= 20, which is not very different from the log K_1 = 18.3 obtained in this study. If indeed complexes with type I structures are precursors of the more stable type II structures in the complex formation reactions of cyclam, the low stability of the Co(II) complex, and presumably also the Ni(II) complex, must contribute to the very slow reactions of these metal ions with cyclam.

In Table III are shown the constants for the binding of hydroxide ion to the TMC complexes. It is seen that for Co(II) the constant is very much higher than log K_1 for the formation of the monohydroxo complex of the Co(II) aquo ion. This can be understood as being due to the lower coordination number of Co(II) in its TMC complex and probably also to the relatively distorted coordination geometry, which must provide poor overlap for the four in-plane bonds, leading to a very strong axial bond. This effect seems to be general for the Co(II) complex in that we have found a log K_1 of 1.3 for the binding of chloride to the Co(II)–TMC complex as compared with 0.5 for the aquo ion.

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Cyanide Exchange Kinetics for Planar Tetracyanometalate Complexes by Carbon-13 NMR

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The planar tetracyanometalate ions $M(CN)_4^{n-}$ where M = Ni(II), Pd(II), Pt(II), and Au(III) are extremely stable complexes in aqueous solution ($\beta_4 \cong 10^{30}$, 10^{63}, 10^{65-75}, and 10^{85}, respectively),[2,3] but they have been reported to undergo CN^- exchange at rates too fast to measure by using radioisotope tracer techniques (exchange complete in less than 1–2 min).[4–6] As a result, these ions have been frequently cited as examples of thermodynamically *stable* yet kinetically *labile* complexes. Unfortunately the rapid rates encountered in the earlier studies[4–6] precluded quantitative rate information and rate law determination. Our ^{13}C magnetic resonance investigation of these complexes[7] showed that the rate of $^{13}CN^-$ exchange with $Pt(^{13}CN)_4^{2-}$ in D_2O was within the range accessible by NMR kinetic methods and thus ^{13}C NMR should be a viable method for obtaining quantitative rate data on CN^- exchange. We report here some additional ^{13}C NMR rate studies of CN^- exchange with $Pd(CN)_4^{2-}$, $Pt(CN)_4^{2-}$, and $Au(CN)_4^-$; CN^- exchange with $Ni(CN)_4^{2-}$ was also investigated but was found to be too fast to be followed by ^{13}C NMR.

Table I. Rate Data

$[CN^-]$, M	ΔW, Hz	k_{obsd}, s^{-1}	k_2, $M^{-1}\,s^{-1}$
	$Pd(CN)_4^{2-}$ [a]		
0.036	1.5	4.7	131
0.104	3.5	11.0	106
0.120	3.5[b]	14.0	117
0.214	7.5	24	110
0.321	12.5	39	122
0.447	18	56	126
0.081	3.5[c,d]	11.0	136
0.081	5.0[c,e]	15.7	194
0.081	6.0[c,f]	18.2	225
0.081	7.3[c,g]	23	284
	$Pt(CN)_4^{2-}$ [h]		
0.057	0.05	1.57	28
0.120	1.00	3.14	26
0.138	1.30[i,j]	4.00	29
0.203	1.75	5.5	27
0.341	2.75	8.6	25
0.477	4.0	12.6	26
0.238	2.2[d,i]	6.9	29
0.238	3.4[e,i]	10.7	45
0.238	4.6[f,i]	14.4	60
0.238	5.2[g,i]	18.0	76
	$Au(CN)_4^-$ [k]		
0.035	41.0[l]	130	3700
0.098	122	380	3900
0.127	160	500	3900
0.162	208	660	4100
0.198	251	790	4000
0.103	152[d,m]	480	4640
0.103	220[e,m]	690	6700
0.103	325[f,m]	1020	9900
0.103	460[g,m]	1440	14000

[a] $[Pd(CN)_4^{2-}]$ = 0.117 M; 24.0 °C; line width for complex in absence of added CN^- 1.00 Hz. [b] $[Pd(CN)_4^{2-}]$ = 0.089 M, $[NaClO_4]$ = 0.31 M. [c] $[Pd(CN)_4^{2-}]$ = 0.111 M. [d] 30.0 °C. [e] 40.0 °C. [f] 50.0 °C. [g] 60.0 °C. [h] $[Pt(CN)_4^{2-}]$ = 0.082 M; 24.0 °C; line width for complex in absence of added CN^- 1.50 Hz. [i] $[Pt(CN)_4^{2-}]$ = 0.091 M. [j] $[NaClO_4]$ = 0.31 M. [k] $[Au(CN)_4^-]$ = 0.182 M; 24.0 °C; line width for complex in absence of added CN^- 2.00 Hz. [l] $[Au(CN)_4^-]$ = 0.114 M, $[NaClO_4]$ = 0.30 M. [m] $[Au(CN)_4^-]$ = 0.159 M.

