3.2
	7.0	1.5	4.6
	8.9	1.1	5.8
	0.98	1.8	1.1
	21	1.5	11
	16	1.9	9.8
	21	1.3	12
	16	1.6	8.7
	14	1.5	8.4
	18	1.5	10
	50	1.1	25
(b) pH-stat kinetics, μ = 1.0 M (NaCl)			
7.61	5.0	1.1	5.9
7.41			3.8
7.14			2.5
6.93			1.7
6.46			0.62

term independent of OH^- concentration ~$0.4 \times 10^{-4}\ s^{-1}$ (at 0.05 M biacetyl) but the poor stoichiometry for the overall process and the scatter in the rate data did not entice a full-scale kinetic investigation.

In the formation kinetics for high concentrations of biacetyl (0.5 M) the absorbance plots showed an inflection point early in the trace which was resolved as two consecutive reactions. The rate constants extracted graphically from the data were 2.5×10^{-3} and $1.1 \times 10^{-2}\ s^{-1}$. The former rate constant is for the formation step and the latter rate constant agrees with that obtained for the reduction of the isolated Ru(III) diimine complex under the same conditions (Table I).

Mechanism

The overall rate law is consistent with a mechanism involving deprotonation of the $Ru(NH_3)_6^{3+}$ ion followed by addition of the coordinated amide ion to the carbonyl center as shown in Figure 1. The condensation reaction appeared to be independent of the buffer concentration, and we were unable to ascertain if amide ion attack, subsequent proton transfer, or elimination of water from the carbinolamine was rate determining. However, related condensations indicate that the deprotonation of a cis ammonia and cyclization of the chelate would not be rate determining.[1,4,6] Approximately one in 10-40 proton exchanges leads to capture of the chelate.[6] For related reactions, with Co(III) as the metal center, the carbinolamine formation is usually much faster than the elimination of water. However, this may not apply to Ru(III) where the radial extension of the d electrons is greater[15] and the diimine product should be stabilized by metal to ligand dπ-pπ donation. Such stabilization could be a substantial influence for the elimination reaction.

While the condensation might be relatively well understood through the kinetics and comparisons with analogous reactions, the reduction path is much less clear. In 1 M OH^- the $Ru^{III}(Me_2diim)$ complex could oxidize water but the same rate of reduction at lower pH values and the multiplicity of products indicate other sources for the reduction step. The buffers appear to be unlikely prospects, especially since carbonate buffers are ineffective and although biacetyl has a reducing capacity through the carbanion, this route seems to be eliminated by the slower rates observed in high biacetyl concentrations.

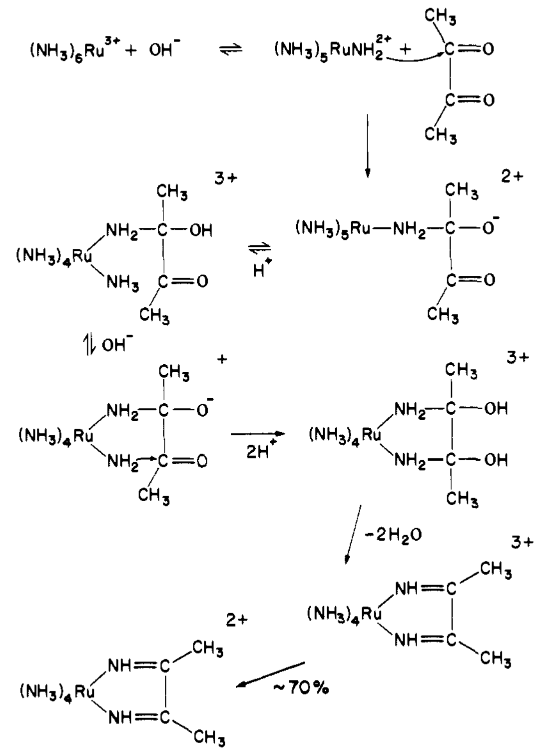


Figure 1. Proposed mechanism of addition of biacetyl to the $Ru(NH_3)_6^{3+}$ ion.

