X-ray Structure Determination.[7] Details of data collection and structure solution are summarized in Table I. Atomic coordinates are listed in Table II, and Table III contains selected bond lengths and angles. A picture of the molecule showing the atomic labeling scheme is presented in Figure 1.

1 exists in the solid state in dimeric units. Two dmpm ligand molecules[8] serve as bridges between the $Ni(CO)_2$ groups forming an eight-membered ring. This ring adopts a boat conformation, and the halves of the molecule are related by a pseudo-2-fold axis. The nonbonded Ni–Ni distance is 4.39 Å.

The coordination geometry of the Ni and P atoms may be described as tetrahedral with P–Ni–P angles of 108.5 (1) and 109.2 (1)°. The P–C–P angles of 119.1 (1) and 119.5 (2)° are 10° larger than the ideal tetrahedral angle. The Ni–P bond lengths of 2.200 (1)–2.219 (1) Å are somewhat longer than those observed in $(dmpe)(PPh_3)Ni(C_2H_4)$[3] and $(dmpe)Ni(C_2Ph_2)$[4] (2.155–2.179 Å). The average P–C (bridging) distance in **1** (1.842 (5) Å) is comparable to known values.[3,4] Inspection of intermolecular distances showed no contacts smaller than 3.5 Å (nonhydrogen atoms).

Acknowledgment. We thank Professor O. Stelzer, Wuppertal, for a sample of dmpm and Dr. R. Mynott of this institute for the carbon-13 NMR studies.

Supplementary Material Available: Tables of atomic coordinates and thermal parameters and bond lengths and angles (2 pages). Ordering information is given on any current masthead page. According to policy instituted Jan 1, 1986, the tables of calculated and observed structure factors (17 pages) are being retained in the editorial office for a period of 1 year following the appearance of this work in print. Inquiries for copies of these materials should be directed to the Editor.

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(7) In addition to several locally written programs, the following programs were used: TRACER by Lawton and Jacobson for cell reduction; DATAP by Coppens, Leiserowitz, and Rabinovich for data reduction; DIFABS by Walker and Stuart for empirical absorption correction; Sheldrick's SHELX-76/84 for Fourier calculations and initial least-squares refinement; GFMLS, a highly modified version of ORFLS, by Hirshfeld, Coppens, Leiserowitz, and Rabinovich for subsequent full-matrix least-squares refinement; Davis' DAESD for bond distance and angle calculations; Roberts and Sheldrick's XANADU for best plane and torsion angle calculations; Johnson's ORTEP for the molecular drawings. See: *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4.

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Kinetics and Mechanism of the Ligand Substitution Reactions of Pentacyano(ligand)ruthenate(II) Complexes

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The ligand substitution reactions of pentacyanoferrate(II) complexes, $Fe(CN)_5L^{(3-n)-}$, have been the subject of considerable interest for a number of years.[1-8] An extensive series of complexes, substituted with N-, O-, S-, and P-donor ligands L^{n+}, have been synthesized from the labile $Fe(CN)_5OH_2^{3-}$ ion. Kinetic, thermodynamic, and volume of activation[3] data from numerous mechanistic studies are consistent with a dissociative mechanism for ligand substitutions in these complexes. Correlations between the spectroscopic properties of the $Fe(CN)_5L^{(3-n)-}$ complexes and other low-spin d^6 species such as $Ru(NH_3)_5L^{(2+n)+}$,[1] and recently $Ru(CN)_5L^{(3-n)-}$,[9] have been established. These low-spin iron species also represent models for biological systems and have been used in the investigations of specific binding groups in amino acids[8] and in redox reactions with metalloproteins.[10]

Table I. Rate and Activation Parameters for Ligand Substitution of L^{n+} by Y^{m+} in $Ru(CN)_5L^{(3-n)-}$ Complexes (pH 7.0, I = 0.10 M)

