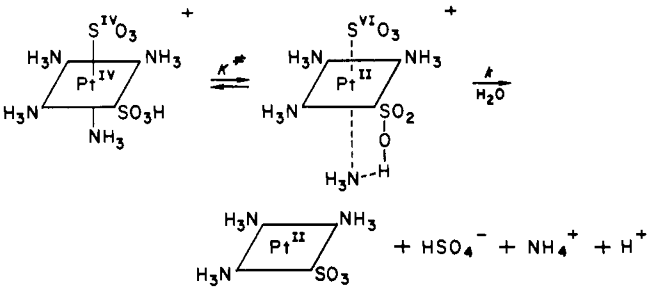
Scheme II



10^{-3} s^{-1} for the S-bonded (sulfito)pentaammine and the O-bonded tren species (entry no. 4) to 10^{-2} s^{-1} for the O-bonded pentaammine complex. The only platinum (IV) species for which we observed redox is no. 7, the S-bonded bis(sulfito) congener, with a rate about 2.5-fold slower than that of the S-bonded cobalt(III) example (no. 2). This somewhat slower electron transfer for the Pt(IV)/S(IV) system is most likely a result of differences in reactivity of Pt(IV) and Co(III) as oxidants, since theory predicts a decrease by a factor of only 2–4 in going from a one-electron to a comparable two-electron transfer system,[23] though this figure is derived for gaseous systems only. There is also the necessity of drastic stereochemical rearrangement in the Pt(IV) to Pt(II) conversion unlike the case for the Co^{III}/Co^{II} system.

Another comparison of interest concerns the reactions which clearly involve O-bonded to S-bonded sulfito isomerization, nos. 3 and 6 (Table XI). These have very similar rate constants at 25 °C, although the temperature parameters are rather different. It is noteworthy that reaction no. 5, which we have concluded previously[7] does *not* involve sulfito isomerization but only S-bonded addition, is the only clearly second-order process in the tabulation. It also has a pseudo-first-order rate constant much in excess of the simple first-order isomerization rate of no. 3 even in sulfite as dilute as 0.01 M ($k \cong 4 \times 10^{-3}$ s^{-1}, as compared to $\sim 3 \times 10^{-4}$ s^{-1}). It is of further interest that reaction no. 6, in which S-bonded sulfite replacement of NH_3 occurs accompanied by O- to S-bonded isomerization, is rate limited by the latter process, since no sulfite concentration dependence is observed. The above discussion thus suggests that sulfite replacement of normally "stable" cis ligands such as OH^- (reaction no. 5) or NH_3 (reaction no. 6) can take place much more rapidly than isomerization in systems of this type.

Acknowledgment. Financial support of this research from the Charles D. and Frances H. Larkin Foundation of the State University of New York at Buffalo is gratefully acknowledged. The authors are also grateful to V. K. Joshi of this laboratory, who independently confirmed the preparative procedure for aquopentaammineplatinum(IV) perchlorate.

Registry No. I, 86767-51-3; II, 86767-52-4; III, 86767-53-5; $[Pt(NH_3)_5OH_2](ClO_4)_4$, 86767-49-9; SO_2, 7446-09-5; HSO_3^-, 15181-46-1.

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Notes

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Redox Potentials of Bis(1,4,7-triazacyclononane) Complexes of Some First Transition Series Metals(II, III). Preparation of Bis(1,4,7-triazacyclononane)nickel(III) Perchlorate

