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Preparation of Pyrazine-Bridged, Polymeric Complexes of Ruthenium(II)

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Methods are described for the preparation of the series of polymeric complexes $[(\text{bipy})_2\text{ClRu(pyz)}[\text{Ru(bipy)}_2\text{pyz}]_n\text{RuCl(bipy)}_2](\text{PF}_6)_{2n+2}\cdot(n+2)\text{H}_2\text{O}$ ($n = 1$–4, pyz is pyrazine, bipy is 2,2′-bipyridine) and for the preparation of precursor nitrosyl and nitrite polymeric complexes. The preparations utilize the reactivity of coordinated NO and NO_2^- in bis(2,2′-bipyridine)ruthenium(II) complexes and are dependent on sequential, stepwise substitution at two coordination sites. Controlled substitution has been obtained by using labile solvent-complex intermediates. The series of dimeric complexes $[(\text{bipy})_2\text{ClRu(L)RuCl(bipy)}_2](\text{PF}_6)_2\cdot 2\text{H}_2\text{O}$ [L is pyrazine, 4,4′-bipyridine, or *trans*-1,2-bis(4-pyridyl)ethylene] has also been prepared.

Introduction

In the preparative chemistry of inert metal complexes use has been made of intermediates in which a limited number of coordination sites are occupied by weakly bound solvent molecules, *e.g.*[2]

$$(\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}_2(\text{OC(CH}_3)_2)^+ \longrightarrow \left[\begin{array}{l} \xrightarrow{+\text{L}} (\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{L}^+ + (\text{CH}_3)_2\text{CO} \\ \quad \text{L} = \text{CO}, (\text{C}_2\text{H}_5)_2\text{S}, \text{CH}_3\text{CN}, \text{P(C}_6\text{H}_5)_3 \\ \xrightarrow{+\text{X}^-} (\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{X} + (\text{CH}_3)_2\text{CO} \\ \qquad \text{X} = \text{Cl, Br, I, NCS, SCN, NO}_3 \end{array}\right.$$

Several methods have been reported for the preparation of labile intermediates in weakly coordinating solvents, including light-catalyzed displacement of CO,[3] oxidative cleavage of metal-metal bonds,[2] and reactions of coordinated ligands in which the ligand is converted chemically into a non- or weakly binding form. Synthetically important reactions of coordinated ligands include the nitrosation of coordinated azide reported by Haim and Taube[4] and utilized synthetically by Hurst and Taube[5]

$$\text{Co(NH}_3)_5\text{N}_3{}^{2+} + \text{NO}^+ + \text{S} \rightarrow \text{Co(NH}_3)_5\text{S}^{3+} + \text{N}_2 + \text{N}_2\text{O}$$
$$\text{S} = \text{solvent}$$

and the reverse reaction between bound nitrosonium ion and free azide ion which we have reported.[6]

$$\text{Ru(bipy)}_2\text{(NO)Cl}^{2+} + \text{N}_3^- + \text{S} \rightarrow \text{Ru(bipy)}_2\text{SCl}^+ + \text{N}_2 + \text{N}_2\text{O} \qquad (1)$$
$$\text{bipy} = 2,2'\text{-bipyridine}; \text{S} = \text{H}_2\text{O}, \text{CH}_3\text{CN}, \text{CH}_3\text{OH}, (\text{CH}_3)_2\text{CO}$$

When reaction 1 is carried out in acetone or methanol, the resulting solvent complexes have proven to be useful synthetic intermediates for the preparation of a series of bis(2,2′-bipyridine)ruthenium(II) complexes.[7]

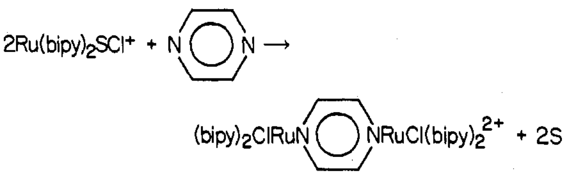
Selectively labile intermediates have also been used for the preparation of complexes in which metal ions are linked by bridging ligands,[8,9] *e.g.*[10]

$$2\text{Ru(NH}_3)_5\text{H}_2\text{O}^{2+} + \text{pyz} \rightarrow (\text{NH}_3)_5\text{Ru(pyz)Ru(NH}_3)_5{}^{4+} + 2\text{H}_2\text{O}$$
$$\text{pyz} = \text{pyrazine}$$

We have been able to prepare a series of ligand-bridged bis(2,2′-bipyridine)ruthenium(II) dimers by similar reactions. Of far greater interest is that by exploiting more fully the chemistry of NO^+ and NO_2^- bound to bis(2,2′-bipyridine)ruthenium(II), we have been able to prepare polymeric complexes of controlled chain length in which ruthenium(II) ions are linked by pyrazine. Part of this work has appeared in a preliminary communication.[11]

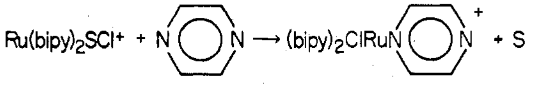
Results and Discussion

Dimeric Complexes. Reaction 1 can be carried out in acetone or methanol giving solvent complexes, $\text{Ru(bipy)}_2\text{SCl}^+$ (S is acetone or methanol), in which only the solvent molecule is easily displaced under mild conditions. By adding controlled amounts of pyrazine to solutions containing the solvent complex, a dimeric 2:1, pyrazine-bridged complex is formed.