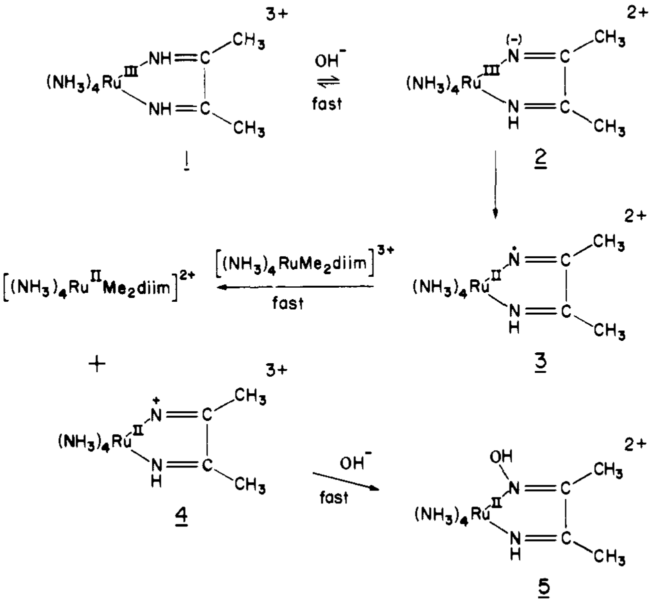
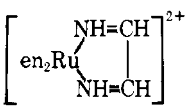


Figure 2. A feasible mechanism for the reduction of $[Ru^{III}(NH_3)_4Me_2diim]^{3+}$ to the Ru(II) ion.

A likely route,[20] however, is an intramolecular oxidation of the ligand (Figure 2) probably by deprotonation of the imine NH (**2**) and subsequent electron transfer to give a coordinated $—\dot{N}=$ radical (**3**). A subsequent fast reaction of the radical and another Ru(III) diimine ion could lead to the Ru(II) diimine complex and a chelated diimine carbonium ion (**4**) which should capture OH^- to give the Ru(II) monooxime complex (**5**), Figure 2. Such a route, however, yields 50% Ru(II) diimine and 50% Ru(II) oxime complexes and, although this route has been identified by Li Chum and Krumholz[20] for analogous Fe chemistry, the oxime had not been identified here. It is conceivable that such an oxime complex could reduce the Ru(III) diimine so that more than 50% conversion of Ru(III) → Ru(II) could be obtained for each mole of oxime produced. The diimine Ru(II) complex isolated as the perchlorate was anhydrous and confusion with a possible oxime complex was thereby eliminated.

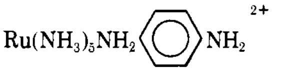
The reduction mechanism requires complete deprotonation of imine N–H above pH 7 in order for the reaction to be independent of OH^- concentration and it is quite likely that the Ru(III) diimine ion is sufficiently acidic to meet this requirement. In Co(III) imine chemistry, the imine protons appear to be $\sim 10^6$-fold more acidic than coordinated ammonia[1] and the Ru(III) ammonia complex is much more acidic than the Co(III) analogue.

A substantial driving force for the reaction is the metal to ligand donation of charge through $d\pi$–$p\pi$ orbitals of appropriate symmetry which enormously stabilizes the Ru(II) diimine complex. The degree of stabilization from such a source has been detailed earlier[15] and the present system provides some additional information. The acidity of the imine proton has now fallen sharply and the imine is nowhere near as reactive as analogous Co(III) systems. The nitromethane carbanion does not add to the imine carbon atom[2] and BH_4^- does not reduce it to amine.[1] On the contrary, this stabilization of Ru(II) imines is almost certainly a major factor in the facile oxidation of $Ru(en)_3^{2+}$ (en = 1,2-diaminoethane) to III,[21,22]



III

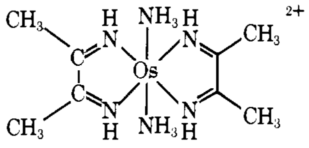
and IV to the *p*-benzoquinone imine complex,[23] and related



IV

reactions.[24]

Osmium. $Os(NH_3)_6^{3+}$ reacts rapidly with biacetyl in basic solution to give a dark brown solution from which the cation V was isolated as the perchlorate salt. ^1H NMR spectra in D_2O



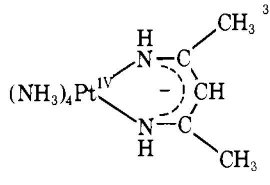
V

show only one sharp signal at δ −3.3 ppm relative to tetramethylsilane attributed to the CH_3 group and there is an intense absorption at 443 nm. The ^1H NMR spectra prescribes a trans configuration unless there is an accidental degeneracy of the methyl signals.