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and Heinz-Josef Küppers

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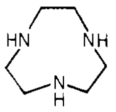
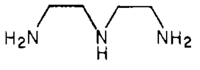
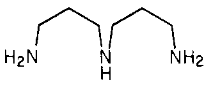
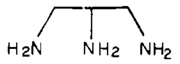
Since its original preparation in 1972[1] and the subsequent synthesis of a series of transition-metal complexes,[2] it has been recognized that the cyclic amine 1,4,7-triazacyclononane ($[9]aneN_3$) is a strong tridentate chelating ligand.[3] To date, only octahedral complexes containing two such ligands of cobalt(III),[1] nickel(II),[2–4] and copper(II)[2] have been isolated and characterized. The three N donors can only coordinate facially, which is in contrast to the well-known open-chain amines (2-aminoethyl)-1,2-ethanediamine (dien) and (3-aminopropyl)-1,3-propanediamine (dpt), the cobalt(III) species of which are dominated by the meridional structures.[5,6] Recently, the facially coordinating ligand 1,2,3-triaminopropane (ptn) has become available in good yields,[7] and the $[Co(ptn)_2]^{3+}$ and $[Ni(ptn)_2]^{2+}$ complexes[7,8] have been isolated. We have now extended the series of bis(triamine)metal(II, III) complexes and have studied their relationship in aqueous solution, determining formal redox potentials of the couples $[([9]aneN_3)_2M]^{3+/2+}$ (M = Mn, Fe, Co, Ni).


$[9]aneN_3$


dien


dpt


ptn

Results and Discussion

Syntheses of Complexes. A series of bis(1,4,7-triazacyclononane)metal(II) complexes have been synthesized by following a procedure described by Pedersen[9] for the preparation of chromium(III)–amine complexes in excellent yields. The appropriate metal chloride, $MCl_2 \cdot xH_2O$ (M = Mn, Fe, Co, Ni), was dissolved in dimethyl sulfoxide at 190 °C. At this

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Table I. UV-Visible Absorption Spectra of $[([9]aneN_3)_2M]$ Complexes

M	λ_{max}, nm (ϵ, L mol^{-1} cm^{-1})	d^n	μ_{eff},^{a} μ_B	ref
Cr(III)	340 (64), 439 (88)	d^3	not measd	this work
Fe(II)	601 (6), 387 (17), 288 (560)	d^6	diamag	this work
Fe(III)	500 (sh), 430 (82), 336 (288)	d^5	2.3	this work
Co(III)	458 (100), 333 (89)	d^6	diamag	1
Co(II)	318 (sh), 462 (5.9), 545 (sh), 630 (1.4), 850 (2.4)	d^7	4.8	this work
Ni(II)	870 (sh), 800 (7), 505 (5), 308 (12)	d^8	2.8	2
Ni(III)	570 (65), 312 (7.2 × 10^3)	d^7	2.0	this work

^{a} 20 °C.