(2)

By reversing the order of addition, and adding the solvent complex to excess pyrazine, gives the 1:1 (Ru-pyrazine) complex free of the dimer.



(3)

Both complexes have been isolated as hexafluorophosphate salts. The analogous dimeric 2:1 and 1:1 complexes of 4,4′-bipyridine have also been prepared by the same methods. For all of the complexes reported here the configuration around each ruthenium ion is apparently cis.[12,13]

The 1:1 complexes can themselves react as ligands by using the uncoordinated donor site on the bound pyrazine. By using the reactivity as ligands, we have also prepared unsymmetrical dimeric complexes in stepwise reactions, *viz.*

$$\text{Ru(bipy)}_2\text{(NO)NO}_2{}^{2+} + \text{N}_3^- + \text{S} \rightarrow \text{Ru(bipy)}_2\text{SNO}_2{}^+ + \text{N}_2 + \text{N}_2\text{O} \qquad (4)$$

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[1] National Science Foundation Undergraduate Research Participant, summer 1970.

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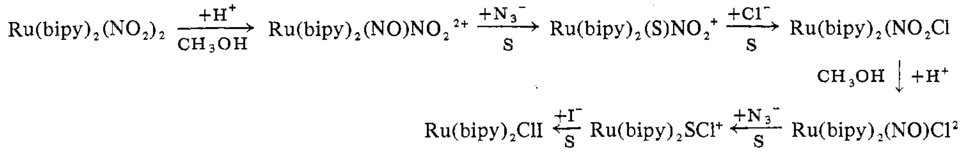
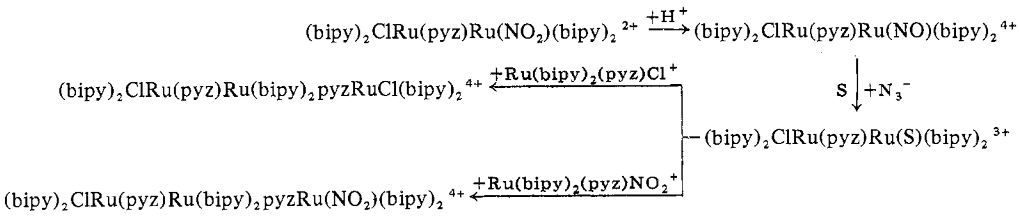
Scheme I



$$\begin{tikzcd}
Ru(bipy)_2(NO_2)_2 \arrow[r, "+H^+", "CH_3OH"'] & Ru(bipy)_2(NO)NO_2{}^{2+} \arrow[r, "+N_3{}^-", "S"'] & Ru(bipy)_2(S)NO_2{}^+ \arrow[r, "+Cl^-", "S"'] & Ru(bipy)_2(NO_2Cl \arrow[d, "CH_3OH"', "+H^+"] \\
 & Ru(bipy)_2ClI & Ru(bipy)_2SCl^+ \arrow[l, "+I^-"', "S"] & Ru(bipy)_2(NO)Cl^{2+} \arrow[l, "+N_3{}^-"', "S"]
\end{tikzcd}$$

Scheme II



$$\begin{tikzcd}
 & (bipy)_2ClRu(pyz)Ru(NO_2)(bipy)_2{}^{2+} \arrow[r, "+H^+"] & (bipy)_2ClRu(pyz)Ru(NO)(bipy)_2{}^{4+} \arrow[d, "S"', "+N_3{}^-"] \\
(bipy)_2ClRu(pyz)Ru(bipy)_2pyzRuCl(bipy)_2{}^{4+} & & (bipy)_2ClRu(pyz)Ru(S)(bipy)_2{}^{3+} \arrow[ll, "+Ru(bipy)_2(pyz)Cl^+"'] \arrow[dll, "+Ru(bipy)_2(pyz)NO_2{}^+"] \\
(bipy)_2ClRu(pyz)Ru(bipy)_2pyzRu(NO_2)(bipy)_2{}^{4+} & &
\end{tikzcd}$$

$$Ru(bipy)_2SNO_2{}^+ + Ru(bipy)_2(pyz)Cl^+ \rightarrow (bipy)_2ClRu(pyz)Ru(NO_2)(bipy)_2{}^{2+} + S \qquad (5)$$

