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Template Condensation of Formaldehyde with Triamines. Synthesis and Characterization of Nickel(II) Complexes with the Novel Hexaaza Macrotricyclic Ligands 1,3,6,9,11,14-Hexaazatricyclo[12.2.1.1^{6,9}]octadecane and 1,3,6,10,12,15-Hexaazatricyclo[13.3.1.1^{6,10}]eicosane

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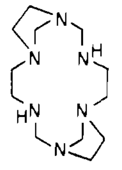
Metal template syntheses often provide selective routes toward products that are not obtainable in the absence of metal ion. Recently, the facility of template syntheses involving formaldehyde and amines to yield complexes of multidentate and macrocyclic ligands has been demonstrated.[1-7] In these reactions, formaldehyde links two amine moieties in the cyclization to yield methylenediamine (NCH_2N) linkages. It has been known that methylenediamine groups are unstable when they contain primary or secondary amines.[8] In addition, it has been revealed that methylenediamine groups containing secondary nitrogens are also stabilized by coordination to metal ion.[2-4]

Utilizing the characteristics of methylenediamine linkages, we have designed and synthesized Ni(II) macrotricyclic complexes of A and B by the simple template condensation of formaldehyde and appropriate triamines.[9] The complexes are quite interesting because fully saturated hexaaza macrocyclic ligands acting as tetradentates have very rarely been reported.[7] Furthermore, the formation of 1,3-diazacyclopentane or 1,3-diazacyclohexane ring moieties from the reaction of two amine groups of a multiamine with aldehydes or ketones has occurred only in limited cases.[6,10-14]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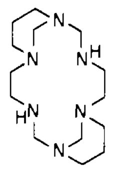
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This paper is an account of the synthesis and characterization of the Ni(II) complexes of 1,3,6,9,11,14-hexaazatricyclo[12.2.1.1^{6,9}]octadecane (A) and 1,3,6,10,12,15-hexaazatricyclo[13.3.1.1^{6,10}]eicosane (B). The X-ray crystal structure of [Ni(A)]$Cl_2 \cdot 2H_2O$ is also described.

Experimental Section

Instrumentation. Conductance measurements were performed by using an Industrial Instruments Model RC 216 B2 conductivity bridge in conjunction with a Beckman Model C1-BB1 conductivity cell with a cell constant of 0.10 cm^{-1}. Infrared spectra were measured with a Shimadzu IR-440 spectrophotometer. Electronic absorption spectra were recorded with a Perkin-Elmer Lambda 5 UV/vis spectrophotometer. ^1H and ^{13}C NMR spectra were recorded with a Bruker WP 80 SY SER ECBAF 223 FT NMR spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Synthesis. All solvents and chemicals used in syntheses were of reagent grade and were used without further purification. *Caution*! Some of the compounds containing perchlorate anions must be regarded as potentially explosive and should be handled with caution.

[Ni(A)]$Cl_2 \cdot 2H_2O$. To a stirred methanol solution (50 mL) of $NiCl_2 \cdot 6H_2O$ (11.9 g) were added diethylenetriamine (10.3 g) and 36% aqueous formaldehyde (24.3 mL), and the mixture was heated at reflux for 4 h until a brownish yellow solution resulted. The solution was filtered to remove insoluble material and allowed to stand overnight at room temperature. The yellow crystals that formed were filtered, washed with cold methanol and diethyl ether, and air-dried. The same product resulted even if ethylenediamine or methylamine was added to the initial reaction mixture and heated at reflux. Crystals for X-ray crystallographic work were selected from the crude products; yield ~90%. Anal. Calcd for $NiC_{12}H_{30}N_6Cl_2O_2$: C, 34.02; H, 7.20; N, 20.01. Found: C, 34.18; H, 7.10; N, 20.29.

