Tripositive Mercury. Low Temperature Electrochemical Oxidation of 1,4,8,11-Tetraazacyclotetradecanemercury(II) Tetrafluoroborate

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Abstract: A complex of mercury(III) has been synthesized by electrochemical oxidation of $[Hg(Cyclam)][BF_4]_2$ (Cyclam = $[14]aneN_4$ or 1,4,8,11-tetraazacyclotetradecane) in propionitrile at −78°. Accessibility to mercury in a formally tripositive state is consistent with its ionization potentials and with known oxidation states and oxidation potentials of neighboring elements. Measurements by cyclic voltammetry, electron spin resonance, and visible spectroscopy establish that the half-life of $[Hg([14]aneN_4)]^{3+}$ is 5 s at −78°. The oxidation potential of $[Hg([14]aneN_4)]^{2+}$ shifts markedly as the temperature is lowered and becomes appreciably lower than the ligand oxidation potential. For $[Hg([14]aneN_4)]^{3+}$, the g factor is 2.014, the hyperfine coupling constant is 2124 MHz for ^{199}Hg, and ^{14}N hyperfine coupling is not observed, consistent with a d^9 configuration for mercury.

The following considerations of Born–Haber cycles, differences in successive ionization potentials, and oxidation potentials of $[ML]^{2+}$ where M is Fe, Co, Ni, or Cu and L is a saturated, tetranitrogen macrocyclic ligand, led us to the experiments described herein and to the general conclusion that compounds of tripositive mercury, and perhaps zinc and cadmium, with relatively nonoxidizable ligands should be obtainable.

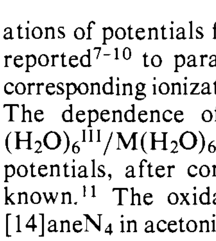
Steps in the Born–Haber cycle for the formation of ionic compounds include:

$$M(s) \xrightarrow{\Delta H_{subl}} M(g) \xrightarrow{\Sigma_1{}^n\ IP} M^{n+}(g)$$

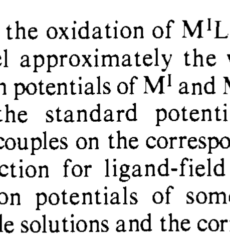
The heats of sublimation required for the step, M(s) → M(g), are less for Zn, Cd, and Hg than for Cu, Ag, and Au as tabulated in Table I. Although the sums of the first three ionization potentials are large for copper, silver, and gold, compounds of Cu^{III}, Ag^{III}, and Au^{III} are well known. The $\Sigma_1{}^3IP$ values for cadmium and mercury *are less* than the corresponding values for copper and silver as tabulated above. Also, $\Sigma_1{}^3IP$ is only 216 kJ/mol larger for Zn than for Cu. The final step in the Born–Haber cycle involves condensation of ions, possibly complex ions, and the relevant values of the lattice energies and/or coordinate bond energies are difficult to estimate. The radii[4] of M^I or M^{II}, having the same coordination number and oxidation state, differ only slightly if at all within each pair: Cu ≥ Zn, Ag ≥ Cd, and Au ≥ Hg. If similar relationships hold for M^{III} and other factors remain constant, the energy released in the final step should be comparable within each pair: Cu ≤ Zn, Ag ≤ Cd, and Au ≤ Hg. However, Zn^{III}, Cd^{III}, and Hg^{III} each possess one more d electron than Cu^{III}, Ag^{III}, and Au^{III} respectively, and the additional electron would probably be weakly antibonding from crystal field considerations. In summary for the above elements in the same periods, the total energies required for sublimation and ionization are comparable (actually 223 kJ/mol less for Cd^{III} than for Ag^{III} and 269 kJ/mol less for Hg^{III} than for Au^{III}), and the energies released in the final step probably would not differ greatly.