Polymeric Complexes. In bis(2,2′-bipyridine)ruthenium(II) complexes, coordinated NO reacts rapidly with azide ion giving synthetically useful solvent complexes (reactions 1 and 4). Also, coordinated nitrite ion can be converted chemically into nitrosyl.[14]

$$Ru(bipy)_2(NO_2)_2 + 2H^+ \rightarrow Ru(bipy)_2(NO)NO_2{}^{2+} + H_2O \qquad (6)$$

As outlined in Scheme I, the two reactions, when appropriately combined, allow for the sequential, stepwise preparation of complexes in which substitution at two coordination sites can be independently controlled. There are two important limitations in Scheme I and in subsequent schemes. The nitrosyl complexes must be isolated as solids, usually as the $PF_6{}^-$ salt, before being reacted with azide ion, and stoichiometric amounts of azide ion must be used in order to avoid the formation of azido complexes.[15] In most of the preparations described here, steps which involve solvent complexes have been carried out in acetone–methanol solvent mixtures in order to minimize solubility problems. In the preparations it is unclear whether acetone or methanol is the bound solvent molecule.

Reactions between labile metal complexes and pyrazine give ligand-bridged polymeric complexes but of uncontrolled chain length,[16-18] *e.g.*

$$n CoCl_2 + 2n pyz \rightarrow [CoCl_2(pyz)_2]_n$$

Controlled, stepwise polymerization is possible for bis(2,2′-bipyridine) complexes since combinations of reactions like 3–6 allow sequential, stepwise substitution at two coordination sites (Scheme II). If in the last step in Scheme II $Ru(bipy)_2(pyz)NO_2{}^+$ is used to displace S, the resulting complex has a $Ru-NO_2$ unit at the end of the chain. Complexes with the general formula $(bipy)_2ClRu(pyz)[Ru(bipy)_2(pyz)]_nRu(NO_2)(bipy)_2{}^{+2n+2}$, of which $(bipy)_2ClRu(pyz)Ru(NO_2)(bipy)_2{}^{2+}$ is the simplest member, can be recycled through Scheme II adding one unit to the polymeric chain length for each cycle. We have used Scheme II for the preparation of the series of polymeric complexes $(bipy)_2ClRu(pyz)[Ru(bipy)_2pyz]_nRu(NO_2)(bipy)_2{}^{+2n+2}$ (n = 1–3), $(bipy)_2ClRu(pyz)[Ru(bipy)_2pyz]_nRu(NO)(bipy)_2{}^{+2n+4}$ (n = 0–3), and $(bipy)_2ClRu(pyz)[Ru(bipy)_2pyz]_nRuCl(bipy)_2{}^{+2n+2}$ (n = 1–4).

Longer chain complexes can be prepared in single steps by using coupling reactions like reaction 2. For chains containing an even number of ruthenium ions, the coupling agent is the bridging ligand, *viz.*

$$\begin{tikzcd}
(bipy)_2ClRu(pyz)Ru(NO)(bipy)_2{}^{4+} \arrow[r, "+N_3{}^-", "S"'] & (bipy)_2ClRu(pyz)Ru(S)(bipy)_2{}^{3+} \arrow[dl, "+{}^1/_2 pyz"] \\
(bipy)_2ClRu(pyz)[Ru(bipy)_2pyz]_2RuCl(bipy)_2{}^{6+} &
\end{tikzcd}$$

and for chains with odd numbers of ions, $Ru(bipy)_2(pyz)_2{}^{2+}$ is the coupling agent, *viz.*

$$\begin{tikzcd}
Ru(bipy)_2(NO)Cl^{2+} \arrow[r, "+N_3{}^-", "S"'] & Ru(bipy)_2SCl^+ \arrow[d, "+{}^1/_2 Ru(bipy)_2(pyz)_2{}^{2+}"] \\
 & (bipy)_2ClRu(pyz)[Ru(bipy)_2pyz]RuCl(bipy)_2{}^{4+}
\end{tikzcd}$$

The polymeric complexes have been isolated as hexafluorophosphate salts which are soluble in polar organic solvents, most notably acetone and acetonitrile. The longer chain complexes show an increasing solubility in water. Several of the complexes appear to undergo a light-catalyzed decomposition in acetonitrile which is apparently a light-induced solvolysis.[15] In the absence of light, all of the complexes are stable in acetone or acetonitrile for periods of at least several hours. As shown by infrared and by elemental analyses, most of the salts reported here contain waters of crystallization. The waters of crystallization are held tenaciously since they cannot be removed by drying *in vacuo* over P_4O_{10}, and they are retained even when the salts are recrystallized from organic solvents.