L^{n+}	Y^{m+}	10^5k_{-L}, s^{-1}	ΔH^*, kcal mol^{-1}	ΔS^*, cal K^{-1} mol^{-1}
N-mepyz$^+$	Me_2SO	6.31	24.5 ± 0.5	5 ± 2
	py	5.97		
	im	6.74		
	pyz	5.91		
pyrpyr$^+$	Me_2SO	4.17	24.0 ± 0.4	2 ± 1
	py	3.79		
	im	4.32		
bpy	Me_2SO	6.79	22.2 ± 0.2	−3 [illegible] 1
pyz	Me_2SO	1.77	22.4 ± 1.7	−5 ± 5
	N-mepyz$^+$	1.57		
py	Me_2SO	3.34	25.6 ± 1.3	7 ± 4
	N-mepyz$^+$	3.39		
im	N-mepyz$^+$	10.7	22.2 ± 0.7	−2 ± 2
	py	11.7		
isonic$^-$	Me_2SO	1.67	25.1 ± 0.3	4 ± 1
	N-mepyz$^+$	1.33		
Me_2SO	N-mepyz$^+$	0.850	24.4 ± 0.4	−1 ± 1
	py	0.812		
	pyz	0.774		

In contrast to the work on the pentacyanoferrate(II) complexes, very little has been reported on the analogous ruthenium(II) system until recently. The replacement of the coordinated water ligand in $Ru(CN)_5OH_2^{3-}$ by other ligands, such as aromatic nitrogen heterocycles, gives rise to an equally extensive series of substituted pentacyanoruthenate(II) complexes.[11] We have recently reported the results of a kinetic study of the substitution reactions of the $Ru(CN)_5OH_2^{3-}$ ion,[12] which implicates an ion-pair dissociative mechanism, with a water exchange rate of 10 ± 5 s^{-1}, 1 order of magnitude lower than found for the $Fe(CN)_5OH_2^{3-}$ ion.

In the present paper the results of a kinetic study of the ligand-exchange reactions of substituted pentacyanoruthenate(II) complexes are reported. The rate and activation parameters for the dissociation of L^{n+}, where L^{n+} is dimethyl sulfoxide or a nitrogen heterocycle, from $Ru(CN)_5L^{(3-n)-}$ have been determined and are compared with values for the analogous pentacyanoferrate(II) complexes and for other ruthenium(II) complexes.

Experimental Section

Materials. Imidazole, isonicotinic acid, 1-(4-pyridyl)pyridinium chloride hydrochloride, pyrazine (Gold Label), and 4,4′-bipyridine hydrate from Aldrich and dimethyl sulfoxide and pyridine from Fisher were used as received. N-Methylpyrazinium iodide was prepared by the methylation of pyrazine by methyl iodide in chloroform.[1,13] The pentacyanoaquoruthenate(II) ion, $Ru(CN)_5OH_2^{3-}$, was prepared from the reaction of the $Ru(CN)_6^{4-}$ ion (From $K_4Ru(CN)_6{\cdot}3H_2O$, Alfa) with bromine in aqueous solution.[11] Solutions of the substituted penta-

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Table II. Rate and Equilibrium Constants for Ligand Substitution in Pentacyano(ligand)ruthenate(II) and Pentacyano(ligand)ferrate(II) Complexes

	$Ru(CN)_5L^{(3-n)-}$			$Fe(CN)_5L^{(3-n)-}$		
ligand L	k_L,[a] $M^{-1}\ s^{-1}$	10^5k_{-L},[b] s^{-1}	$10^{-5}K$, M^{-1}	k_L, $M^{-1}\ s^{-1}$	10^3k_{-L}, s^{-1}	$10^{-5}K$, M^{-1}
N-methylpyrazinium	47.2	6.31	7.5	550[c]	0.28[g]	20
pyridylpyridinium	44.4	4.17	11	2050[d]	2.6[d]	7.9
bipyridine	14.4	6.79	2.1	365[d]	0.62[g]	5.9
pyrazine	10.5	1.77	5.9	380[c]	0.42[g]	9.0
pyridine	5.4	3.34	1.6	365[c]	1.10[g]	3.3
imidazole	5.1	10.7	0.48	240[e]	1.33[e]	1.8
isonicotinate	3.5	1.67	2.1	60[d]	0.40[d]	1.5
dimethyl sulfoxide	13.1[b]	0.85	15	240[f]	0.075[f]	32