Table I. Spectral and Conductance Data for Nickel(II) Macrotricyclic Complexes

complex	IR, cm^{-1}	electronic spectra[a] λ_{max}, nm (ϵ, M^{-1} cm^{-1})	Λ_M,[a] Ω^{-1} cm^{-2} M^{-1}
[Ni(A)]$Cl_2 \cdot 2H_2O$		444 (72)	
[Ni(A)]$(ClO_4)_2$	ν_{NH} 3165	443 (72), 447 (80)[b]	238
[Ni(B)]$(ClO_4)_2$	ν_{NH} 3259	468 (58), 465 (95)[b]	198
[Ni(A)$(NCS)_2$][c]	ν_{NH} 3205 ν_{CN} 2050 ν_{CS} 780		
[Ni(B)$(NCS)_2$][c]	ν_{NH} 3242 ν_{CN} 2060 ν_{CS} 780		
[Ni(Me_2[14]aneN_6)]-$(ClO_4)_2$[d]		446 (40)	
[Ni(Et_2[14]aneN_6)]-$(ClO_4)_2$[d]		445 (47)	

[a] Measured in aqueous solutions at 20 °C unless specified otherwise. [b] Measured in CH_3NO_2. [c] No suitable solvents were found for the measurement of λ_{max} and Λ_M. [d] Reference 7. Me_2[14]aneN_6 = 1,8-dimethyl-1,3,6,8,10,13-hexaazacyclotetradecane; Et_2[14]aneN_6 = 1,8-diethyl-1,3,6,8,10,13-hexaazacyclotetradecane.

[Ni(A)]$(ClO_4)_2$. [Ni(A)]$Cl_2 \cdot 2H_2O$ (0.8 g) was dissolved in hot water (40 mL), and an aqueous solution (5 mL) of excess $LiClO_4 \cdot 3H_2O$ (1.4 g) was added with stirring. The solution was allowed to stand in the refrigerator until yellow crystals formed, which were filtered, washed with methanol, and air-dried. Anal. Calcd for $NiC_{12}H_{26}N_6Cl_2O_8$: C, 28.15; H, 5.12; N, 16.41. Found: C, 27.95; H, 4.93; N, 16.32.

[Ni(B)]$(ClO_4)_2$. To a methanol solution (100 mL) of $NiCl_2 \cdot 6H_2O$ (11.9 g) were added *N*-(2-aminoethyl)-1,3-propanediamine (12.1 g) and 36% aqueous formaldehyde (30.9 mL), and the mixture was stirred and heated at reflux for 5 h until a yellow solution resulted. The solution was allowed to cool at room temperature and filtered to remove the insoluble material. A saturated aqueous solution of excess $LiClO_4$ or perchloric acid was added to the filtrate with stirring, and the mixture was stored in a refrigerator until yellow crystals formed. The crystals were filtered, washed with methanol, and dried in vacuo. The product was recrystallized from hot water; yield ~70%. Anal. Calcd for $NiC_{14}H_{30}N_6Cl_2O_8$: C, 31.13; H, 5.61; N, 15.56. Found: C, 31.07; H, 5.64; N, 15.22.

[Ni(A)]$(PF_6)_2$ and [Ni(B)]$(PF_6)_2$. To an acetonitrile suspension of the corresponding perchlorate salt was added excess NH_4PF_6 dissolved in acetonitrile. The complex went into solution, and the white precipitate of NH_4ClO_4 was removed by filtration. Water was added dropwise to the filtrate to induce crystallization. The yellow crystals were filtered, washed with a 5:1 mixture of water and acetonitrile, and dried in vacuo. ^{13}C NMR (CD_3NO_2): [Ni(A)]$(PF_6)_2$, δ 48.3, 49.1, 56.1, 56.3, 70.9, 76.4; [Ni(B)]$(PF_6)_2$, δ 24.5, 46.2, 48.3, 57.6, 60.5, 71.5, 75.0.