Conductivity data for the complexes $[Ru(bipy)_2(pyz)Cl](PF_6)$ and $[(bipy)_2ClRu(pyz)[Ru(bipy)_2pyz]_nRuCl(bipy)_2](PF_6)_{2n+2}\cdot(n + 2)H_2O$ (n = 0–2) in acetone at 25.0 ± 0.3° are given in Table I. The conductivity data are consistent with the expected values for the various charge types in dilute solution.[19]

Infrared Spectra. In the complex $Ru(bipy)_2(NO)NO_2{}^{2+}$, bound nitrite ion is present only as the nitro (N-bound) isomer. Both nitro and nitrito (O-bound nitrite) complexes result from the reaction between the nitrosyl complex and

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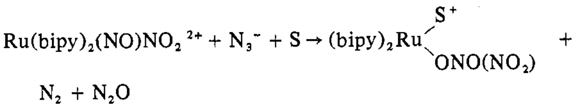
Table I. Conductivity Data at 25.0 ± 0.3° in Acetone

Complex	Conductivity, $cm^2\ ohm^{-1}\ mol^{-1}$ [a]
$[Ru(bipy)_2(pyz)Cl](PF_6)$	163
$[(bipy)_2ClRu(pyz)RuCl(bipy)_2](PF_6)_2 \cdot 2H_2O$	315
$[(bipy)_2ClRu(pyz)[Ru(bipy)_2pyz]\text{-}RuCl(bipy)_2](PF_6)_4 \cdot 3H_2O$	518
$[(bipy)_2ClRu(pyz)[Ru(bipy)_2pyz]_2\text{-}RuCl(bipy)_2](PF_6)_6 \cdot 4H_2O$	636

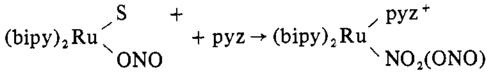
[a] Average of at least two determinations at concentrations $<10^{-4}$ *M*.

azide ion in acetone (S)



$$Ru(bipy)_2(NO)NO_2{}^{2+} + N_3{}^- + S \rightarrow (bipy)_2Ru\begin{matrix} S^+ \\ ONO(NO_2) \end{matrix} + N_2 + N_2O$$

but the nitrito isomer is highly favored (>95%).[7] Displacement of coordinated acetone from $Ru(bipy)_2[(CH_3)_2CO]\text{-}ONO^+$ gives mixtures in which both nitro and nitrito isomers are important,[7] *e.g.*



$$(bipy)_2Ru\begin{matrix} S \\ ONO \end{matrix}{}^{+} + pyz \rightarrow (bipy)_2Ru\begin{matrix} pyz^+ \\ NO_2(ONO) \end{matrix} \qquad (7)$$

The complex $Ru(bipy)_2(pyz)NO_2^+$ used in Scheme II was prepared using reaction 7 so that the series of complexes $(bipy)_2ClRu(pyz)[Ru(bipy)_2pyz]_n\ Ru(NO_2)(bipy)_2{}^{+2n+2}$ are actually mixtures of nitro and nitrito isomers. The presence of both isomers can be seen clearly in the infrared (Table II).

Both nitro and nitrito isomers react essentially quantitatively with acid in methanol, *e.g.*

$$(bipy)_2ClRu(pyz)Ru(NO_2)(bipy)_2{}^{2+} + 2H^+ \rightarrow (bipy)_2ClRu(pyz)Ru(NO)(bipy)_2{}^{4+} + H_2O$$

since the resulting nitrosyl complexes are obtained in high yield (~90%). In the infrared the nitrosyl complexes have very intense ν_{NO} bands in the region 1940-1950 cm^{-1} (Table II) as expected.[20]

In Table II are also given data for the characteristic centrosymmetric pyrazine stretch at ~1600 cm^{-1} [ν(pyz)]. The transition is infrared allowed for the 1:1 complexes which contain unidentate pyrazine and Raman allowed for bidentate pyrazine.[21] As expected, ν(pyz) is absent in the infrared spectra of the pyrazine-bridged complexes.

Experimental Section

Infrared spectra were recorded on Perkin-Elmer 421 or Beckman IR-12 spectrophotometers in KBr pellets. Sodium azide and potassium azide were recrystallized from water and then ethanol-water before use. Water was deionized and then distilled from alkaline permanganate. Acetone and methanol (Reagent Grade) were dried over magnesium sulfate and molecular sieves, respectively. The preparation of the nitrosyl complexes $[Ru(bipy)_2(NO)Cl](PF_6)_2$ and $[Ru(bipy)_2(NO)(NO_2)](PF_6)_2$ was described previously.[20]