[a] Reference 12 (I = 0.10 M). [b] This work (I = 0.10 M). [c] Reference 1b (I = 0.50 M, except for *N*-mepyz$^+$, where I = 1.00 M). [d] Macartney, D. H., unpublished results (I = 0.10 M). [e] Reference 5 (I = 0.10 M). [f] Reference 14 (I = 1.00 M). [g] Reference 1a (I = 1.00 M).

cyano(ligand)ruthenate(II) complexes (10^{-4} M) were prepared by the addition of a 10-fold excess of the appropriate ligand to the nitrogen-saturated solutions of the $Ru(CN)_5OH_2^{3-}$ ion. The mixed solutions were allowed to stand for 30 min to ensure complete reaction before kinetic measurements on the dissociation reactions were started.

Kinetic Measurements. Kinetic measurements were made by using a Bausch and Lomb Spectronic 2000 spectrophotometer, modified with a cell block thermostated by means of an external water bath. The ligand dissociation reactions were followed by monitoring at the λ_{max} of the $Ru(CN)_5L^{(3-n)-}$ reactant or $Ru(CN)_5Y^{(3-m)-}$ product species.[12] Pseudo-first-order conditions of excess ligand concentrations (Y is primarily dimethyl sulfoxide or the *N*-methylpyrazinium cation) were employed, and the reactions were monitored for 2–3 half-lives. Infinity absorbance readings were recorded after 8–10 half-lives, and first-order rate constants were determined from least-squares plots of ln ($A_t - A_\infty$) or ln ($A_\infty - A_t$) against time. The pH of the reaction solutions was maintained at 7.0 with use of phosphate buffers. All of the solutions were prepared at an ionic strength of 0.10 M with added sodium chloride.

Results and Discussion

The formation of substituted pentacyanoruthenate(II) complexes from the $Ru(CN)_5OH_2^{3-}$ ion (eq 1) has been shown to follow an ion-pair dissociative mechanism.[12] The observed

$$Ru(CN)_5OH_2^{3-} + L^{n+} \underset{k_{-L}}{\overset{k_L}{\rightleftharpoons}} Ru(CN)_5L^{(3-n)-} + H_2O \quad (1)$$

first-order rate constant k_{obsd} displayed a first-order dependence on $[L^{n+}]$, with k_L dependent on the charge and size of L^{n+}. The lack of an intercept in the plots of k_{obsd} against $[L^{n+}]$ suggested that ligand exchange in $Ru(CN)_5L^{(3-n)-}$ is very much slower than the replacement of H_2O in $Ru(CN)_5OH_2^{3-}$. The kinetics of ligand exchange in $Ru(CN)_5L^{(3-n)-}$ complexes were determined by following the dissociation of L^{n+} in the presence of an excess of a second incoming ligand Y^{m+}:

$$Ru(CN)_5L^{(3-n)-} + Y^{m+} \rightarrow Ru(CN)_5^{(3-m)-} + L^{n+} \quad (2)$$

In this study L^{n+} is dimethyl sulfoxide (Me_2SO) or a nitrogen heterocycle: pyridine (py), pyrazine (pyz), imidazole (im), bipyridine (bpy), isonicotinate (isonic$^-$), pyridylpyridinium (pyrpyr$^+$), and *N*-methylpyrazinium (*N*-mepyz$^+$). The entering ligand Y^{m+} was primarily dimethyl sulfoxide or the *N*-methylpyrazinium cation. Dimethyl sulfoxide forms a very stable colorless complex with pentacyanoruthenate(II) (k_L = 13 $M^{-1}\ s^{-1}$). The *N*-methylpyrazinium complex (λ_{max} = 524 nm) is also very stable and forms rapidly in solution.[12] Both ligands have frequently been employed in kinetics studies of substitution reactions of $Fe(CN)_5L^{3-}$ complexes.[1,8,14]