The relationship between the magnitude of the difference of successive ionization potentials and the stability of oxidation states has been discussed by Ahrens[5] and others: if the difference in IP of M^{n-1} and M^{n-2} is in the range 1200–2400 kJ, both the M^{n-1} and M^n oxidation states can be stabilized; if the difference is greater than ~2400 kJ, the higher oxidation state is not usually obtainable by chemical methods. In Table II, differences of successive ionization potentials, $IP_{(M^{n-1})} - IP_{(M^{n-2})}$, are tabulated and the higher oxidation states are listed on the left if previously unknown in compounds and on the right if stable in compounds. Certainly Hg^{III} and possibly Zn^{III} and Cd^{III} are in the range where complexation or lattice formation with these ions should lead to stable species.

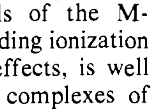
The oxidation potentials for the process $M^{II}L^{2+} \rightarrow M^{III}L^{3+} + e$ are *roughly* linearly related to the third ionization potential of M(gas) in systems where (a) M represents elements Fe, Co, Ni, and Cu in the same period with zinc and (b) the ligand (or ligands), L, is (are) not oxidized electrochemically.[6-10] Linear variations of oxidation potential with the third ionization potential have been shown for the tetraphenylporphyrin series $[M^{II}(TPP)]$ and for the phthalocyanine series $[M^{II}(Pc)]$ where M is Fe, Co, or Ni.[6] For $[Cu^{II}(TPP)]$ and $[Cu^{II}(Pc)]$, oxidation of the ligands, not copper, occurs.[6] For certain complexes of the ligands, *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane ($Me_6[14]aneN_4$ or Tet*a* below) and 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene ($Me_6[14]4,11$-dieneN_4 or Trans-Diene), the variations of potentials for the oxidation of M^IL and $M^{II}L$ were reported[7-10] to parallel approximately the variation of the corresponding ionization potentials of M^I and M^{II}, respectively. The dependence of the standard potentials of the $M(H_2O)_6{}^{III}/M(H_2O)_6{}^{II}$ couples on the corresponding ionization potentials, after correction for ligand-field effects, is well known.[11] The oxidation potentials of some complexes of $[14]aneN_4$ in acetonitrile solutions and the corresponding third ionization potentials of the metal are collected in Table III. For each of the above series of complexes of tetranitrogen macrocyclic ligands, plots of oxidation potentials as a function of third ionization potentials can be used to estimate approximately, either by interpolation or by extrapolation, the oxidation potentials for the processes: $Zn^{II}L = Zn^{III}L + e$, $Cd^{II}L = Cd^{III}L + e$, and $Hg^{II}L = Hg^{III}L + e$. By this approach, formation of



Tet*a*
($Me_6[14]aneN_4$)



Trans–Diene
(Me[14]4, 11–dieneN_4)



Cyclam
($[14]aneN_4$)

Table I. Heats of Sublimation and Ionization Potentials

	ΔH_{subl},[1] kJ/mol	$\Sigma_1{}^3\text{IP}$,[2] kJ/mol	$\Delta H_{\text{subl}} + \Sigma_1{}^3\text{IP}$, kJ/mol
Cu	338.4	6257	6595
Ag	284.6	6165	6450
Au	366	6081[3]	6447
Zn	130.8	6472.6	6603
Cd	112	6115	6227
Hg	61.3	6117	6178

tripositive cadmium (IP_3 = 3616 kJ) and tripositive mercury (IP_3 = 3300 kJ) is predicted to be feasible and formation of tripositive zinc (IP_3 = 3833 kJ) may be possible if ligand oxidation can be avoided. The extrapolated oxidation potentials, ~1.9 to 2.5 V, for $Zn^{II}L$ complexes are well within the anodic range[16] obtainable in acetonitrile with Et_4NBF_4 as the supporting electrolyte; however, oxidation of ligands probably will preclude preparation of $Zn^{III}L$. The potentials for $M^{II}L \rightarrow M^{III}L$, where L is a tetranitrogen macrocyclic ligand, are much less positive than for $M^{II}(H_2O)_n \rightarrow M^{III}(H_2O)_n$ and reflect the stabilization, by stronger coordination of the metal, of the oxidized state relative to the reduced state.[17] As another example, the $Fe^{II} \rightarrow Fe^{III}$ redox potential is −0.150 V for iron protoporphyrin but is +0.771 V for the simple hydrated ion.[17,18]

In view of the above observations, the preparation of a macrocyclic complex of tripositive mercury was undertaken. Ligand oxidation was made relatively difficult by choosing $[14]aneN_4$ instead of an unsaturated ligand for this project.