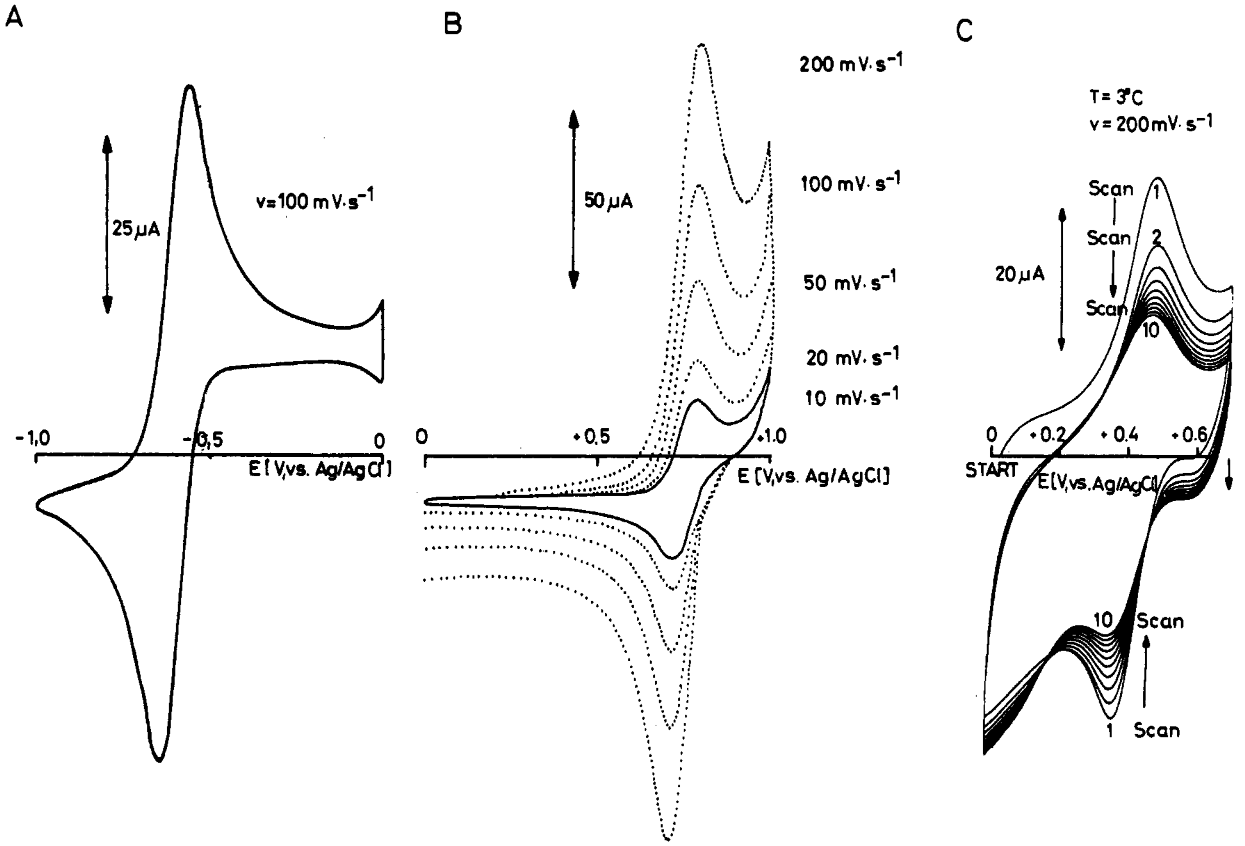

Figure 1. (A) Cyclic voltammogram of $[([9]aneN_3)_2Co]^{3+/2+}$ at 25 °C (0.1 M $LiClO_4$). (B) Cyclic voltammograms of $[([9]aneN_3)_2Ni]^{3+/2+}$ at 25 °C (0.1 M $LiClO_4$). (C) Cyclic voltammograms of $[([9]aneN_3)_2Mn]^{3+/2+}$ at 3 °C (0.1 M KCl).

temperature, the former water of crystallization of the dichlorides was allowed to evaporate, and at temperatures between 20 and 70 °C the cyclic amine dissolved in ethanol (~1 M) was added. In all cases, precipitates of $[([9]aneN_3)_2M]Cl_2$ formed immediately.

$[([9]aneN_3)_2Ni]Cl_2$ had been prepared previously.[2] The crystals of $[([9]aneN_3)_2Co]Cl_2$ had a nondescript gray color and were not stable in air. In aqueous solution and in the solid state, oxidation to the yellow $[([9]aneN_3)_2Co^{III}]^{3+}$ cation by dioxygen occurred. The UV-visible spectrum (Table I) and the magnetic moment (4.8 μ_B) are typical for a d^7 high-spin Co(II)-N_6 chromophore of high symmetry. Similar data are reported for $[Co(sep)]^{2+}$ and $[Co(en)_3]^{2+}$.[10] The stability of $[([9]aneN_3)_2Co]^{2+}$ in aqueous solution (pH 5-7) is high. At 25 °C no decomposition due to hydrolysis was observed for at least 3 h. The same ion formed readily from the yellow $[([9]aneN_3)_2Co^{III}]^{3+}$ cation by reduction with Zn in aqueous solution. Oxidation by dioxygen produces H_2O_2 and the cobalt(III) species. Crystals of $[([9]aneN_3)_2Mn]Cl_2$ are colorless. Aqueous solutions at pH 7 and 25 °C are relatively stable to decomposition, but they are air sensitive. Crystals of $[([9]aneN_3)_2Fe]Br_2·3H_2O$ are faint blue and diamagnetic as was judged from a magnetic measurement of a powdered sample (Faraday method). Aqueous solutions are stable at 25 °C but are air sensitive.