Preparations. $[Ru(bipy)_2(L)X](PF_6)$ [L = Pyrazine, X = Cl or NO_2; L = 4,4′-Bipyridine (4,4′-bipy) or *trans*-1,2-Bis(4-pyridyl)-ethylene (BPE), X = Cl]. In a typical reaction, $(bipy)_2Ru(NO)Cl^{2+}$ (0.200 g, 0.260 mmol) was dissolved in 20 ml of acetone giving a light yellow solution. A stoichiometric amount of KN_3 (0.0211 g, 0.260 mmol) was dissolved in 5-10 ml of methanol by warming. The clear potassium azide solution was added dropwise and slowly to the $(bipy)_2Ru(NO)Cl^{2+}$ solution. Care was taken to add the KN_3 solution quantitatively. An immediate reaction occurred giving a purple-brown solution of the solvent complex accompanied by gas evolution. The purple-brown solution was stirred 15 min and then filtered to remove KPF_6. The filtered solution was added dropwise to a solution of pyrazine in acetone (0.200 g, 2.500 mmol in 5 ml). The solution was stirred and heated at 35-40° for 0.5 hr giving a deep red-brown solution. Anhydrous ether (~200 ml) was added to the solution giving a red-brown solid. The solid was filtered and reprecipitated twice from acetone-ether and then dried over P_4O_{10} *in vacuo* overnight, yield 80%. *Anal.* Calcd for $[Ru(bipy)_2(pyz)Cl]\text{-}(PF_6)$: C, 42.77; H, 3.00; N, 12.47; F, 16.91. Found: C, 42.50; H, 2.98; N, 12.19; F, 16.71. Calcd for $[Ru(bipy)_2(pyz)NO_2](PF_6) \cdot H_2O$: C, 41.02; H, 3.13; N, 13.95. Found: C, 40.53; H, 2.87; N, 13.18. Calcd for $[Ru(bipy)_2(BPE)Cl](PF_6) \cdot 2H_2O$: C, 47.32; H, 3.73; N, 10.35; Cl, 4.37; F, 14.04. Found: C, 46.90; H, 3.53; N, 10.34; Cl, 5.00; F, 14.41. Calcd for $[Ru(bipy)_2(4,4'\text{-}bipy)Cl]\text{-}(PF_6) \cdot H_2O$: C, 46.91; H, 3.42; N, 10.94; Cl, 4.62; F, 14.84. Found: C, 46.48; H, 3.61; N, 10.89; Cl, 4.57; F, 14.74.

$[Ru(bipy)_2(pyz)_2](PF_6)_2$. $Ru(bipy)_2Cl_2 \cdot 2H_2O$ (0.534 g, 1.10 mmol) was added to water (50 ml) and the resulting suspension heated at reflux under nitrogen for 30 min. A tenfold excess of pyrazine (0.881 g, 11.00 mmol) was added to the red-brown solution of $Ru(bipy)_2(H_2O)Cl^+$ formed and heating was continued for 15 min giving a yellow-orange solution. The yellow-orange solution was heated on a steam bath for 1-2 hr and filtered, and 10 ml of a saturated aqueous solution of NH_4PF_6 was added dropwise to the filtrate. A yellow-orange solid precipitated which was recrystallized from acetone-ether, yield 69.5%. *Anal.* Calcd for $[Ru(bipy)_2\text{-}(pyz)_2](PF_6)_2$: C, 38.9; H, 2.78; N, 12.98. Found: C, 38.74; H, 2.65; N, 12.73.

$[(bipy)_2ClRu(L)RuX(bipy)_2](PF_6)_2$ [L = Pyrazine, X = Cl or NO_2; L = *trans*-1,2-Bis(4-pyridyl)ethylene or 4,4′-Bipyridine, X = Cl). The bridged dimers were prepared successfully by two routes: (1) by reacting the solvent complex intermediate $Ru(bipy)_2(S)Cl^+$ with a stoichiometric amount of the appropriate 1:1 ligand-Ru complex, *e.g.*, $Ru(bipy)_2(pyz)X^+$ (X = Cl, NO_2), and (2) by reacting the solvent complex with 0.5 equiv of the appropriate bridging ligand. All of the preparations were carried out in the absence of light. In a typical preparation for $[(bipy)_2ClRu(pyz)RuCl(bipy)_2](PF_6)_2 \cdot 2H_2O$, KN_3 (0.0211 g, 0.260 mmol) was dissolved in warm methanol (5 ml). The potassium azide solution was added slowly dropwise to an acetone solution of $Ru(bipy)_2(NO)Cl^{2+}$ (0.260 mmol). The resulting solution was stirred for 15 min and warmed to 40°, and pyrazine (0.0104 g, 0.130 mmol) in acetone (5 ml) was added dropwise. The solution was stirred at 35-40° for 0.5 hr after which time it was added to excess ether. The solid which precipitated was collected on a frit, washed with ether, and recrystallized from dichloromethane-pentane. The solid was dried *in vacuo* over P_4O_{10}, yield 52%. *Anal.* Calcd for $[(bipy)_2ClRu(pyz)RuCl(bipy)_2](PF_6)_2 \cdot 2H_2O$: C, 40.53; H, 3.10; N, 10.74; Cl, 5.44; F, 17.49. Found: C, 40.43; H, 2.91; N, 10.27; Cl, 5.68; F, 17.74. Calcd for $[(bipy)_2ClRu(BPE)\text{-}RuCl(bipy)_2](PF_6)_2 \cdot 2H_2O$: C, 44.42; H, 3.30; N, 9.96; Cl, 5.04; F, 16.23. Found: C, 44.00; H, 3.21; N, 10.03; Cl, 4.87; F, 15.56. Calcd for $[(bipy)_2ClRu(4,4'\text{-}bipy)RuCl(bipy)_2](PF_6)_2 \cdot 2H_2O$: C, 43.51; H, 3.22; N, 10.15. Found: C, 42.76; H, 2.87; N, 10.05.