It is interesting now to consider how the Os(II) complex attaches two diimine moieties while Ru(II) only captures one. The answer probably lies with the redox potential differences between $Os(NH_3)_6^{2+/3+}$ (−1 V est) and $Ru(NH_3)_6^{2+/3+}$ ($\sim$0.1 V).[15] Addition of two diimines is required to stabilize the Os(II) oxidation state at 0.53 V (ac polarography), approximately 0.75 V per α-diimine grouping. This stabilization factor is higher than that for the Ru(II) α-diimine complex (0.44 V) to achieve approximately the same potential and probably reflects the greater radial extension of the d orbitals for the Os(II) oxidation state. Once the divalent oxidation state is reached, the ammonia acidities fall sharply and the rate of addition of the ligand is presumably slower than the self-condensation of biacetyl. An experiment with $[Ru(NH_3)_4(Me_2diim)]^{3+}$, biacetyl, and base showed that the complex reduced rapidly to the Ru(II) complex and no sign of addition of another chelate was detected.

Platinum. $Pt(NH_3)_6^{4+}$ ion is rather acidic (pK_a = 7.9) by comparison with most ammonia complexes and the coordinated amide ion is therefore readily accessible. Correspondingly, NH_2^- attached to Pt(IV) might be expected to be a poorer nucleophile than when attached to Ru(III) for example. $Pt(NH_3)_6^{4+}$ and biacetyl or 1,2-cyclohexanedione, reacted in neutral conditions, gave no isolable complex. However, it is likely that the α-diketones condense. Whether the complexes are too soluble or whether they equilibrate rapidly with $Pt(NH_3)_6^{4+}$ is not yet known. One factor which seems certain is a reduction in the extent of π-donation from metal to ligand relative to Ru(II),[15] for example, and a consequent destabilization of the imine complex.

The hexaammine and acetylacetone react rapidly, however, in the vicinity of the pK_α of acetylacetone and a yellow complex was isolated as the perchlorate salt, VI. The equivalence of the methyl groups in the ^1H NMR spectrum indicates there is delocalization of the charge over the entire ring. The chelate readily brominates at the methine center and the reaction was followed conveniently by ^1H NMR spectroscopy. As the methine signal vanished, the growth of a new methyl signal and the decline of the old was observed. The same type of complex was also isolated using trifluoroacetylacetone and there was evidence for condensation of more than one ligand per metal ion.[25]



VI

This work demonstrates the formation and stabilization of imine-type chelates by intermolecular reactions where the coordinated nucleophile captures the organic moiety without leaving the metal center. The metals used clearly have different potentials for forming and stabilizing the coordinated organic adduct and it is obvious that Ru(II) and Os(II) for example inactivate the coordinated imine relative to the same type of ligand bound to Co(III). The factors which have been outlined in the article should contribute to the prospect for planned syntheses using metal chelates.

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Infrared and Visible Circular Dichroism and Magnetic Circular Dichroism Studies on Cobalt(II)-Substituted Blue Copper Proteins

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Abstract: The near-infrared, visible, and near-ultraviolet circular dichroism (CD) and magnetic circular dichroism (MCD) spectra of the cobalt(II) derivatives of *Rhus vernicifera* stellacyanin, *Pseudomonas aeruginosa* azurin, and bean plastocyanin are reported. Bands attributable to transitions to $^4T_1(^4F)$ in a distorted tetrahedral Co(II) center have been observed in the near-infrared region. The centers of gravity of $^4T_1(^4F)$ are estimated to be 8250, 8375, and 8450 cm^{-1} above the $^4A_2$ ground state in the Co(II) derivatives of stellacyanin, azurin, and plastocyanin, respectively. In addition, one component of a split $^4A_2 \rightarrow {}^4T_2$ band has been observed at 5600 cm^{-1} in cobalt(II) stellacyanin. The average positions of the ligand field states are described satisfactorily by taking $Dq = 490$ and $B = 730$ cm^{-1} for all three cobalt(II)-substituted proteins. The ligand field analysis as well as MCD spectral comparisons suggest that the donor groups of the three blue copper sites are probably the same. It is proposed that each blue copper site involves a rather rigidly constrained ligand structure. The variation in the distortion of the site from tetrahedral symmetry in the three blue proteins is not large.