The reactions of $Ru(CN)_5L^{(3-n)-}$ in the presence of an excess of Y^{m+} resulted in a first-order formation of $Ru(CN)_5Y^{(3-m)-}$ or loss of $Ru(CN)_5L^{(3-n)-}$. Deviations of the first-order behavior after 4 or 5 half-lives (~24 h) were observed in some reactions and are attributed to possible side processes, such as cyanide substitution and dimer formation.[15] Over the range of $[Y^{m+}]$ = 0.001–0.100 M the rate of dissociation k_{obsd} increases or (for L^{n+} = Me_2SO) decreases to a limiting value (Figure 1). The limiting rate constants and the corresponding activation parameters for the complexes in this study are presented in Table I. The dissociations of the $Ru(CN)_5L^{(3-n)-}$ complexes were also studied in the presence of several different ligands. Varying the nature of Y^{m+} had a negligible effect, within experimental error, on the limiting rate of dissociation (Table I).

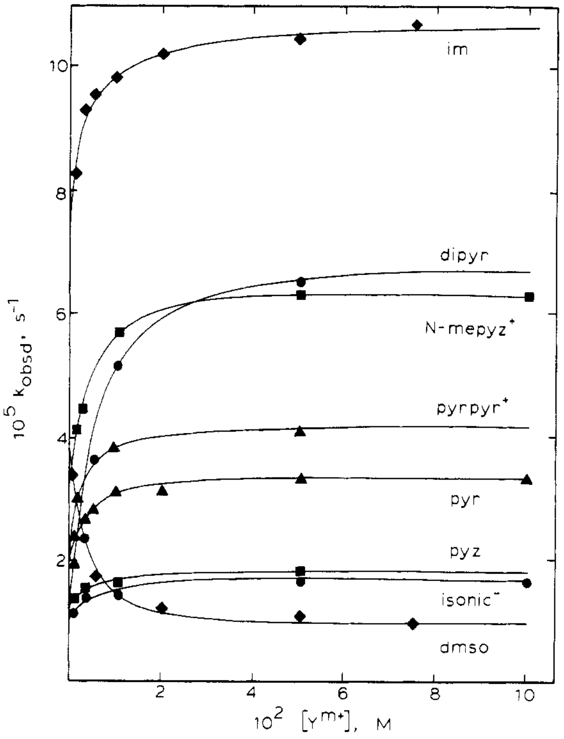

Figure 1. Dependences of the observed rate constants for the dissociation of $Ru(CN)_5L^{(3-n)-}$ on the concentration of the entering ligand Y^{m+} at 25 °C. The ligand Y^{m+} is *N*-methylpyrazinium when L^{n+} is dimethyl sulfoxide or imidazole and is dimethyl sulfoxide for the remaining reactions.

The dissociative mechanism of ligand substitution is proposed for the exchange of the L and Y ligands in the pentacyano(ligand)ruthenate(II) complexes, on the basis of the saturation of k_{obsd} at high $[Y^{m+}]$, the dependence of k_{-L} on the nature of L^{n+}, and the lack of a dependence of k_{-L} on the nature of Y^{m+}:

$$Ru(CN)_5L^{(3-n)-} \underset{k_L}{\overset{k_{-L}}{\rightleftharpoons}} Ru(CN)_5OH_2^{3-} + L^{n+} \quad (3)$$

$$Ru(CN)_5OH_2^{3-} + Y^{m+} \underset{k_{-Y}}{\overset{k_Y}{\rightleftharpoons}} Ru(CN)_5Y^{(3-m)-} \quad (4)$$