$[(bipy)_2ClRu(pyz)[Ru(bipy)_2pyz]_nRuX(bipy)_2](PF_6)_{2n+2}$ (X = Cl, *n* = 1-4; X = NO_2, *n* = 1-3). Three procedures were used for the preparations of the polymeric complexes. (1) All of the complexes were prepared by reacting stoichiometric amounts of the appropriate 1:1 ligand-Ru complexes $Ru(bipy)_2(pyz)X^+$ with the solvent complex $(bipy)_2ClRu(pyz)[Ru(bipy)_2pyz]_xRu(S)(bipy)_2{}^{+2X+3}$ (*x* = 0, . . ., *n* − 1) which had been generated by the reaction between the corresponding nitrosyl complex and azide ion. (2) For the complex $(bipy)_2ClRu(pyz)[Ru(bipy)_2pyz]_2Ru(Cl)(bipy)_2{}^{6+}$ in which there is an even number of ruthenium ions in the chain, the solvent complex $(bipy)_2ClRu(pyz)Ru(S)(bipy)_2{}^{3+}$ was allowed to react with 0.5 equiv of pyrazine. (3) For the complex $(bipy)_2ClRu(pyz)\text{-}[Ru(bipy)_2pyz]RuCl(bipy)_2{}^{4+}$ in which there is an odd number of ruthenium ions, $Ru(bipy)_2(S)Cl^+$ was allowed to react with 0.5 equiv of $Ru(bipy)_2(pyz)_2{}^{2+}$. All of the preparations were carried out in the absence of light. In a typical preparation $[(bipy)_2\text{-}ClRu(pyz)Ru(NO)(bipy)_2](PF_6)_4$ (0.3880 g, 0.250 mmol) was dissolved in acetone (15 ml) and to it was added slowly (dropwise) KN_3 (0.0203 g, 0.250 mmol) in warm methanol (5 ml). As it was added, the azide ion reacted rapidly with gas evolution and the solution color changed from red brown to purple brown. After complete addition of azide ion, $[Ru(bipy)_2(pyz)NO_2](PF_6)$ (0.1711 g, 0.250 mmol) dissolved in the minimum volume of acetone was added slowly changing the solution color back to red brown. The red-brown solution was warmed at 35-40° with stirring for 0.5 hr and filtered, and the filtrate was added to excess ether giving a red-brown precipitate. The solid was dissolved in acetone to remove KPF_6 and reprecipitated with ether. It was then washed twice with warm water (50-60°), recrystallized from acetone-ether, air-dried, and then

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Table II. Characteristic Infrared Bands in cm^{-1} [a]

Complex	ν(pyz)	ν(NO)		
		Nitrosyl	Nitro	Nitrito
$[(\mathrm{bipy})_2\mathrm{Ru}(\mathrm{pyz})\mathrm{Cl}](\mathrm{PF}_6)$	1588 (s)			
$[(\mathrm{bipy})_2\mathrm{Ru}(\mathrm{pyz})\mathrm{NO}_2](\mathrm{PF}_6)\cdot\mathrm{H}_2\mathrm{O}$	1585 (s)		1338 (s), 1294 (s)	1393 (sh), 1133 (s, br)
$[(\mathrm{bipy})_2\mathrm{ClRu}(\mathrm{pyz})\mathrm{Ru}(\mathrm{NO}_2)(\mathrm{bipy})_2](\mathrm{PF}_6)_2\cdot 2\mathrm{H}_2\mathrm{O}$			1340 (s), 1295 (2)	1395 (sh), 1135 (s, br)
$[(\mathrm{bipy})_2\mathrm{ClRu}(\mathrm{pyz})\mathrm{Ru}(\mathrm{NO})(\mathrm{bipy})_2](\mathrm{PF}_6)_4$		1940 (vs)		
$[(\mathrm{bipy})_2\mathrm{ClRu}(\mathrm{pyz})[\mathrm{Ru}(\mathrm{bipy})_2\mathrm{pyz}]\mathrm{Ru}(\mathrm{NO})(\mathrm{bipy})_2](\mathrm{PF}_6)_6$		1942 (vs)		

[a] In KBr pellets; ±4 cm^{-1}. Abbreviations used are very strong (vs), strong (s), shoulder (sh), and broad (br).