Experimental Section

Preparation of Ligands and Metal Complexes. The metal salts, acids, and solvents used in the preparation of the complexes were all of reagent grade and used without further purification. Infrared spectra of KBr pellets prepared from solid samples were recorded on Beckman IR-5 and IR-10 instruments. Potentially explosive perchlorate salts were prepared in small quantities (less than 0.5 g) and never heated above 100 °C.

Cyclam ($[14]aneN_4$) and $[Ni([14]aneN_4)][ClO_4]_2$ were prepared by published procedures.[19] Anal. ($C_{10}H_{24}N_4$): C, 59.77; H, 12.26; N, 28.38; 63% yield. ($C_{10}H_{24}N_4Cl_2O_8Ni$): C, 26.52; H, 5.24; N, 12.17; 65% yield.

1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecane. This ligand (*N,N′,N″,N‴*-tetramethylcyclam or $[14]ane(NMe)_4$) was prepared by a modification of the Eschweiler–Clarke procedure for the alkylation of amines by the reaction of $[14]aneN_4$ with formaldehyde and formic acid.[20] Anal. ($C_{14}H_{32}N_4$): C, 65.33; H, 12.73; N, 22.14; 60% yield.

Conversion of Cyclam ($[14]aneN_4$) Complexes to *N,N′,N″,N‴*-Tetramethylcyclam ($[14]ane(NMe)_4$) Complexes. The initial and unsatisfactory efforts to prepare $[M([14]ane(NMe)_4)][ClO_4]_2$ complexes involved repeated treatment of the corresponding $[M([14]aneN_4)][ClO_4]_2$ complexes in liquid ammonia[21] first with KNH_2 and then with CH_3I. Attempts under a variety of conditions to N-methylate the coordinated $[14]aneN_4$ in $Ni([14]aneN_4)^{2+}$ by reaction with diazomethane did not lead to carbene insertion but rather to reaction with the solvent or formation of polymethylene or to disproportionation of the copper(I) catalyst.

$[Ni([14]ane(NMe)_4)][ClO_4]_2$ was prepared from $[Ni([14]aneN_4)][ClO_4]_2$ and demsyl ion ($CH_3S(O)CH_2^-$) in dimethyl sulfoxide followed by treatment with methyl iodide as described by Barefield.[22] Anal. ($C_{14}H_{32}N_4Cl_2O_8Ni$): C, 32.74; H, 6.07; N, 10.65.

$(H_2[14]aneN_4)(ClO_4)_2$ and $(H_2[14]aneN_4)(BF_4)_2$. Protonation of the ligand was achieved by titrating a weighed amount of $[14]aneN_4$ with 2 equiv of dilute (1 M) HBF_4 or $HClO_4$. Solutions were evaporated to dryness on a rotary evaporator, redissolved in hot methanol and cooled to 0°. The crystals were filtered and washed with cold methanol and dried in vacuo between 65° and 100° for at least 2 days. Infrared spectra showed a strong absorption near 1610 cm^{-1} attributable to the protonated amine. Anal. ($C_{10}H_{26}N_4Cl_2O_8$): C, 29.95; H, 6.73; N, 13.87. ($C_{10}H_{26}N_4B_2F_8$): C, 32.50; H, 7.48; N, 14.79.

Table II. Differences of Successive Ionization Potentials

M^n unknown	$IP_{(M^{n-1})} - IP_{(M^{n-2})}$ (kJ/mol)[a]	M^n known
N(VI)	43 823	
C(V)	31 609	
Ti(V)	5 399	
Na(II)	4 067	
Ca(III)	3 767	
Sn(V)	3 044	
K(II)	2 632	
Pb(V)	2 555	
In(IV)	2 506	
	2 342	Mn(VII)
	2 330	Fe(IV)
Rb(II)	2 229	
Zn(III)	2 099	
	2 052	Cr(VI)
Cs(II)	2 046	
Cd(III)	1 985	
	1 970	N(V)
	1 904	Ni(IV)
	1 787	V(V)
	1 656	Cl(VII)
	1 641	Ni(III)
	1 596	Cu(III)
	1 594	Ce(IV)
	1 522	Ti(IV)
Hg(III)	1 490	
	1 287	Ag(III)
	1 235[b]	Au(III)

[a] Reference 2. [b] Reference 3.

