

Table III. Analytical Data

complex	color	% C		% H		% N		% metal		% halide	
		calcd	found	calcd	found	calcd	found	calcd	found	calcd	found
$[(C_6H_{15}N_3)_2Cr]Br_3 \cdot 5H_2O$	yellow	22.51	22.4	6.30	6.1	13.13	13.3	8.12	8.2	37.45	37.6
$[(C_6H_{15}N_3)_2Mn]Cl_2$	colorless	37.51	37.6	7.87	8.0	13.87	22.2				
$[(C_6H_{15}N_3)_2Fe]Br_2 \cdot 3H_2O$	faint blue	27.29	26.8	6.87	6.9	15.91	15.2	10.58	10.5	30.25	30.7
$[(C_6H_{15}N_3)_2Fe]Br_3 \cdot 5H_2O$	orange	22.38	22.4	6.26	6.1	13.05	13.0	8.67	8.8	37.22	37.0
$[(C_6H_{15}N_3)_2Co]Cl_2$	gray	37.12	37.0	7.79	7.6	21.65	21.4			18.26	18.3
$[(C_6H_{15}N_3)_2Ni](ClO_4)_2$	violet	27.9	27.8	5.9	6.0	16.2	16.3				
$[(C_6H_{15}N_3)_2Ni](ClO_4)_3 \cdot H_2O$	yellow	22.75	22.6	5.09	5.0	13.27	13.5			47.10	47.1

Experimental Section

The triamines used in this study were obtained commercially ((3-aminopropyl)-1,3-propanediamine) or synthesized according to procedures described in the literature (1,4,7-triazacyclononane,¹⁹ 1,2,3-triaminopropane⁷). Analytical data for the new complexes are summarized in Table III.

Preparation of Complexes. The complexes $[(9\text{aneN}_3)_2Co]Br_3 \cdot 5H_2O$,¹ $[(9\text{aneN}_3)_2Ni]Cl_2 \cdot 4H_2O$,² $[Co(dpt)_2](ClO_4)_3$,^{6a} and $[Co(pnt)_2](ClO_4)_3$ ⁷ were prepared according to previously published procedures.

A general method for the synthesis of bis(1,4,7-triazacyclononane)metal(II) (metal = Mn, Fe, Co, Ni) complexes follows: A 4-mmol sample of dichloride, $MCl_2 \cdot xH_2O$, was dissolved in 30 mL of dimethyl sulfoxide at 190 °C. The volume of this solution was reduced to 20 mL by evaporation at 190 °C. To the cooled solution (20 °C) was added 10 mL of an ethanolic solution of 1,4,7-triazacyclononane (1 M) with stirring. Precipitates of $[(9\text{aneN}_3)_2M]Cl_2$ formed immediately, which were filtered off, washed with ethanol and ether, and dried. Except $[(9\text{aneN}_3)_2Ni]Cl_2$, all other complexes are air sensitive in the solid state and in solution. Therefore, all preparations were carried out under an argon atmosphere. In general, the yields were better than 60%. $[(9\text{aneN}_3)_2Fe]Cl_2$ was converted to the blue bromide salt $[(9\text{aneN}_3)_2Fe]Br_2 \cdot 3H_2O$ from an oxygen-free, aqueous solution of the chloride with sodium bromide.

$[(9\text{aneN}_3)_2Cr]Br_3 \cdot 5H_2O$. $CrCl_3 \cdot 6H_2O$ (1 g) was dissolved in 50 mL of dimethyl sulfoxide at 190 °C, and 10 mL of this solution was allowed to evaporate. To the cooled solution was added 10 mL of 1,4,7-triazacyclononane in ethanol (1 M) at 70 °C. The temperature was slowly raised to 170 °C and maintained for 30 min, after which time the yellow precipitate of $[(9\text{aneN}_3)_2Cr]Cl_3$ was filtered off and dissolved again in 10 mL of water at 50 °C. To this solution was added 5 mL of concentrated NaBr solution. After the mixture was cooled, yellow crystals of $[(9\text{aneN}_3)_2Cr]Br_3 \cdot 5H_2O$ precipitated; yield 1.6 g.