[Ni(A)$(NCS)_2$] and [Ni(B)$(NCS)_2$]. To a saturated aqueous solution of [Ni(A)]$(ClO_4)_2$ or [Ni(B)]$(ClO_4)_2$ was added excess KSCN dissolved

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Scheme I

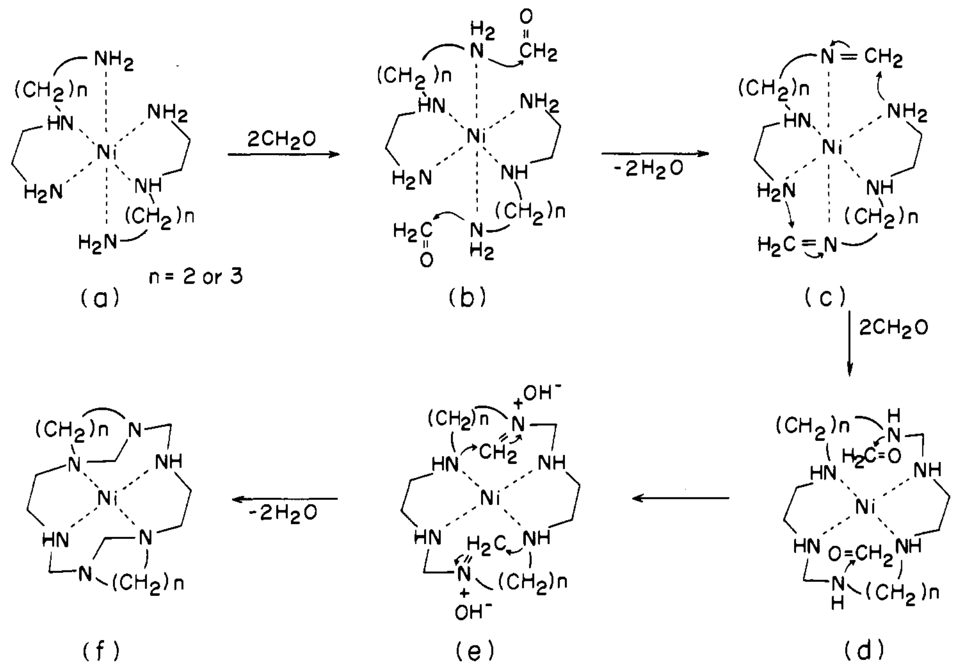


Table II. Atomic Coordinates and Equivalent Thermal Parameters for Non-Hydrogen Atoms of $[Ni(A)]Cl_2 \cdot 2H_2O$[a]

atom	x	y	z	U_{eq}[b]
Ni[c]	0	0	0	23
C(2)	1283 (6)	2684 (12)	7 (9)	42
N(3)	296 (5)	2094 (8)	191 (5)	29
C(4)	−26 (8)	2567 (10)	1118 (6)	38
C(5)	−974 (8)	1857 (11)	1235 (7)	40
N(6)	−907 (4)	231 (7)	978 (4)	25
C(7)	−619 (7)	−802 (11)	1765 (6)	32
C(8)	−1176 (8)	−2278 (13)	1626 (7)	46
N(9)	−1732 (5)	−2073 (9)	785 (5)	39
C(18)	−1852 (6)	−445 (11)	737 (7)	31
Cl	1334 (2)	−3510 (3)	1111 (2)	45
O(W)	1862 (2)	−209 (10)	1946 (8)	86

[a] Positional parameters ×10^4, thermal parameters ×10^3 Å^2. [b] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a^*_i a^*_j a_i a_j$. [c] Site occupancy factor 0.5.

Table III. Bond Distances (Å) and Angles (deg) for $[Ni(A)]Cl_2 \cdot 2H_2O$

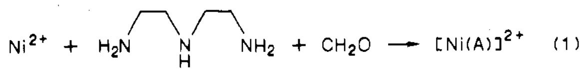
Ni–N(3)	1.906 (7)	Ni–N(6)	1.934 (6)
N(1)–C(2)	1.428 (14)	C(2)–N(3)	1.512 (11)
N(3)–C(4)	1.491 (12)	C(4)–C(5)	1.489 (15)
C(5)–N(6)	1.479 (11)	N(6)–C(7)	1.522 (11)
N(6)–C(18)	1.504 (10)	C(7)–C(8)	1.530 (15)
C(8)–N(9)	1.473 (13)	N(9)–C(18)	1.440 (12)
N(6)–Ni–N(3)	86.3 (3)	N(11)–Ni–N(6)	93.7 (3)
C(2)–N(3)–Ni	120.5 (6)	C(4)–N(3)–Ni	109.6 (5)
C(5)–N(6)–Ni	109.4 (5)	C(7)–N(6)–Ni	108.7 (5)
C(18)–N(6)–Ni	112.0 (5)	N(3)–C(2)–N(1)	115.3 (8)
C(4)–N(3)–C(2)	110.4 (8)	C(5)–C(4)–N(3)	105.3 (7)
N(6)–C(5)–C(4)	108.5 (8)	C(7)–N(6)–C(5)	113.6 (7)
C(8)–C(7)–N(6)	105.4 (7)	N(9)–C(8)–C(7)	106.4 (8)
N(9)–C(18)–N(6)	106.0 (7)	C(10)–N(9)–C(8)	113.3 (8)
C(18)–N(6)–C(5)	112.6 (7)	C(18)–N(6)–C(7)	100.4 (6)
X(18)–N(9)–C(8)	103.0 (8)	C(18)–N(9)–C(10)	112.7 (8)