Table III. Oxidation Potentials of Some Complexes of $[14]aneN_4$

	E_{ox},[a] V	IP_3,[b] kJ
$Cu^{II}([14]aneN_4)^{2+}$	1.42[c]	3554
$Ni^{II}([14]aneN_4)^{2+}$	0.98[c,d]	3394
$Ag^{II}([14]aneN_4)^{2+}$	0.90[c]	3361
$Fe^{II}(Me_2[14]aneN_4)^{2+}$	0.51[e]	2958

[a] *E* at $i = 0.85 i_{\max}$ in cyclic voltammogram vs. SCE at 25°. [b] Reference 2. [c] Reference 12. [d] Reference 13. [e] Reference 14; Assuming $E_{Ag/0.1 M Ag^+} = +0.34$ V; E_{ox} for $Ni^{II}([14]aneN_4)^{2+}$ and $Ni^{II}(Me_2[14]aneN_4)^{2+}$ differ by only 0.01 V (ref 15).

$[Cu([14]aneN_4)][ClO_4]_2$. Cupric carbonate (1.51 mmol of Cu) was added to 30 ml of water and acidified to pH 2 with $HClO_4$. This solution was added dropwise to $[14]aneN_4$ (1.51 mmol) dissolved in 30 ml of water. An intense maroon color developed immediately. After reacidification to pH 2, the solution was evaporated to dryness. The resulting crystals were washed with hot methanol, then with ether, and dried at 65° in vacuo for 2 days. Anal. ($C_{10}H_{24}N_4Cl_2O_8Cu$): C, 26.44; H, 5.74; N, 11.61; 88% yield.

$[Ag([14]aneN_4)][ClO_4]_2$ was prepared by disproportionation of the Ag(I) salt in the presence of the ligand.[23,24] Anal. ($C_{10}H_{24}N_4Cl_2O_8Ag$): C, 23.39; H, 4.66; N, 10.51; 30% yield.

$[Zn([14]aneN_4)][BF_4]_2$ was prepared by the addition of a minimum amount of 50% HBF_4 to dissolve ZnO (9.2 mmol) followed by the addition of a methanolic solution of $[14]aneN_4$ (9.2 mmol). The solution was evaporated to dryness and the white solid was redissolved in methanol, reprecipitated with ether and cooling, washed, and dried at 65° in vacuo for several hours. Anal. ($C_{10}H_{24}N_4B_2F_8Zn$): C, 27.28; H, 5.37; N, 12.57; 62% yield.

$[Cd([14]aneN_4)][ClO_4]_2$ was prepared in a similar manner from $HClO_4$ and $Cd(OH)_2$. Anal. ($C_{10}H_{24}N_4Cl_2O_8Cd$): C, 21.70; H, 5.08; N, 10.40.

$[Hg([14]aneN_4)][BF_4]_2$ and $[Hg([14]aneN_4)][ClO_4]_2$. The fluoroborate salt was prepared by slow addition of a 0.3 M solution of $Hg(BF_4)_2$, prepared from HgO and HBF_4, to a methanolic solution of the ligand (0.15 M) at 0°. The pH was monitored until it decreased to 5, and the solution was evaporated to dryness. The white crystalline material was redissolved in a minimum amount of absolute methanol, reprecipitated at 0°, filtered, washed with ether, and dried at 40° in vacuo for 2 days. Lower pH of the final mixture resulted in increased yields of the protonated ligand salts. Higher concentrations and temperatures cause some darkening of the solution. The perchlorate salts were prepared in an analogous manner. Infrared spectra were similar to those of other metal complexes of $[14]aneN_4$. Anal. ($C_{10}H_{24}N_4B_2F_8Hg$): C, 21.07; H, 4.17; N, 9.68; 83% yield. ($C_{10}H_{24}N_4Cl_2O_8Hg$): C, 19.36; H, 4.03; N, 8.67.