The same procedure as described above has been used to prepare $[([9]aneN_3)_2Cr]Br_3·5H_2O$ from Me_2SO solutions of $CrCl_3·6H_2O$. Beautiful yellow crystals of the bromide salt were obtained from recrystallizations of the chloride in water with sodium bromide. Using $FeCl_3·6H_2O$ as starting material, this procedure yielded orange crystals of $[([9]aneN_3)_2Fe]Br_3·5H_2O$. Aqueous solutions of the latter at pH 7 and 25 °C were stable to hydrolysis. The magnetic moment of 2.3 μ_B indicates a low-spin d^5 electron configuration of Fe(III).

When violet-red $[([9]aneN_3)_2Ni](ClO_4)_2$ (pH 2) was treated with potassium peroxodisulfate at 20 °C, a color change to orange-brown was observed within a few minutes. Upon addition of sodium perchlorate, gold-brown crystals of $[([9]aneN_3)_2Ni](ClO_4)_3$ precipitated. The UV-visible spectrum of the cation $[([9]aneN_3)_2Ni]^{3+}$ (Table I) and its magnetic moment of 2.0 μ_B are in agreement with a low-spin d^7 configuration of a Ni(III) center in a pseudooctahedral environment of six N donors.[11-13] Again, aqueous solutions of this species were stable in the absence of reductants. Addition of

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Table II. Formal Reduction Potentials of Bis(triamine)metal(II)/Bis(triamine)metal(III) Couples vs. NHE at 25 °C

	$E°$, V	ΔE_p,[a] mV	
$[([9]aneN_3)_2Cr]^{3+/2+}$	−1.14[b]	63	reversible[e]
$[([9]aneN_3)_2Mn]^{3+/2+}$	+0.62[c]	120[d]	quasi-reversible[f]
$[([9]aneN_3)_2Fe]^{3+/2+}$	+0.13[c]	60	reversible[f]
$[([9]aneN_3)_2Co]^{3+/2+}$	−0.41[b]	70	reversible[e]
$[([9]aneN_3)_2Ni]^{3+/2+}$	+0.95[b]	75	quasi-reversible[f]
$[Ni(ptn)_2]^{3+/2+}$	+0.93	115	quasi-reversible[f]
$[Co(ptn)_2]^{3+/2+}$	−0.34	70	reversible[e]
$[Co(dpt)_3]^{3+/2+}$	+0.28[b]	60	reversible[e]

[a] Scan rate 50 mV s^{-1}. [b] Measured in 0.1 M $LiClO_4$. [c] Measured in 0.1 M KCl at 3 °C. [d] Scan rate 200 mV s^{-1}. [e] Hanging-mercury-drop electrode. [f] Glassy-carbon electrode.

sodium iodide or sodium bromide yielded iodine or bromine and $[([9]aneN_3)_2Ni^{II}]^{2+}$.

Electrochemistry. Cyclic voltammograms of the $[([9]aneN_3)_2M^{III}]^{3+}$ ion (~10^{-3} M) in 0.1 M KCl (or 0.1 M $LiClO_4$), where M(III) = Cr(III), Fe(III), Co(III) (shown for Co(III) in Figure 1a), exhibited one wave in the potential range +1.0 to −1.5 V vs. Ag/AgCl. The peak-to-peak separations (Table II) and an i_{pa}/i_{pc} ratio of 1.0 indicated the electrochemical reversibility for the respective one-electron redox process. Formal redox potentials summarized in Table II indicate a strong stabilization of the oxidation state +3 for the chromium and cobalt complexes, the reduced species being strong reductants; contrasting is the $[([9]aneN_3)_2Fe^{III}]^{3+}$ complex, which appears to be a weak oxidant.