Our understanding of the structure of the blue (or type 1)[2] site in copper proteins has developed rapidly in recent years.[3-8] This understanding is based in part on spectroscopic[6,7] and magnetic[8] studies of the high-spin cobalt(II) derivatives of *Rhus vernicifera* stellacyanin, bean plastocyanin, and *Pseudomonas aeruginosa* azurin. The former experiments have been particularly revealing, as the electronic spectrum of a high-spin cobalt(II) center depends strongly on coordination geometry.[9-11] Our previous work was limited, however, to absorption measurements, and to the visible and ultraviolet spectral regions, where interpretation is complicated by overlap of the highest energy, spin-allowed d-d and the lowest energy charge transfer excitations. We have extended our absorption studies, therefore, to include circular dichroism (CD) and magnetic circular dichroism (MCD) measurements, as each spectroscopic method is associated with different selection rules and allows complementary information to be obtained. Further, the different selection rules associated with the dichroism methods have allowed us to investigate the low energy near-infrared ligand field transitions that often are obscured in absorption owing to protein and solvent vibrational overtone bands. From this investigation we have been able to reach definite conclusions regarding the geometry of the Co(II) binding site in the blue protein derivatives.

Experimental Section

Bean plastocyanin was purified by a standard procedure.[12] Stellacyanin was extracted and purified as described previously.[13] Azurin from *Pseudomonas aeruginosa* (strain no. 10145, American type culture collection) was obtained by a literature method.[14] The cobalt(II) derivatives of the three blue proteins were prepared as described earlier.[6,7] Protein samples for the near-infrared CD work were lyophilized and equilibrated twice with D_2O and finally dissolved in deuterated Tris buffer (0.025 M, pH 8.1). The protein concentrations used were in the range 0.5–1.0 mM.

Absorption spectra were obtained using a Cary 17 spectrometer. The CD and MCD spectra in the visible region were measured on a Cary 61 spectropolarimeter. Measurements in the near-infrared region were performed on a specially designed instrument that has been described previously.[15,16] The sign of the CD was determined using a nickel(II) tartrate solution. Magnetic circular dichroism measurements were made using a Varian superconducting magnet. Fields of approximately 40 kG were used in the experiments. CD and MCD are reported in $\Delta\epsilon$ and $[\theta]_M$ units, being normalized to a field of 10 kG in the case of MCD. The MCD spectra were corrected for the presence of natural optical activity.

Results and Discussion

Figures 1–3 present the visible–uv absorption, CD, and MCD spectra of cobalt(II) derivatives of stellacyanin, plastocyanin, and azurin. The absorption and MCD spectra are seen to be quite similar for the three proteins, whereas the CD curves exhibit substantial differences. Through a comparison of the absorption and MCD spectra, the charge transfer manifold can be distinguished from the ligand field region. The charge transfer transitions exhibit a characteristic MCD spectrum, which shifts over the series independently of the ligand field bands at lower energy. No d → d transitions are found to be at energies above 20 500 cm^{-1}, a region in each absorption spectrum that is obscured by the charge transfer bands. The lack of a d-d band centered at ~22 000 cm^{-1} rules against a square pyramidal structure, as such cobalt(II) complexes are expected to exhibit a $^4A_2 \rightarrow {}^4A_2$ transition at approximately this energy.[17]

Further, the MCD spectra in the region of 12 500–20 500 cm^{-1} (Figures 1–3) may be compared to those of Co(II) model complexes.[18-21] These comparisons allow us to exclude trigonal bipyramidal Co(II) complexes as models for the metal-binding site. Although such complexes exhibit two absorption bands[17] in the visible region, their MCD spectra show large negative