The mercury complexes were photosensitive in the finely powdered form and showed considerable graying after prolonged exposure to intense light.

$[Hg(Me_6[14]aneN_4)]Cl_2 \cdot H_2O$ was prepared by the dropwise addition of a solution of anhydrous mercuric chloride (0.01 mol) in 50 ml of acetonitrile to a 250-ml solution of $Me_6[14]aneN_4$ (0.01 mol) in acetonitrile. The mixture was refluxed for 30 min and filtered hot. Cooling to 0 °C gave a crude product which was recrystallized from hot ethanol. Anal. ($C_{16}H_{38}N_4Cl_2OHg$): C, 33.21; H, 6.78; N, 9.38; 81% yield.

$[Hg(Me_6[14]aneN_4)][BF_4]_2$ was obtained from $[Hg(Me_6[14]aneN_4)]Cl_2$ by ion exchange techniques. Typically, 1–2 g of the chloro complex was dissolved in 50–100 ml of methanol and placed on a column of Dowex 1-X8 in the BF_4^- form. Slow elution with methanol and evaporation of the solvent gave a crude product which was repeatedly recrystallized from acetonitrile, in which the chloride salt is only slightly soluble, until ir spectra indicated the absence of the chloro complex. Anal. ($C_{16}H_{36}N_4B_2F_8Hg$): C, 29.27; H, 5.71; N, 8.32.

Electrochemical Preparation of Mercury and Cadmium Complexes. To obtain small high-purity samples of complexes for cyclic voltammetry and to avoid the difficult crystallization and purification procedures discussed above, the metals were electrochemically oxidized in anhydrous acetonitrile containing either tetrabutylammonium fluoroborate or hexafluorophosphate. Weighed amounts of $[14]aneN_4$ were added either before or after electrolysis. Since the complexes are soluble in acetonitrile and since free $[14]aneN_4$ is only slightly soluble at 25° and not oxidized at the potentials required for metal dissolution, the extent of complexation could be followed by visual inspection as confirmed by coulometric measurements. Typically, a strip of cadmium foil or a bead of mercury (touching a platinum electrode) was oxidized in acetonitrile in the low-temperature preparative cell (see below for description) at 25°. The solution could be cooled for voltammetry. No product isolation was attempted.

Electrochemical measurements and preparations were made using a Princeton Applied Research Model 373 potentiostat/galvanostat in conjunction with a ramp and function generator constructed locally. Voltammograms and current–time curves for coulometry were recorded on a Houston Instruments Omnigraphic 2000 X-Y recorder. Rapid scans (greater than 1 V/s) were recorded photographically as their oscilloscope traces.

Solvents were purified by published procedures.[25] Acetonitrile was refluxed over calcium hydride, then distilled under reduced pressure. This was followed by rapid, vacuum distillation from P_2O_5. Butyronitrile and propionitrile were distilled under reduced pressure from calcium hydride, then from a mixture of $KMnO_4$ and $NaHCO_3$. Final drying was accomplished by adding activated (heated to 300 °C) alumina. Occasionally alumina was added to the electrochemical cell to scavenge water and to improve the shapes of voltammetric waves at high potentials.[26]

Tetrabutylammonium perchlorate and tetrabutylammonium hexafluorophosphate were recrystallized from absolute ethanol. Tetrabutylammonium tetrafluoroborate was recrystallized by dissolution in a slight excess of absolute methanol followed by addition of water to induce crystallization. Supporting electrolytes were dried between 65° and 100° in vacuo for at least 2 days before use and stored over P_2O_5.