in a minimum amount of water. The solution was kept in a refrigerator until the pink precipitate formed. The precipitate was filtered, washed with methanol, and dried in vacuo. Anal. Calcd for $NiC_{14}H_{26}N_8S_2$: C, 39.18; H, 6.11; N, 26.11. Found: C, 39.65; H, 6.14; N, 25.58. Calcd for $NiC_{16}H_{30}N_8S_2$: C, 42.01; H, 6.83; N, 24.63. Found: C, 42.03; H, 6.61; N, 24.50.

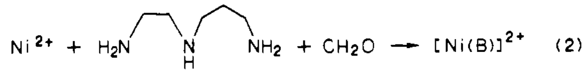
X-ray Crystallography. Crystal data for $[Ni(A)]Cl_2 \cdot 2H_2O$: $NiC_{12}H_{30}N_6Cl_2O$, orthorhombic, space group *Pbca* (No. 61), a = 14.142 (3) Å, b = 8.779 (2) Å, c = 14.648 (2) Å, V = 1818.6 (6) Å^3, Z = 4, D(calcd) = 1.534 g cm^{-3}, μ(Mo Kα) = 13.40 cm^{-1}. A rectangular crystal (0.30 × 0.45 × 0.30 mm) was used to collect 1692 unique reflections (one octant, Rigaku AFC 4 diffractometer, graphite monochromator, $4° \leq 2\theta \leq 51°$, 18 °C), of which 816 were considered observed ($6\sigma(F_0)$). The structure was solved by heavy-atom methods. All non-hydrogen atoms were refined anisotropically. The positional parameters of the hydrogen atoms were refined, while the isotropic thermal parameters were fixed with values 1.3 times those of the bonded atoms. At convergence, $R(F)$ = 0.0524, $R_w(F)$ = 0.0521, GOF = 0.879, Δ/σ = 0.783 (U_{13} of O(W)), and $\Delta(\rho)$ = 1.05 e Å^{-3}. All calculations used SHELX 76.[15] The final atomic parameters are listed in Table II. Bond distances and angles are listed in Table III.

Results and Discussion

Syntheses and Properties. Template condensations of triamines with formaldehyde in the presence of Ni(II) ion produced the Ni(II) macrotricyclic complexes $[Ni(A)]X_2$ and $[Ni(B)]X_2$ (X = Cl, ClO_4, PF_6) as described in eq 1 and 2.



$$Ni^{2+} + H_2N\!\!\diagup\!\!\diagdown\!\!\underset{H}{N}\!\!\diagup\!\!\diagdown\!\!NH_2 + CH_2O \longrightarrow [Ni(A)]^{2+} \quad (1)$$



$$Ni^{2+} + H_2N\!\!\diagup\!\!\diagdown\!\!\underset{H}{N}\!\!\diagup\!\!\diagdown\!\!\diagup\!\!NH_2 + CH_2O \longrightarrow [Ni(B)]^{2+} \quad (2)$$

Complexes $[Ni(A)]^{2+}$ and $[Ni(B)]^{2+}$ contain six nitrogen atoms in the ligands, all of which are involved in four methylenediamine (NCH_2N) linkages. In accordance with the characteristics of methylenediamine linkages stated previously, four nitrogen atoms are tertiary while the remaining two are secondary and are coordinated to the Ni(II) ion. The complexes contain two 1,3-diazacyclopentane or 1,3-diazacyclohexane ring moieties fused to the macrocyclic ligands. Reports of the formation of such rings from the reaction of two amine groups of the multiamine with aldehydes or ketones are quite rare.[6,10–14] The proposed synthetic routes for $[Ni(A)]^{2+}$ and $[Ni(B)]^{2+}$ are shown in Scheme I.