For this mechanism the observed rate constants may be expressed as

$$k_{obsd} = \frac{k_{-L}k_Y[Y^{m+}] + k_{-Y}k_L[L^{n+}]}{k_Y[Y^{m+}] + k_L[L^{n+}]} \quad (5)$$

As the concentration of Y^{m+} is increased, with $[L^{n+}]$ held constant, k_{obsd} will increase until the conditions of $k_{-L}k_Y[Y^{m+}] \gg k_{-Y}k_L[L^{n+}]$

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Inorg. Chem. 1986, 25, 2101-2104 2101

and $k_Y[Y^{m+}] \gg k_L[L^{n+}]$ are met. At this point, k_{obsd} will approach the value of k_{-L}, where k_{-L} is the limiting rate of dissociation of L^{n+} from $Ru(CN)_5L^{(3-n)-}$. Similarily, as $[Y^{m+}]$ is decreased, the observed rate constant approaches the rate of dissociation, k_{-Y}, of Y^{m+} from $Ru(CN)_5Y^{(3-m)-}$. The expression in eq 5 is consistent with the observed dependence of the rate on $[Y^{m+}]$ for the substitution reactions in this study. With k_{-L} for the complexes with nitrogen heterocycles being greater (Table I) than the corresponding rate constant for the dimethyl sulfoxide complex, k_{obsd} increases to a limiting value (Figure 1) with increasing $[Me_2SO]$. In the substitution reactions of the dimethyl sulfoxide complex, an increase in $[Y^{m+}]$ results in a decrease in k_{obsd} to a limiting value.

Rate constants and activation parameters have been reported for formation and dissociation reactions of the analogous $Fe(CN)_5L^{(3-n)-}$ complexes.[1,5,14] The enthalpies of activation associated with k_{-L} are similar for the two systems while the entropy values are slightly lower (5–10 cal K^{-1} mol^{-1}) for the ruthenium complexes. The decreased entropies of activation are suggestive of a shift from a purely dissociative (D) mechanism toward an interchange (I_d) process for the ruthenium system, but such a shift is not clearly supported by the kinetic behavior. The rate and equilibrium constants for the pentacyano(ligand) complexes of Ru(II) and Fe(II) are summarized in Table II. The ruthenium complexes are more inert than the iron species with respect to substitution of L^{n+}, including the coordinated water molecule. The decreased lability is expected because of the relatively stronger Ru–L bonds. The larger radial extension of the 4d orbitals on ruthenium would allow for greater π back-bonding to the cyanide ligands and to the N-heterocycle in the sixth position. The increased back-donation would enhance the M(III) character of Ru(II) relative to that of Fe(II) and account for the slower exchange in $Ru(CN)_5OH_2^{3-}$. For the ligands used in this study the equilibrium constants calculated from k_L/k_{-L} for the Fe(II) complexes are similar to those for the corresponding Ru(II) complexes. The trends in k_L and k_{-L} are also similar for the two metal systems, with dimethyl sulfoxide the most inert and imidazole the most labile with respect to substitution. Ligand-exchange rate constants have been reported for some other octahedral ruthenium(II) complexes of the type $Ru(NH_3)_5L^{2+}$,[16,17] and $Ru(edta)L^{2-}$.[18] The rates of ligand substitution in these complexes are of similar magnitude and are found to be dependent on the nature of L, consistent with a dissociatively activated process.

The results of the present kinetic study and previous work on substitution of the $Ru(CN)_5OH_2^{3-}$ ion[12] have demonstrated that these pentacyano(ligand)ruthenate(II) complexes are relatively inert species in solution. Shepherd and co-workers[9,19] have recently employed these complexes and binuclear derivatives in spectroscopic studies for a comparison of the behavior of the low-spin d^6 moieties $Fe(CN)_5^{3-}$, $Ru(CN)_5^{3-}$, and $Ru(NH_3)_5^{2+}$. Further kinetic studies on $Ru(CN)_5L^{(3-n)-}$ complexes with other ligand types, including bridging metal species, are in progress in our laboratory.