Working and counter electrodes were fabricated from platinum wire, gauze, or foil. Platinum electrodes were cleaned in nitric acid for several minutes and washed with solvent before drying at 55–100°. A Princeton Applied Research Model 9311 saturated calomel reference electrode at room temperature was connected to the solutions through a nonaqueous salt bridge and cracked glass tip. Reproducible voltammograms were obtained after one scan out to 1.5–2.0 V vs. SCE. Attempts to improve reversibility of most of the voltammetric waves by preconditioning of the electrode were unsuccessful.[15]

Low-temperature cyclic voltammograms were obtained on less than 5 ml of solution (1–8 mM electroactive species, 10–50 mM supporting electrolyte) by using a conventional 25-ml pear shaped flask with side arm (to accommodate the reference electrode bridge). Electrodes, thermocouple wire, and nitrogen gas and sample tubes penetrated a rubber septum at the top. After purging, an atmosphere of nitrogen was maintained above the solution. Low-temperature coulometry and small scale electrolysis for the preparation of complexes were performed in a U-shaped tube. The two chambers were separated by a fine fritted glass disk. The counter electrode was positioned in one side. In the other was placed a glass finger made with a fine fritted disk at the bottom. This contained 1–5 ml of solution, a small stirring bar, and the working and reference (platinum) electrodes. Electrode potentials were referenced to the SCE by sweeping a voltammogram with a third platinum button working electrode and calibrating the scale vs. Pt to a known peak position vs. SCE.

Occasionally samples were withdrawn for spectroscopic examination. Stainless steel syringe needles and plastic syringes and tubing were used throughout since the strongly complexing ligands reacted with the brass fittings on glass syringes to give $Cu([14]aneN_4)^{2+}$.

Electron spin resonance spectra were scanned with a Varian E-4 spectrometer operating at 9.1985 GHz in conjunction with the potentiostat and the locally constructed flow cell shown in Figure 1. Cooling of 20 to 100 ml of solution down to −100° was accomplished with cold nitrogen gas which was circulated around the bulk solution by a glass rod baffle and passed along the flat cell and out a small hole at the bottom. An evacuated jacket extending through the active area of the ESR cavity prevented condensation of moisture. The portion within and below the ESR cavity was made of quartz. Downward flow was controlled by a needle valve or tubing clamp attached to 1 mm o.d. polyethylene tubing at the bottom of the cell. A cap clamped to the top accommodated the working and reference electrodes (platinum), nitrogen gas inlet and sample port, and thermocouple wires. Electrodes were positioned to give optimum signal response. The counter electrode was always below the spectrometer cavity. To minimize dielectric loss with different solvents at low temperatures, quartz "T" spacers were inserted from above leaving as little as 0.4 mm solution thickness (3.0 mm width throughout).

Ultraviolet/Visible Measurements. Spectra were recorded on a Cary 14 spectrophotometer. Electrochemically generated species were examined using the flow cell of Figure 1 without the quartz spacer (1.5 × 3.0 × 23 mm flat cell dimensions). The reference sample contained the unoxidized complex in acetonitrile or propionitrile at 25°.

Results and Discussion

Cyclic Voltammetry. Low temperature cyclic voltammograms of several complexes of $[14]aneN_4$ in nitrile solvents are presented in Figure 2. At 25°, the cyclic voltammograms of $[Hg([14]aneN_4)][BF_4]_2$ and $[Hg([14]aneN_4)][ClO_4]_2$ have a broad shoulder with a maximum at +1.8 V. At lower temperatures, the latter wave shifts[25] to less positive potentials (+1.73 V at −40° and +1.60 V at −78°), quasi-reversibility is exhibited, and the coupled chemical reaction becomes less apparent. Further cooling to −95° or the use of butyronitrile causes no significant change, and the lower solubility of the complex becomes the limiting factor in obtaining good voltammograms. From analysis of i_{ox}, i_{red}, and scan rates,[27] the half-life is ca. 1 s at −40° and ca. 5 s at −78° for the initial oxidation product. The oxidative wave at +1.6 V arises from a one-electron process as shown by a comparison (see insert, Figure 2) of the i_{ox} value with that observed for the oxidation of $Cu([14]aneN_4)^{2+}$ to $Cu([14]aneN_4)^{3+}$ under identical conditions. For the oxidation of $[Cu(Me_6[14]aneN_4)][ClO_4]_2$, n equals 1[7] and the resulting $[Cu(Me_6[14]aneN_4)][ClO_4]_3$ exhibits a visible spectrum similar to the initial oxidation product of $[Cu([14]aneN_4)][BF_4]_2$. The cyclic voltammogram of $[Hg(Me_6[14]aneN_4)][BF_4]_2$ at 25° shows irreversible processes at 1.83 and 2.29 V.