$[(9\text{aneN}_3)_2Fe]Br_3 \cdot 5H_2O$. $FeCl_3 \cdot 6H_2O$ (0.5 g) was dissolved in 20 mL of Me_2SO at 140 °C and the resultant solution cooled to 20 °C. A 5-mL portion of 1,4,7-triazacyclononane dissolved in ethanol (1 M) was added with stirring. The yellow-brown precipitate was filtered off (0.6 g) and was recrystallized from a minimum amount of water at 20 °C by adding solid sodium bromide. Orange-red crystals were filtered off, washed with ethanol and ether, and air-dried; yield 0.4 g.

$[(9\text{aneN}_3)_2Ni](ClO_4)_3$. A 0.5-g sample of $[(9\text{aneN}_3)_2Ni](ClO_4)_2$, which was prepared from an aqueous solution of the chloride salt with sodium perchlorate, was dissolved in 20 mL of water. $K_2S_2O_8$ (3 g) was dissolved in 50 mL of water, and 2 mL of concentrated perchloric acid was added. After 2 h at 0 °C, the precipitated $KClO_4$ was filtered off. A 3-mL sample of the resulting oxidant was added to the above solution containing the nickel(II) complex. A color change from red-violet to brown was observed. After this solution was stirred for 20 min at 20 °C, 1 g of solid sodium perchlorate was added, which initiated the precipitation of gold-brown crystals. After 2 h at 0 °C, these crystals were filtered off, washed with ethanol and ether, and air-dried; yield 0.5 g.

Apparatus. Cyclic voltammograms were recorded with Princeton Applied Research equipment, which included the Model 173/179 potentiostat-galvanostat and the Model 175 programmer. Voltammograms were recorded at scan rates from 5 to 200 $mV s^{-1}$ on an X-Y recorder (Kipp & Zonen). The electrochemical cell (Metrohm)

employed the standard three-electrode configuration: the working electrode (hanging mercury drop or glassy carbon), a Pt-wire auxiliary electrode, and the reference electrode (Ag/AgCl in saturated KCl). In general, potentials were measured at 25 ± 1.0 °C under a nitrogen atmosphere. Solutions were $\sim 10^{-3}$ M in sample and 0.1 M in supporting electrolyte (KCl or $LiClO_4$). Potentials were corrected to the normal hydrogen electrode (NHE) by adding 0.200 V to the measured potential. $E_{1/2}$ values were taken as the average of the anodic and cathodic peak potentials. Electrochemical reversibility was judged on the basis of the peak-to-peak separation (ΔE_p) for the complementary cyclic voltammetric waves relative to the theoretical value of 59 mV for a reversible one-electron process and an i_{pc}/i_{pa} ratio of 1.0.¹⁴

The magnetic susceptibilities of powdered samples were measured by using the Faraday method, and diamagnetic corrections were applied with use of published tables.²⁰

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Registry No. $[(C_6H_{15}N_3)_2Cr]Br_3$, 86709-76-4; $[(C_6H_{15}N_3)_2Mn]Cl_2$, 86709-77-5; $[(C_6H_{15}N_3)_2Fe]Br_2$, 86709-78-6; $[(C_6H_{15}N_3)_2Fe]Br_3$, 86709-79-7; $[(C_6H_{15}N_3)_2Co]Cl_2$, 86709-80-0; $[(C_6H_{15}N_3)_2Ni](ClO_4)_2$, 60296-44-8; $[(C_6H_{15}N_3)_2Ni](ClO_4)_3$, 86709-82-2; $[Co(dpt)_2](ClO_4)_3$, 86709-84-4; $[Co(pnt)_2](ClO_4)_3$, 86709-86-6; $[Ni(pnt)_2]^{2+}$, 86709-87-7.

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Formation Constants of Some Complexes of Tetramethylcyclam

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The complexes of the ligand tetramethylcyclam (TMC) (Figure 1), first reported by Barefield et al.,^{1,2} adopt an unusual five-coordinate structure, which is kinetically determined.² It has been suggested³ that complexes with this structure, shown as I in Figure 2, are formed as the first step in the metal ion entering the cavity of macrocycles such as cyclam itself. Cyclam complexes can undergo inversion at the nitrogen to give the thermodynamically more stable isomer II, which is not possible for TMC complexes because of the tertiary nitrogens. Another class of macrocyclic ligands with tertiary nitrogens is the acetate derivatives such as 1,4,8,11-tetraazacyclotetradecane-*N,N',N'',N'''*-tetraacetate (CTA), whose formation constants are already known.⁴ Kaden et al.⁵ have

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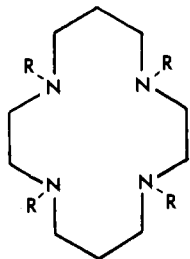


Figure 1. Ligands discussed in this work: R = H, cyclam; R = CH₃, TMC (tetramethylcyclam); R = CH₂COO⁻, CTA (cyclamtetraacetate).