Complexes $[Ni(A)](ClO_4)_2$ and $[Ni(B)](ClO_4)_2$ exhibit remarkable stability against ligand dissociation in acidic solutions. No absorbance change was observed for aqueous solutions of $[Ni(A)](ClO_4)_2$ (7.6×10^{-3} M) and of $[Ni(B)](ClO_4)_2$ (2.9×10^{-3} M) upon the addition of $HClO_4$ (0.15 M) in 24 h.

The values of molar conductance (Table I) of $[Ni(A)](ClO_4)_2$ and $[Ni(B)](ClO_4)_2$ indicate that the complexes are 1:2 electrolytes.[17] The infrared spectra (Table I) of $[Ni(A)](ClO_4)_2$ and

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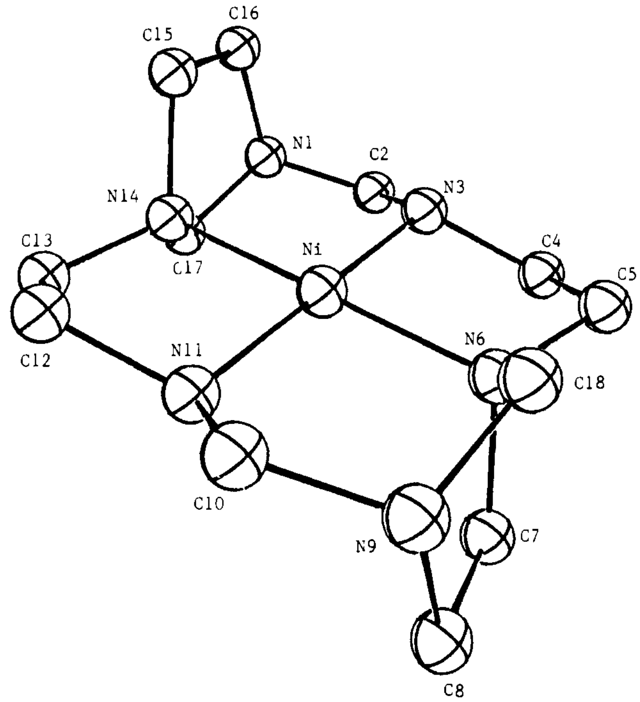
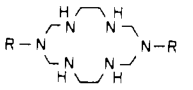


Figure 1. ORTEP view of the cation for $[Ni(A)]Cl_2·2H_2O$ with the atomic numbering scheme.

$[Ni(B)](ClO_4)_2$ show single absorptions attributed to ν_{NH} of the coordinated secondary amines. A much higher ν_{NH} value (3259 cm^{-1}) for $[Ni(B)](ClO_4)_2$ than that (3165 cm^{-1}) for $[Ni(A)](ClO_4)_2$ indicates that the Ni–N interaction in $[Ni(B)](ClO_4)_2$, containing 1,3-diazacyclohexane ring moieties in the macrocycle, is much weaker than in $[Ni(A)](ClO_4)_2$, containing 1,3-diazacyclopentane ring moieties. The electronic absorption spectra (Table I) of $[Ni(A)]^{2+}$ and $[Ni(B)]^{2+}$ show that the complexes have square-planar $Ni^{II}–N_4$ chromophores.[18-21] The λ_{max} value of $[Ni(A)]^{2+}$ is similar to that of $[Ni(R_2[14]aneN_6)]^{2+}$ (**1**), which