dried over $\mathrm{P}_4\mathrm{O}_{10}$ *in vacuo* overnight, yield 60%. *Anal.* Calcd for $[(\mathrm{bipy})_2\mathrm{ClRu}(\mathrm{pyz})[\mathrm{Ru}(\mathrm{bipy})_2\mathrm{pyz}]_n\mathrm{RuCl}(\mathrm{bipy})_2](\mathrm{PF}_6)_{2n+2}\cdot(n+2)\mathrm{H}_2\mathrm{O}$ ($n = 1$): C, 38.78; H, 2.94; N, 10.64; Cl, 3.37. Found: C, 38.38; H, 2.76; N, 10.80; Cl, 3.25. Calcd ($n = 2$): C, 38.01; H, 2.89; N, 10.59; Cl, 2.44. Found: C, 38.27; H, 3.09; N, 10.74; Cl, 2.30. Calcd ($n = 3$): C, 39.00; H, 2.87; N, 10.62. Found: C, 39.90; H, 3.02; N, 11.35. Calcd ($n = 4$): C, 37.25; H, 2.87; N, 10.55. Found: C, 38.01; H, 3.10; N, 10.06.

$[(\mathrm{bipy})_2\mathrm{ClRu}(\mathrm{pyz})[\mathrm{Ru}(\mathrm{bipy})_2\mathrm{pyz}]_n\mathrm{Ru}(\mathrm{NO})(\mathrm{bipy})_2](\mathrm{PF}_6)_{2n+4}$. The nitrosyl complexes were prepared in methanol by adding acid to the corresponding nitrite complexes. As an example the preparation of $[(\mathrm{bipy})_2\mathrm{ClRu}(\mathrm{pyz})\mathrm{Ru}(\mathrm{NO})(\mathrm{bipy})_2](\mathrm{PF}_6)_4$ is given below. $[(\mathrm{bipy})_2\mathrm{ClRu}(\mathrm{pyz})\mathrm{Ru}(\mathrm{NO}_2)(\mathrm{bipy})_2](\mathrm{PF}_6)_2$ (0.500 g, 0.391 mmol) was suspended with stirring in methanol (30 ml). To the suspension was added dropwise 6 ml of 70% HPF_6 and stirring was continued for several minutes. Ether was added and the deep red-brown precipitate was collected on a frit, reprecipitated three times from acetone–ether, washed twice with ether, air-dried, and finally dried over $\mathrm{P}_4\mathrm{O}_{10}$ *in vacuo* overnight, yield 90%. *Anal.* Calcd for $[(\mathrm{bipy})_2\mathrm{ClRu}(\mathrm{pyz})\mathrm{Ru}(\mathrm{NO})(\mathrm{bipy})_2](\mathrm{PF}_6)_4$: C, 34.04; H, 2.32; N, 9.92; Cl, 2.29. Found: C, 33.86; H, 2.32; N, 9.83; Cl, 2.14. Calcd for $[(\mathrm{bipy})_2\mathrm{ClRu}(\mathrm{pyz})[\mathrm{Ru}(\mathrm{bipy})_2\mathrm{pyz}]\mathrm{Ru}(\mathrm{NO})(\mathrm{bipy})_2](\mathrm{PF}_6)_6$: C, 34.17; H, 2.59; N, 9.96; Cl, 1.49. Found: C, 35.10; H, 2.55; N, 9.97; Cl, 1.39. Elemental analyses were not obtained for the remainder of the nitrosyl and nitrite complexes since they were utilized as intermediates for the preparation of the longer chain polymeric complexes.