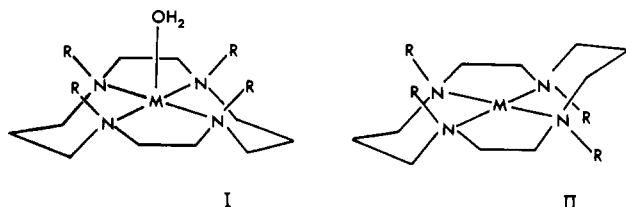


Figure 2. The *trans*-(*R**S**R**S*)-I and *trans*-(*R**S**S**R*)-II isomers of metal complexes of cyclam-type ligands. Isomer I is thought to be the five-coordinate precursor to II, with inversion at two adjacent nitrogens by base-catalyzed loss of protons. For ligands where R is an alkyl group, inversion cannot occur, and we observe only isomer I.

Table I. p*K*_a Values

	tetramethylcyclam		cyclam ^c
	μ = 0.1 ^a	μ = 0.5 ^b	
p <i>K</i> ₁	9.34 ± 0.02	9.70	11.59
p <i>K</i> ₂	8.99 ± 0.02	9.31	10.62
p <i>K</i> ₃	2.58 ± 0.04	3.09	1.61
p <i>K</i> ₄	2.25 ± 0.05	2.64	2.42

^a This work; 25 °C, 0.1 M NaNO₃; mean of three titrations.
^b 25 °C; ref 7. ^c 25 °C, ionic strength 0.5; ref 7.

shown that it is likely that in a rather similar di-C-dimethylated analogue of CTA metal ions such as Co(II) and Ni(II) are not, as might be expected, bound to the four nitrogen donors, as has been shown² for the TMC complexes, but rather to only two of the ring nitrogens, plus two acetates. The lability of the TMC complexes means that determination of the formation constants should be possible by straightforward glass-electrode techniques. Because of the interest attached to the TMC complexes, we undertook a study of the complexes of the more labile metal ions Cu(II), Co(II), Zn(II), Cd(II), and Hg(II) by potentiometric and spectroscopic means.

Experimental Section

TMC was obtained as the free ligand from Strem Chemicals. It was used to prepare a stock solution, which was standardized by acid titration. Stock solutions of the metal nitrates were prepared and used for the potentiometric titrations, which were carried out at 25 °C and in 0.1 M NaNO₃ by previously reported⁶ procedures. For Cu(II) and Hg(II), equilibrium was reached in a matter of minutes after each addition of acid in the potentiometric titration, while for Co(II), the most slowly reacting of these metal ions, this required 2 h or more. As a check on the steadiness of the potentials, *E*^o, the standard potential of the cell, was determined before and after the titrations with Co(II), which lasted 2–3 days, and found not to have changed significantly. The p*K*_a values determined for TMC are shown in Table I, where they are compared with those reported⁷ at 25 °C

Table II. log *K*₁ Values

	TMC ^a	cyclam	CTA ^b	trien ^c
Cu(II)	18.3	27.2 ^d	18.6	20.4
Co(II)	7.58		15.8	11.0
Zn(II)	10.4	15.5 ^e	14.7	12.1
Cd(II)	9.0		15.5	10.8
Hg(II)	20.3	23.0 ^f		25.0

^a This work; 25 °C, 0.1 M NaNO₃. ^b Reference 4; 25 °C, 0.1 M KCl. ^c Reference 8. ^d Reference 9. ^e Reference 10. ^f Reference 11.

Table III. Constants for the Binding of Hydroxide to TMC Complexes

	log <i>K</i> ₁ (OH ⁻) ^a	log <i>K</i> ₁ (OH ⁻) ^b	log <i>k</i> ₁ (OH ⁻) ^c (aquo ion)
Cu(II)	<i>d</i>		6.65
Ni(II)		3.72	4.13
Zn(II)	5.44		4.60
Co(II)	5.76	5.28	3.9
Cd(II)	5.60		3.9

^a This work; 25 °C, 0.1 M NaNO₃. Refers to the process M(TMC)²⁺ + OH⁻ ⇌ M(TMC)OH⁺. ^b Reference 13; *I* = 0.5. ^c Refers to the process M²⁺ + OH⁻ ⇌ MOH⁺. ^d No evidence of deprotonation of complex even at high pH.