R = CH_3 or C_2H_5

$[Ni(R_2[14]aneN_6)]^{2+}$ (**1**)

contains a fully saturated 14-membered hexaaza macrocyclic ligand.[7] However, $[Ni(B)]^{2+}$ absorbs at ~25 nm longer wavelengths than $[Ni(A)]^{2+}$ in aqueous solutions, indicating that a macrotricyclic ligand containing six-membered 1,3-diazacyclohexane ring moieties exerts a much weaker ligand field than one containing five-membered 1,3-diazacyclopentane ring moieties. The results show that the $Ni^{II}–N$ interaction and the ligand field strength of the macrocyclic complex vary widely, depending on the small ring moieties fused to the macrocycle even if the same main framework of the macrocycle is retained. ^{13}C NMR spectra of PF_6^- salts of $[Ni(A)]^{2+}$ and $[Ni(B)]^{2+}$ show six and seven unique carbon peaks, respectively, in CH_3NO_2-d_3, as summarized in the Experimental Section. These are consistent with the ligand structures proposed.

Complexes $[Ni(A)](ClO_4)_2$ and $[Ni(B)](ClO_4)_2$ react with excess KSCN in aqueous solutions to give the six-coordinate complexes $[Ni(A)(NCS)_2]$ and $[Ni(B)(NCS)_2]$, whose IR spectra (Table I) show that the nitrogen atoms of NCS^- ligands are coordinated to the Ni(II) ion.[22]

Structure of $[Ni(A)]Cl_2·2H_2O$. An ORTEP view of the $[Ni(A)]^{2+}$ cation with the atomic numbering scheme is presented in Figure 1. The cation possesses a crystallographic center of symmetry. The nickel ion is coordinated to the two tertiary and two secondary nitrogen atoms with a square-planar geometry. Both the chloride ions and the water molecules are placed above and below the coordination plane with displacements of 3.962 (3) and 3.884 (11) Å, respectively, from the nickel ion.

The 14-membered macrocyclic ring is ruffled and contains two five- and two six-membered chelate rings. The five-membered chelate ring assumes a half-chair conformation. The N–C–C–N torsion angle in the ethylenediamine moiety is 48.7 (7)°. The six-membered chelate ring assumes a conformation intermediate between the normal chair and half-chair conformations. The intracyclic torsion angles range from −30.6 (7) to 79.5 (8)°. The N–C–C–N bite angle and the bite distance in the five-membered chelate ring are 86.3 (3)° and 2.627 (9) Å, respectively. Those in the six-membered chelate ring are 93.7 (3)° and 2.801 (9) Å, respectively. These values are commonly observed ones in Ni(II) macrocyclic complexes.[4,23-26]

The 1,3-diazacyclopentane ring moiety assumes an envelope conformation with an N–C–C–N torsion angle of 1.1 (7)°. Two centrosymmetrically related ring moieties are almost perpendicular to the coordination plane with a dihedral angle of 105°. C(7) and C(8) are displaced by −1.288 (9) and −0.939 (11) Å from the coordination plane. Displacements of the four hydrogen atoms attached to C(7) and C(8) from the coordination plane range from −2.02 (9) to −1.06 (10) Å so that the thickness of the ligand amounts to ca. 3 Å on either side of the plane. H(3) is located toward the same direction of the 1,3-diazacyclopentane ring fused to the six-membered chelate ring including N(3).

There are four tertiary nitrogens, N(1), N(6), N(9), and N(14), and two secondary nitrogens, N(3) and N(11), in the ligand. The average N–C distance (1.45 ± 0.02 Å) involving uncoordinated tertiary N(1) is shorter by ca. 0.05 Å than that (1.50 ± 0.02 Å) involving coordinated tertiary N(6).

The Ni–N(6) distance [1.934 (6) Å] is longer by 4σ than the Ni–N(3) distance [1.907 (7) Å]. That is, Ni–N distances involving tertiary nitrogens are significantly longer than those involving secondary nitrogens. It has been observed that N-methylation of the secondary nitrogen donors of the macrocyclic complexes results in a decrease of the ligand field strength, and this has been explained by an increase in the Ni–N distances in the N-methylated complexes.[27-29] It is noteworthy that this observation was made for the complexes which contain either all tertiary or all secondary nitrogen donors in the ligand. For the complexes that contain both secondary and tertiary nitrogen donors in a ligand, there seems no consistent trend in the Ni–N bond distances. In the present study and for the six-coordinate complex $[Ni(\mathbf{2})](ClO_4)_2$,[30] Ni–N(tert) distances are significantly longer than Ni–N(sec) distances. However, no significant differences exist in the square-planar complex $[Ni(\mathbf{3})](ClO_4)_2$.[4]