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Registry No. $[\mathrm{Ru}(\mathrm{bipy})_2(\mathrm{pyz})\mathrm{Cl}](\mathrm{PF}_6)$, 40537-43-7; $[\mathrm{Ru}(\mathrm{bipy})_2(\mathrm{pyz})\mathrm{NO}_2](\mathrm{PF}_6)\cdot\mathrm{H}_2\mathrm{O}$, 40548-18-3; $[\mathrm{Ru}(\mathrm{bipy})_2(\mathrm{BPE})\mathrm{Cl}](\mathrm{PF}_6)\cdot 2\mathrm{H}_2\mathrm{O}$, 40548-19-4; $[\mathrm{Ru}(\mathrm{bipy})_2(4,4'\text{-bipy})\mathrm{Cl}](\mathrm{PF}_6)\cdot\mathrm{H}_2\mathrm{O}$, 40548-20-7; $[\mathrm{Ru}(\mathrm{bipy})_2(\mathrm{pyz})_2](\mathrm{PF}_6)_2$, 40537-44-8; $[(\mathrm{bipy})_2\mathrm{ClRu}(\mathrm{pyz})\mathrm{RuCl}(\mathrm{bipy})_2](\mathrm{PF}_6)_2\cdot 2\mathrm{H}_2\mathrm{O}$, 40548-21-8; $[(\mathrm{bipy})_2\mathrm{ClRu}(\mathrm{BPE})\mathrm{RuCl}(\mathrm{bipy})_2](\mathrm{PF}_6)_2\cdot 2\mathrm{H}_2\mathrm{O}$, 40587-86-8; $[(\mathrm{bipy})_2\mathrm{ClRu}(4,4'\text{-bipy})\mathrm{RuCl}(\mathrm{bipy})_2](\mathrm{PF}_6)_2\cdot 2\mathrm{H}_2\mathrm{O}$, 40548-22-9; $[(\mathrm{bipy})_2\mathrm{ClRu}(\mathrm{pyz})[\mathrm{Ru}(\mathrm{bipy})_2\mathrm{pyz}]\mathrm{RuCl}(\mathrm{bipy})_2](\mathrm{PF}_6)_4\cdot\mathrm{H}_2\mathrm{O}$, 40548-23-0; $[(\mathrm{bipy})_2\mathrm{ClRu}(\mathrm{pyz})[\mathrm{Ru}(\mathrm{bipy})_2\mathrm{pyz}]_2\mathrm{RuCl}(\mathrm{bipy})_2](\mathrm{PF}_6)_6\cdot 2\mathrm{H}_2\mathrm{O}$, 39296-34-9; $[(\mathrm{bipy})_2\mathrm{ClRu}(\mathrm{pyz})[\mathrm{Ru}(\mathrm{bipy})_2\mathrm{pyz}]_3\mathrm{RuCl}(\mathrm{bipy})_2](\mathrm{PF}_6)_8\cdot 3\mathrm{H}_2\mathrm{O}$, 40548-24-1; $[(\mathrm{bipy})_2\mathrm{ClRu}(\mathrm{pyz})[\mathrm{Ru}(\mathrm{bipy})_2\mathrm{pyz}]_4\mathrm{RuCl}(\mathrm{bipy})_2](\mathrm{PF}_6)_{10}\cdot 4\mathrm{H}_2\mathrm{O}$, 39296-35-0; $[(\mathrm{bipy})_2\mathrm{ClRu}(\mathrm{pyz})\mathrm{Ru}(\mathrm{NO})(\mathrm{bipy})_2](\mathrm{PF}_6)_4$, 40537-45-9; $[(\mathrm{bipy})_2\mathrm{ClRu}(\mathrm{pyz})[\mathrm{Ru}(\mathrm{bipy})_2\mathrm{pyz}]\mathrm{Ru}(\mathrm{NO})(\mathrm{bipy})_2](\mathrm{PF}_6)_6$, 40537-46-0; $[(\mathrm{bipy})_2\mathrm{ClRu}(\mathrm{pyz})\mathrm{Ru}(\mathrm{NO}_2)(\mathrm{bipy})_2](\mathrm{PF}_6)_2\cdot 2\mathrm{H}_2\mathrm{O}$, 40537-47-1; $[\mathrm{Ru}(\mathrm{bipy})_2(\mathrm{NO})\mathrm{Cl}](\mathrm{PF}_6)_2$, 29102-12-3; $[\mathrm{Ru}(\mathrm{bipy})_2(\mathrm{NO})(\mathrm{NO}_2)](\mathrm{PF}_6)_2$, 29240-99-1; $\mathrm{Ru}(\mathrm{bipy})_2\mathrm{Cl}_2$, 15746-57-3.

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Oxalate Anation of α-*cis*-Ethylenediamine-*N*,*N*′-diacetatodiaquocobalt(III) Ion in Slightly Acidic Aqueous Medium[1]

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The reaction of α-*cis*-$\mathrm{Co}(\mathrm{EDDA})(\mathrm{OH}_2)_2^+$ with members of the oxalate system in the pH range 4.5–5.2 yields geometrically pure β-*cis*-$\mathrm{Co}(\mathrm{EDDA})(\mathrm{C}_2\mathrm{O}_4)^-$. Evidence indicates that the geometry change occurs at or after the rate-determining step. The reaction appears to proceed *via* ion-pair equilibration followed by rate-determining substitution. Values for the association constants for the ion pairs α-*cis*-$\mathrm{Co}(\mathrm{EDDA})(\mathrm{OH}_2)_2^+,\mathrm{HC}_2\mathrm{O}_4^-$ and α-*cis*-$\mathrm{Co}(\mathrm{EDDA})(\mathrm{OH}_2)_2^+,\mathrm{C}_2\mathrm{O}_4^{2-}$ are 41 and 72, respectively, at 38° and $\mu = 0.50$. In the pH range studied, the species $\mathrm{Co}(\mathrm{EDDA})(\mathrm{OH})(\mathrm{OH}_2)^0$ makes an important contribution to the generation of product.

Introduction

Harris and coworkers have recently reported on their studies of the anation of various aquo-containing cobalt(III) and chromium(III) complexes with members of the oxalate system.[2-4] Effectively they proposed an ion-pair equilibration between complex and the oxalate member prior to the slower rate-determining ligand–water dissociation. Other workers[5] have proposed similar mechanisms for numbers of anation reactions involving coordination complexes.

We have chosen to investigate the oxalate anation of α-*cis*-ethylenediamine-*N*,*N*′-diacetatodiaquocobalt(III) ion (α-*cis*-$\mathrm{Co}(\mathrm{EDDA})(\mathrm{OH}_2)_2^+$) for numbers of reasons.[6]

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