Experimental Section

Isotopically enriched (45% ^{13}C) samples of $K_2M(CN)_4$, M = Ni(II), Pd(II), and Pt(II), and $KAu(CN)_4$, prepared as described earlier,[7] were used for the exchange studies. Exchange reactions were run in D_2O with $K^{13}CN$ (90% ^{13}C; Merck Sharp and Dohme) used as the source of added CN^-. The pHs measured for solutions of each of the complexes used in this study were between 10.3 and 10.8. At the concentrations of CN^- used (0.04–0.5 M), a maximum of about 1% of the cyanide would be converted to HCN by hydrolysis. Therefore, corrections of the $[CN^-]$ due to hydrolysis were negligible. Ionic strength effects on the rates were investigated by adding $NaClO_4$ to solutions containing the metal complex and free CN^- and measuring the line width. In all cases the line width of the high ionic strength solution was within ±0.5 Hz or ±5%, whichever was greater, of the original line width. Therefore, ionic strength effects within the range studied are negligibly small. NMR measurements were made with an IBM NR-80 spectrometer (^{13}C resonance at 20.1 MHz) fitted with a temperature-controlled sample probe. Rate measurements for $Pd(CN)_4^{2-}$, $Pt(CN)_4^{2-}$, and $Au(CN)_4^-$ were determined by the line broadening of the ^{13}C resonance of the complex in the presence of added CN^-. In the case of $Pt(CN)_4^{2-}$, the broadening was measured from the uncoupled central line of the three-line pattern that results from ^{195}Pt ($S = {}^1/_2$, 33.7%) spin coupling. The rates of CN^- exchange were all in the slow-exchange region at the $[CN^-]$ employed, and first-order rate constants, k_{obsd}, were determined by the standard expression[8] $k_{obsd} = \pi(\Delta W)$, where ΔW is the increase in line width observed on adding CN^-. Plots of k_{obsd} vs. $[CN^-]$ were linear for each

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Table II. Rate Constants and Activation Parameters

reaction	k_2(24 °C), M^{-1} s^{-1}	ΔH^*, kJ mol^{-1}	ΔS^*, J K^{-1} mol^{-1}
$Ni(CN)_4^{2-} + CN^- \rightarrow$	$>5 \times 10^5$		
$Pd(CN)_4^{2-} + CN^- \rightarrow$	120	17 ± 2	−178 ± 7
$Pt(CN)_4^{2-} + CN^- \rightarrow$	26	26 ± 3	−143 ± 8
$Au(CN)_4^- + CN^- \rightarrow$	3900	28 ± 1	−100 ± 3
trans-[Ni(PEt$_3$)$_2$(*o*-tol)Cl] + EtOH →	330[a]		
trans-[Pd(PEt$_3$)$_2$(*o*-tol)Cl] + EtOH →	0.58[a]		
trans-[Pt(PEt$_3$)$_2$(*o*-tol)Cl] + EtOH →	6.7×10^{-6} [a]		
$[Pt(dien)Cl]^+ + Br^- \rightarrow$	5.3×10^{-3} [b,d]	59[b]	−96[b]
$[Au(dien)Cl]^{2+} + Br^- \rightarrow$	154[b,c]	54[b]	−17[b]

[a] Reference 11. Values are for solvent reaction in ethanol; k_1 in units of s^{-1}; overall reaction involved pyridine replacement of Cl^-; 25 °C. [b] Reference 12. [c] 20 °C. [d] 25 °C.

complex, and the second-order rate constants, k_2, were determined from the slopes. Activation parameters ΔH^* and ΔS^* were calculated from data taken at four different temperatures from 30 to 60 °C. In the case of $Ni(CN)_4^{2-}$, no line broadening could be detected within experimental error. Therefore, only a lower limit can be placed on the rate of CN^- exchange. On the assumption that the broadening was <1 Hz, k_2 is estimated to be $>5 \times 10^5$ s^{-1} M^{-1} (in the fast-exchange region[9]).