Figure 1B shows the cyclic voltammogram of the couple $[([9]aneN_3)_2Ni^{II}]^{2+/3+}$ in 0.1 M $LiClO_4$. One wave was observed in the potential range +1.2 to −1.5 V vs. NHE. The peak-to-peak separation, ΔE_p, increases with increasing scan rate (10–200 mV s^{-1}) whereas the i_{pa}/i_{pc} ratio remains constant (1.0). This behavior is typical for a quasi-reversible one-electron redox process.[14] The formal redox potential of +0.95 V vs. NHE indicates that the Ni(III) complex is a strong oxidant. This is in good agreement with other Ni(II)/Ni(III) couples containing other macrocyclic N-donor ligands.[12,13] A very similar quasi-reversible electrochemical behavior was observed for the couple $[Ni(ptn)_2]^{2+/3+}$. A formal redox potential of +0.93 V has been determined.

The cyclic voltammogram of $[([9]aneN_3)_2Mn]^{2+}$ in 0.1 M KCl is more complex. At 25 °C one highly irreversible oxidation peak at 0.68 V vs. NHE was observed, but the corresponding reduction peak has not been detected. At lower temperatures (3 °C) and scan rates of 200 mV s^{-1} the cyclic voltammograms shown in Figure 1C has been recorded, which now contained a reduction peak at +0.58 V vs. NHE. Repetitive fast scans showed a time-dependent decrease of i_{pa} and i_{pc}, indicating the chemical decomposition of the $[([9]aneN_3)_2Mn^{III}]^{3+}$ species.

Finally, the cyclic voltammograms of two further cobalt(III) complexes containing two tridentate amine ligands have been measured. The couples $[Co(ptn)_2]^{3+/2+}$ and $[Co(dpt)_2]^{3+/2+}$ exhibit reversible electrochemical behavior (Table II). Interestingly, a dramatic difference of formal redox potentials for the two complexes $[Co(ptn)_2]^{3+}$ ($E°$ = −0.34 V vs. NHE) and $[Co(dpt)_2]^{3+}$ ($E°$ = +0.28 V) is observed. The latter complex is a strong Co(III) oxidant containing an octahedral N_6-donor set whereas the former is a strong reductant in the +2 oxidation state (as is $[Co([9]aneN_3)_2]^{2+}$, $[Co(sep)]^{2+}$,[10] or $[Co(dien)_2]^{2+}$ [15]). Even for the $[Co(NH_3)_6]^{3+/2+}$ couple a formal potential of only +0.10 V vs. NHE has been estimated.[16] The unusual positive potential for $[Co(dpt)_2]^{3+/2+}$ is readily explained in terms of differing Co–N bond lengths in the +2 and +3 oxidation states of the cobalt center. The crystal structure of $[Co(dpt)_2](ClO_4)_3$[6a] reveals that due to steric constraints of the ligands four Co–N bond lengths are rather long (~2.03 Å), resembling distances found for Co(II)–N bonds, whereas only two Co–N bond lengths per bound ligand exhibit the normal Co(III)–N distance of 1.97 Å. Thus, due to the steric requirements of the dipropylenetriamine ligand, the +2 oxidation state of cobalt is already preformed in the ground state of the $[Co(dpt)_2]^{3+}$ cation.

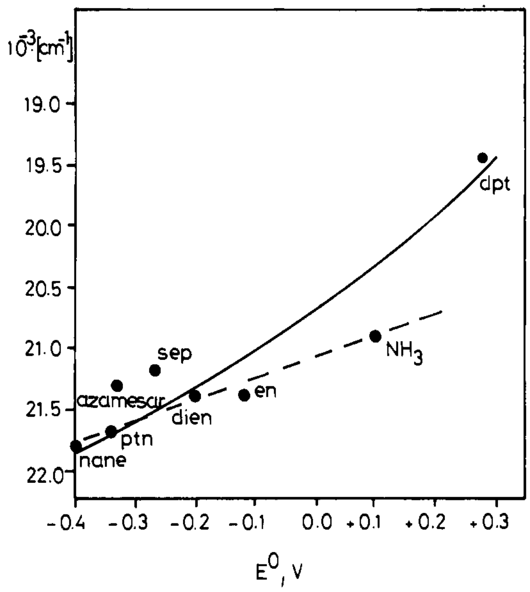

Figure 2. Correlation between the maxima of the first d–d transitions of bis(triamine)cobalt(III) species and the redox potential of $[(triamine)_2Co]^{3+/2+}$ couples (values for $[Co(sep)]^{3+}$, $[Co(azamesar)]^{3+}$, and $[Co(en)_3]^{3+}$ from ref 10; those for $[Co(dien)_2]^{3+}$ from ref 15).