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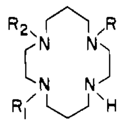
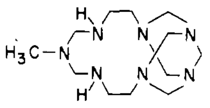


$R_1 = CH_2CH_2C(O)NH_2$
$R_2 = CH_2CH_2C{\equiv}N$

2



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of Korea. We thank Chee-Hun Kwak for technical assistance.

Registry No. $[Ni(A)]Cl_2{\cdot}2H_2O$, 119413-95-5; $H_2N(CH_2)_2NH(CH_2)_2NH_2$, 111-40-0; CH_2O, 50-00-0; $[Ni(A)](ClO_4)_2$, 119478-59-0; $[Ni(B)](ClO_4)_2$, 119413-97-7; $H_2N(CH_2)_2NH(CH_2)_3NH_2$, 13531-52-7; $[Ni(A)](PF_6)_2$, 119478-60-3; $[Ni(B)](PF_6)_2$, 119413-98-8; $[Ni(A)(NCS)_2]$, 119413-99-9; $[Ni(B)(NCS)_2]$, 119414-00-5.

Supplementary Material Available: Tables SI–SIV, listing crystal data and data collection parameters, anisotropic thermal parameters, atomic coordinates and thermal parameters of the hydrogen atoms, and bond lengths and angles involving the hydrogen atoms (4 pages); a table of observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

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Reduction by $^{\bullet}CO_2^-$ of (1-Methyl-4,4′-bipyridinium)pentaamminecobalt(III) Perchlorate and Kinetic Behavior of the Transient Radical in Aqueous Solution

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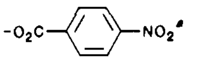
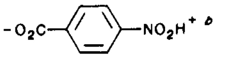
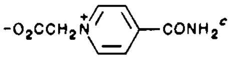
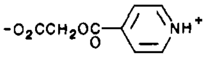
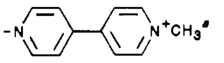
The subject of electron transfer within molecules is an intriguing and much studied topic. A wide variety of systems have been examined including binuclear metal complexes,[2] extended organics,[3] and metalloproteins.[2,4] Cobalt(III) complexes containing reducible aromatic ligands, L, have been much utilized for studying the modes of electron transfer. Typical examples are shown in Table I.[5-7] A popular approach is to effect very rapid *one-electron* reduction of the cobalt complex by using a deficiency of a vigorous reducing agent, usually e_{aq}^- or $^{\bullet}CO_2^-$ generated by pulse radiolysis. A definite amount of reduction is at the ligand center (reaction 1). The loss of the radical center can be easily monitored

$$\mathrm{Co^{III}\text{-}L} \xrightarrow[{}^{\bullet}\mathrm{CO_2^-}]{e_{aq}^-\ \text{or}} \mathrm{Co^{III}\text{-}L^{\bullet-}} \qquad (1)$$

spectrally. In the systems so far examined (Table I) decay of the coordinated radical ligand usually occurs by an intramolecular electron transfer (eq 2) leading to the cobalt(II) species. This

$$\mathrm{Co^{III}\text{-}L^{\bullet-}} \rightarrow \mathrm{Co^{II}\text{-}L} \quad k_1 \qquad (2)$$

Table I. Rate Constants for Decay of $Co(NH_3)_5(L^{\bullet-})^{n+}$ at 23–25 °C

–L	k_1, s^{-1}	k_2, $M^{-1}\,s^{-1}$	$2k_3$, $M^{-1}\,s^{-1}$	ref
 [a]	2.6×10^3			7
 [b]	5		1.5×10^8	7
 [c]	$\leq 2.0 \times 10^4$	1.5×10^9		5
	2.0×10^4	$\leq 6 \times 10^6$		5
	2.5×10^3			6
 [a] mbpy	8.7×10^2	5.4×10^7	2.4×10^8	*d*