Results and Discussion

The CN^--exchange rate data for $Pd(CN)_4^{2-}$, $Pt(CN)_4^{2-}$, and $Au(CN)_4^-$ obtained from ^{13}C NMR are collected in Table I and are consistent with the simple rate law in eq 1. The rate

$$\text{rate} = k_2[M(CN)_4^{n-}][CN^-] \qquad (1)$$

laws for most square-planar substitution reactions have two terms:[10] a term that depends on the substituting reagent analogous to eq 1 and a second term independent of reagent concentration, which in the present case should have the form $k_1[M(CN)_4^{n-}]$. The reagent-dependent term is visualized as resulting from an associative replacement involving a five-coordinate transition state. The reagent-independent term corresponds to a rate-limiting solvent substitution (presumably involving an associative five-coordinate transition state also) followed by a fast solvent replacement by the reagent. Both terms would lead to the same substituted product, in the present case to CN^- exchange. However, careful examination of the data was made for such a CN^--independent term, but plots of k_{obsd} vs. $[CN^-]$ gave good straight lines that passed through the origin within experimental error. If a CN^--independent path for the exchange exists, its contribution to the overall rate is very small and $k_2[CN^-] \gg k_1$. Rate constants and activation parameters are summarized in Table II along with some data for some related reactions for comparison. The slowest rates measured in our experiments correspond to $t_{1/2} \sim 0.5$–2 s so that the lack of quantitative data from the earlier radioisotope studies[4–6] can be easily understood.

The CN^--exchange rates are in the order Ni(II) ≫ Au(III) > Pd(II) > Pt(II) (relative k_2 at 24 °C $>2 \times 10^4$:150:4.6:1), with $Pt(CN)_4^{2-}$ being the most inert. Though data are limited, a similar reactivity order has been observed for other square-planar substitution reactions as the metal ion is changed. For example, in the Cl^- replacement by pyridine in *trans*-[M(PEt$_3$)$_2$(*o*-tol)Cl], the relative rates of the rate-limiting ethanol substitution (reagent-independent path) at 25 °C (Table II) for Ni(II), Pd(II), and Pt(II) are 5×10^6:10^5:1, respectively;[11] for Cl^- replacement by Br^- in $[M(dien)Cl]^{n+}$ the relative rates for Au(III) and Pt(II) are $\sim 3 \times 10^4$:1.[12] It is interesting that the CN^--exchange rate variation between $Pd(CN)_4^{2-}$ and $Pt(CN)_4^{2-}$, and to a lesser extent between $Au(CN)_4^-$ and $Pt(CN)_4^{2-}$, is smaller than for the other reactions among square-planar complexes as the metal ion is changed. From the trend in activation parameters, changes in ΔH^* and ΔS^* are partly compensating for the CN^- exchange. Thus, ΔH^* for CN^- exchange with $Pd(CN)_4^{2-}$ is ~9 kJ mol^{-1} more favorable than for $Pt(CN)_4^{2-}$, but ΔS^* is 35 J K^{-1} mol^{-1} more unfavorable. Similarly the much higher rate for $Au(CN)_4^-$ can be traced to a more favorable (less negative) ΔS^* since the ΔH^* is larger than for either $Pd(CN)_4^{2-}$ or $Pt(CN)_4^{2-}$. A similar trend in ΔS^* is observed for $[M(dien)Cl]^{n+} + Br^-$ (Table II). The exceptionally high reactivity of $Ni(CN)_4^{2-}$ to CN^- exchange is undoubtedly due to the stability of five-coordinate $Ni(CN)_5^{3-}$, which may be similar to reaction intermediates or the associative transition state. Salts of $Ni(CN)_5^{3-}$ have been isolated,[13] but there is no evidence that five-coordinate CN^- complexes of Pd(II), Pt(II), or Au(III) exist either in solution or in the solid state.

Registry No. CN^-, 57-12-5; $Ni(CN)_4^{2-}$, 48042-08-6; $Pd(CN)_4^{2-}$, 15004-87-2; $Pt(CN)_4^{2-}$, 15004-88-3; $Au(CN)_4^{2-}$, 14263-59-3.

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A Molybdenum-95 NMR Study of Some *cis*-Mo(CO)$_4$(PPh$_2$XR)$_2$ and Mo(CO)$_4$(PPh$_2$YPPh$_2$) Complexes. Correlation between Molybdenum-95 NMR Chemical Shifts and UV–Vis Absorption Band Wavelengths

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Recent ^{95}Mo NMR studies of molybdenum(VI) complexes[1–4] and molybdenum(0) carbonyl complexes containing π-arene,[5,6] Schiff base,[7,8] and organophosphine[9–11] ligands have shown the ^{95}Mo chemical shift to be extremely sensitive to the ligand environment (of the molybdenum) and have suggested that this technique may serve as a probe for subtle steric and electronic effects in molybdenum-containing catalysts and enzymes. First, however, a better understanding of the manner in which the steric and electronic properties of the ligands influence the ^{95}Mo chemical shift is desirable. In two previous studies we have shown that the ^{95}Mo chemical shift is sensitive

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