Quite the contrary seems to be the case for the $[Co(ptn)_2]^{3+}$ species.[7] Here, the crystal structure shows six rather short Co(III)–N bond lengths (1.96 Å), which agree well with the steric demands of the ligand 1,2,3-triaminopropane and an electronic d^6 low-spin configuration. A Co–N bond lengthening (Co(II)–N ~ 2.15 Å) in going from Co(III) to Co(II) increases the strain of the coordinated triamines considerably. Therefore, the +3 oxidation state is stabilized over the +2 state. Exactly the same situation has been envisaged for the encapsulated cobalt center in Sargeson's $[Co(sep)]^{3+}$,[10] and for $[Co([9]aneN_3)_2]^{3+}$ the same arguments are believed to be valid.

It is noted that a correlation between the maxima of the first d–d transitions ($^1A_1$–$^1T_1$) of bis(triamine)cobalt(III) complexes and their respective redox potentials may exist. In Figure 2 the correlation is shown. The $[Co(en)_3]^{3+}$ species also roughly conforms to it, whereas the encapsulated complexes $[Co(azamesar)]^{3+}$ and $[Co(sep)]^{3+}$ appear to be offset. Such correlations have been found for Co(III) macrocyclic complexes,[17] but Lintvedt's caveat[18] should be borne in mind. A second more linear correlation is possible among $[Co([9]aneN_3)_2]^{3+}$, $[Co(ptn)_2]^{3+}$, $[Co(dien)_2]^{3+}$, $[Co(en)_3]^{3+}$, and $[Co(NH_3)_6]^{3+}$ in which case the $[Co(dpt)_2]^{3+}$ complex does not fit. But it should be borne in mind that the $[Co(NH_3)_6]^{3+/2+}$ potential represents an estimate[16] and has not been measured experimentally.

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Table III. Analytical Data

complex	color	% C calcd	% C found	% H calcd	% H found	% N calcd	% N found	% metal calcd	% metal found	% halide calcd	% halide 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	21.87	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-triaminopropane[7]). Analytical data for the new complexes are summarized in Table III.

Preparation of Complexes. The complexes $[([9]aneN_3)_2Co]Br_3 \cdot 5H_2O$,[1] $[([9]aneN_3)_2Ni]Cl_2 \cdot 4H_2O$,[2] $[Co(dpt)_2](ClO_4)_3$,[6a] and $[Co(ptn)_2](ClO_4)_3$[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 $[([9]aneN_3)_2M]Cl_2$ formed immediately, which were filtered off, washed with ethanol and ether, and dried. Except $[([9]aneN_3)_2Ni]Cl_2$, 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%. $[([9]aneN_3)_2Fe]Cl_2$ was converted to the blue bromide salt $[([9]aneN_3)_2Fe]Br_2 \cdot 3H_2O$ from an oxygen-free, aqueous solution of the chloride with sodium bromide.

$[([9]aneN_3)_2Cr]Br_3 \cdot 5H_2O$. $CrCl_3 \cdot 6H_2O$ (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 $[([9]aneN_3)_2Cr]Cl_3$ 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 $[([9]aneN_3)_2Cr]Br_3 \cdot 5H_2O$ precipitated; yield 1.6 g.

$[([9]aneN_3)_2Fe]Br_3 \cdot 5H_2O$. $FeCl_3 \cdot 6H_2O$ (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.

$[([9]aneN_3)_2Ni](ClO_4)_3$. A 0.5-g sample of $[([9]aneN_3)_2Ni](ClO_4)_2$, 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; $[Co(ptn)_2](ClO_4)_3$, 86709-86-6; $[Ni(ptn)_2]^{2+}$, 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 suggested[3] 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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