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Registry No. $Ru(CN)_5(N\text{-mepyz})^{2-}$, 84711-78-4; $Ru(CN)_5(pyrpyr)^{2-}$, 101953-46-2; $Ru(CN)_5(bpy)^{3-}$, 86260-22-2; $Ru(CN)_5(pyz)^{3-}$, 96455-66-2; $Ru(CN)_5(py)^{3-}$, 86260-15-3; $Ru(CN)_5(im)^{3-}$, 101953-47-3; $Ru(CN)_5(isonic)^{4-}$, 86260-17-5; $Ru(CN)_5(Me_2SO)^{3-}$, 101953-48-4; Me_2SO, 67-68-5; py, 110-86-1; im, 288-32-4; pyz, 290-37-9; $N\text{-mepyz}^+$, 17066-96-5.

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Synthesis and Photobehavior of Chromium(III) and Rhodium(III) Complexes of the Macrocyclic Ligand *C-meso*-5,7,7,12,14,14-Hexamethyl-1,4,8,11-Tetraazacyclotetradecane

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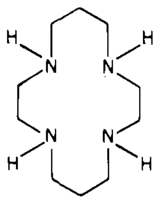
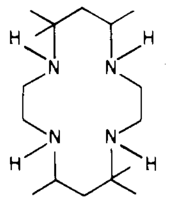
We have recently synthesized the Cr(III) complexes *cis*- and *trans*-$Cr(cyclam)(NH_3)_2^{3+}$ [1] and *trans*-$Cr(cyclam)(CN)_2^+$,[2] and the Rh(III) species *cis*- and *trans*-$Rh(cyclam)(CN)_2^+$,[3] where cyclam is the macrocyclic tetradentate amine ligand, 1,4,8,11-tetraazacyclotetradecane (I). The trans isomers display very unusual photobehavior in room-temperature solution. In addition to the near absence of any discernible photochemistry, they exhibit exceptionally strong, long-lived phosphorescence signals.[1,4,5] Furthermore, in the Cr(III) case, deuteration of the amine N–H protons results in marked increases in the intensity and lifetime of their emission.[1,4]



I
cyclam



II
tet a

In view of the novel photobehavior of these systems, we have extended our studies to include other macrocyclic ligands. We report here the synthesis and photobehavior of the complexes *trans*-$Cr(tet\ a)(NH_3)_2^{3+}$, *trans*-$Cr(tet\ a)(CN)_2^+$, and *trans*-$Rh(tet\ a)(CN)_2^+$, where tet a is *C-meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (II). The tet a ligand contains the same basic 14-membered ring structure of cyclam, with the additional presence of six methyl groups on the ring periphery. Steric hindrance associated with these methyl groups is apparently responsible for the absence of stable cis complexes of the type *cis*-$M(tet\ a)X_2^{n+}$.[7-10] We were therefore interested in learning whether steric factors might substantially affect the photochemical and photophysical properties of tet a complexes with Cr(III) and Rh(III).

Experimental Section

Reagents. The ligand tet $a{\cdot}2H_2O$ was obtained from Strem Chemicals. The complex *trans*-[Cr(tet a)Cl_2]Cl was synthesized by the published method,[7] and the perchlorate salt was isolated by the addition of $NaClO_4$ to an aqueous solution of the chloride salt. The $CrCl_3{\cdot}6H_2O$ and $RhCl_3{\cdot}3H_2O$ were purchased from Fisher Scientific and Alfa Products, respectively.

Measurements. Electronic absorption spectra were recorded on a Cary 118C spectrophotometer, and infrared data were collected on a Perkin-Elmer 283 instrument using KBr pellets. A Markson Electromark ana-

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