In cyclic voltammograms taken at 25°, the waves at 0.98 V (E_{ox} for $i = 0.85 i_{max}$) for $Ni([14]aneN_4)^{2+}$, 1.42 V for $Cu([14]aneN_4)^{2+}$, and 0.90 V for $Ag([14]aneN_4)^{2+}$ are

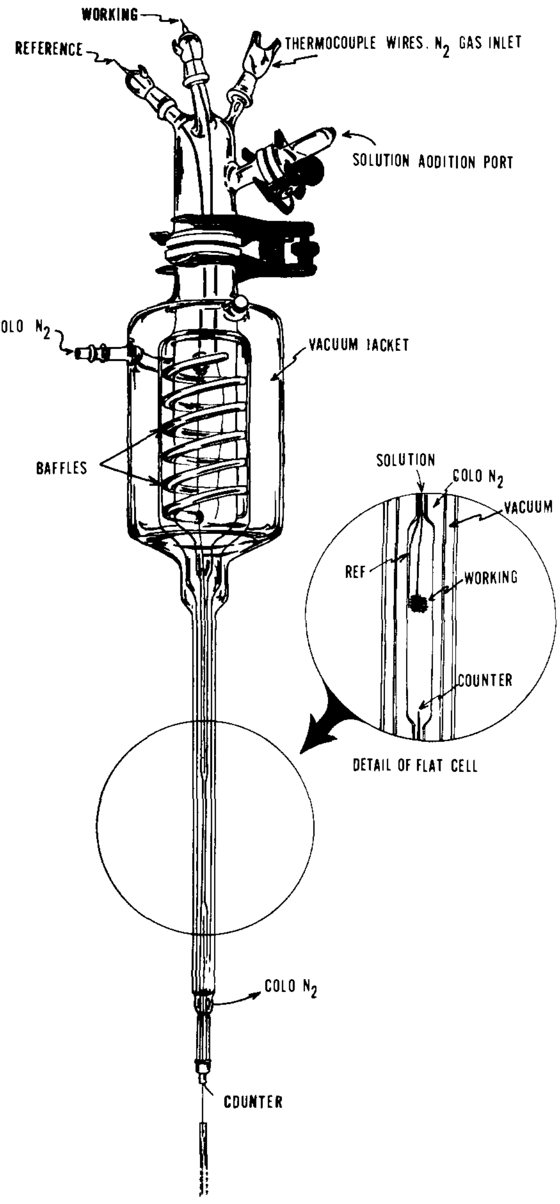


Figure 1. Electrolysis cell for ESR or uv/visible spectroscopy under low temperature and flow conditions. At the bottom is a rubber septum, a syringe needle, 1 mm o.d. polyethylene tubing, and pinch clamp (not shown) for controlling flow rate.