and in 0.5 M KNO₃. The differences observed are similar to those found for other polyamines where data are available at both 0.1 and 0.5 ionic strengths. The stability of the copper complex turned out to be too high for much breakup to occur above pH 2, so that the potentiometric results, where *pH* did not fall much below 0.9, were checked by an electronic spectroscopic study between pH 1 and 2. For Hg(II), the glass electrode was calibrated down to pH 1 to correct for junction potentials in the low-pH region so that the complex could be studied in the pH region where it was being broken up. The Hg(II) constant so determined appeared satisfactory but was further checked by a UV-visible spectroscopic study of the competition reaction between Cu(II) and Hg(II) for the ligand, with the Cu(II):Hg(II) ratio varying from 1:1 to 100:1.

Results and Discussion

The log *K*₁ values for TMC, together with the log *K*₁ values for cyclam, CTA, and trien (trien = 1,4,7,10-tetraazadecane), are shown in Table II, the trien complexes being included as examples of open-chain tetraaza polyamines. One sees that the complexes with TMC are very much less stable than those with cyclam. This difference in stability appears, from Table II, to decrease as the size of the metal ion increases, being least for Hg(II) and most for Cu(II). Models show that steric interactions between the methyl groups become less as the size of the metal ion in the TMC complex becomes larger, which seems a reasonable explanation of the effects observed. The very low stability of the TMC complex of Co(II) must relate to the loss of ligand field stabilization energy experienced by the Co(II) ion in five-coordinate geometry.

For Cu(II), the difference in stability between the CTA and TMC complexes is small, suggesting that there could be at least a considerable percentage of Cu(II) bound by the four nitrogens rather than two nitrogens and two acetate groups in the CTA complex. For the other metal ions, the CTA complexes are considerably more stable than those of TMC, indicating why the metal ions do not take up the TMC type of five-coordinate structure when coordinating to CTA.

The formation constant of Cu(II) complexing with tet a (the C-substituted hexamethylcyclam) to form the blue complex, which may have structure I,³ has been measured¹² as log *K*₁

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= 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 ($\beta_4 \approx 10^{30}, 10^{63}, 10^{65-75},$ 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 studies⁴⁻⁶ precluded quantitative rate information and rate law determination. Our ¹³C magnetic resonance investigation of these complexes⁷ showed that the rate of ¹³CN⁻ exchange with $Pt(^{13}CN)_4^{2-}$ in D₂O was within the range accessible by NMR kinetic methods and thus ¹³C NMR should be a viable method for obtaining quantitative rate data on CN^- exchange. We report here some additional ¹³C 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 ¹³C NMR.

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Table I. Rate Data

[CN ⁻], M	ΔW , Hz	k_{obsd} , s ⁻¹	k_2 , M ⁻¹ s ⁻¹
Pd(CN)₄²⁻ ^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)₄²⁻ ^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)₄²⁻] = 0.117 M; 24.0 °C; line width for complex in absence of added CN⁻ 1.00 Hz. ^b [Pd(CN)₄²⁻] = 0.089 M, [NaClO₄] = 0.31 M. ^c [Pd(CN)₄²⁻] = 0.111 M. ^d 30.0 °C. ^e 40.0 °C. ^f 50.0 °C. ^g 60.0 °C. ^h [Pt(CN)₄²⁻] = 0.082 M; 24.0 °C; line width for complex in absence of added CN⁻ 1.50 Hz. ⁱ [Pt(CN)₄²⁻] = 0.091 M. ^j [NaClO₄] = 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, [NaClO₄] = 0.30 M. ^m [Au(CN)₄⁻] = 0.159 M.

Experimental Section

Isotopically enriched (45% ¹³C) samples of K₂M(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 D₂O with K¹³CN (90% ¹³C; 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 NaClO₄ 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 (¹³C resonance at 20.1 MHz) fitted with a temperature-controlled sample probe. Rate measurements for Pd(CN)₄²⁻, Pt(CN)₄²⁻, and Au(CN)₄⁻ were determined by the line broadening of the ¹³C resonance of the complex in the presence of added CN⁻. In the case of Pt(CN)₄²⁻, the broadening was measured from the uncoupled central line of the three-line pattern that results from ¹⁹⁵Pt (*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 expression⁸ $k_{obsd} = \pi(\Delta W)$, 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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