[a] pH 7. [b] 1 M $HClO_4$. [c] pH 4.5–5.5. [d] This work.

is indicated by the observation of first-order loss of radical signal, with the rate constant k_1 being independent of the concentration of radical complex (i.e. dose of reductant radical used) and of Co^{III}–L complex used (in excess). Only rarely[5] is the first-order loss of Co^{III}–$L^{\bullet-}$ directly dependent on the concentration of Co^{III}–L present, and this is interpreted in terms of reaction 3. Sometimes

$$\mathrm{Co^{III}\text{-}L^{\bullet-}} + \mathrm{Co^{III}\text{-}L} \rightarrow \mathrm{Co^{III}\text{-}L} + \mathrm{Co^{II}\text{-}L} \quad k_2 \qquad (3)$$

the loss of Co^{III}–$L^{\bullet-}$ is second-order,[7] and this is attributed to a disproportionation in acid (eq 4). In all cases (2)–(4), the cobalt(II) product is expected to rapidly dissociate to constituents.

$$2\mathrm{Co^{III}\text{-}L{\cdot}H} \rightarrow \mathrm{Co^{III}\text{-}L} + \mathrm{Co^{II}\text{-}LH_2} \quad 2k_3 \qquad (4)$$

The presence of (3) makes it difficult to determine the value of k_1 (which is a small intercept on a k_{obs} vs [Co^{III}–L] plot). The occurrence of (4) is usually attended by mixed first- and second-order kinetics, since as the concentration of Co^{III}–$L^{\bullet-}$ is reduced, the importance of (4) is superseded by process 2 and k_1 results from the (first-order) end of the decay.

In a continuation of our interest in viologen radicals,[8] we have studied the reduction of the complex $(NH_3)_5Co(mbpy)^{4+}$ ($mbpy^+$ = 1-methyl-4,4′-bipyridinium cation; see Table I) by $^{\bullet}CO_2^-$, observed the coordinated bipyridinyl radical intermediate $(NH_3)_5Co(mbpy^{\bullet})^{3+}$, and noted the three modes of decay outlined above (Table I).

Experimental Section

Materials. 1-Methyl-4,4′-bipyridinium perchlorate and (1-Methyl-4,4′-bipyridinium)pentaamminecobalt(III) perchlorate were prepared as described in the literature[9] with slight modifications. The crude cobalt(III) product in solution was added to a column of CM-Sephadex C25 (Na^+ form). The column was washed with sodium perchlorate solutions (0.1–0.5 M), and $mbpy^+$, Co^{2+}, and $Co(NH_3)_5OS(CH_3)_2{}^{3+}$ were eluted. An orange fraction was eluted with 0.5–0.6 M sodium perchlorate solution. The first portion contained $Co(NH_3)_6{}^{3+}$, and the second portion, which was collected, was evaporated to a small volume. Ethanol addition caused deposition of pink crystals, which were recrystallized twice from water. Anal. Calcd for $[(NH_3)_5Co(mbpy)](ClO_4)_4{\cdot}H_2O$: C, 18.07; H, 3.86; N, 13.41. Found: C, 18.19; H, 3.71; N, 13.43. $\epsilon^{max}{}_{250nm} = 2.16 \times 10^4$, $\epsilon^{max}{}_{275nm} = 1.75 \times 10^4$, $\epsilon^{sh}{}_{340nm} \sim 95$, and $\epsilon^{max}{}_{475nm} = 69.1\ M^{-1}\,cm^{-1}$ in water. (1-Methyl-4,4′-bipyridinium)pentaammineruthenium(III) complex was prepared by adding several pieces of zinc amalgam to 1.0 g of $[Ru(NH_3)_5Cl]Cl_2$ suspended in 30 mL of water for 45 min in argon, with gentle stirring. The resulting solution was added to an argon-degassed solution of [mbpy]Cl (0.85 g in 10 mL of water). After 30 min the blue solution was cooled in ice and filtered. A 0.3-mL portion of 50% sulfuric acid and then 0.46 g of potassium peroxydisulfate were added with stirring. The orange solution after 15

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