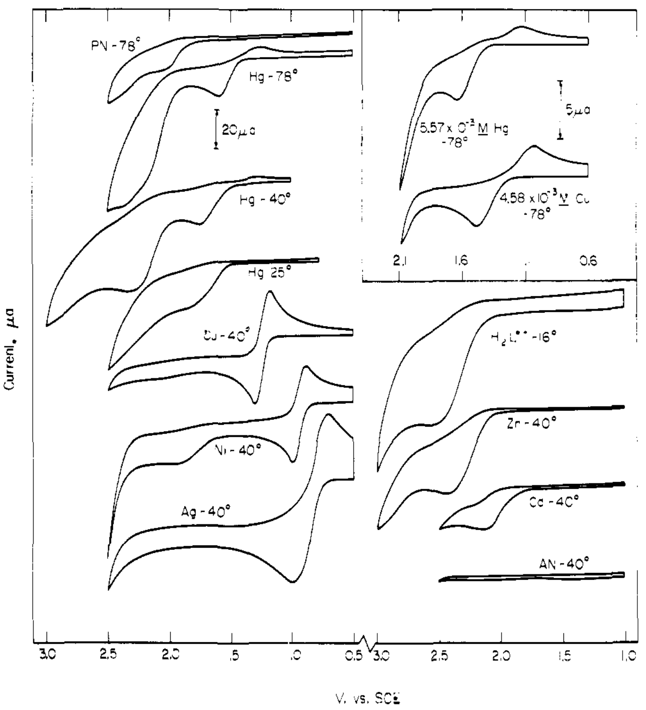


Figure 2. Single sweep cyclic voltammograms of $\mathrm{[14]aneN_4}$ complexes. Saturated calomel reference electrode (25°), platinum working and counter electrodes; 1-8 × 10^{-3} M complex and 5 × 10^{-2} M tetrabutylammonium salts of the anion of each complex; sweep rates, 0.1–0.5 V/s. Complexes: $\mathrm{[Hg([14]aneN_4)][BF_4]_2}$, $\mathrm{[Cu([14]aneN_4)][ClO_4]_2}$, $\mathrm{[Ag([14]aneN_4)][ClO_4]_2}$, $\mathrm{[Ni([14]aneN_4)][ClO_4]_2}$, $\mathrm{[Zn([14]aneN_4)][BF_4]_2}$, $\mathrm{[Cd([14]aneN_4)][PF_6]_2}$ (from the electrochemical oxidation of cadmium foil in the presence of $\mathrm{[14]aneN_4}$), and $\mathrm{H_2L^{2+}} = \mathrm{[H_2[14]aneN_4][BF_4]_2}$. Upper right: 5.57 × 10^{-3} M $\mathrm{[Hg([14]aneN_4)][BF_4]_2}$ and 4.58 × 10^{-3} M $\mathrm{[Cu([14]aneN_4)][ClO_4]_2}$. The solvent was acetonitrile (AN) except for $\mathrm{[Hg([14]aneN_4)][BF_4]_2}$ at −40° and for scans at −78° for which propionitrile (PN) was used.

due to oxidation of the metals: $\mathrm{M^{II}([14]aneN_4)^{2+}}$ to $\mathrm{M^{III}([14]aneN_4)^{3+}}$. These potentials agree with earlier reports for metaloxidations in $\mathrm{Ni([14])aneN_4)^{2+}}$,[15] $\mathrm{Cu(Me_6[14]aneNa_4)^{2+}}$,[17,10] and $\mathrm{Ag([14]aneN_4)^{2+}}$.[24] Oxidations at −40° occur at somewhat lower potentials: +0.95 V for $\mathrm{Ni([14]aneN_4)^{2+}}$, +1.26 V for $\mathrm{Cu([14]aneN_4)^{2+}}$, and +0.85 V for $\mathrm{Ag([14]aneN_4)^{2+}}$. At −78° the wave (insert, Figure 2) for the oxidation of $\mathrm{[Cu^{II}([14]aneN_4)]^{2+}}$ is well-resolved and $E_{ox} - E_{red}$ (at $0.85 i_{max}$) becomes 0.40 V. The general shape and behavior of these waves conform to the theoretical curves published by Van Duyne and Reilley[25] for quasi-reversible heterogeneous electron transfer in the absence of coupled chemical reactions.

With the substitution of methyl groups in the coordinated $\mathrm{[14]aneN_4}$, the potential required for oxidation becomes more positive. E_{ox} at 25° for $\mathrm{[Ni^{II}([14]ane(NMe)_4)][ClO_4]_2}$[20] prepared from pre-formed $\mathrm{[14]ane(NMe)_4}$ and Ni(II) is +1.55 V and for the isomeric $\mathrm{[Ni^{II}([14]ane(NMe)_4)][ClO_4]_2}$[22] prepared from $\mathrm{Ni([14]aneN_4)^{2+}}$ and $\mathrm{CH_3S(O)CH_2^-/CH_3I}$ is +1.56 V.

Irreversible waves occur at +2.2 to 2.5 V vs. SCE (Figure 2) in the cyclic voltammograms of $\mathrm{Ni([14]aneN_4)^{2+}}$, $\mathrm{Cu([14]aneN_4)^{2+}}$, $\mathrm{Zn([14]aneN_4)^{2+}}$, $\mathrm{Cd([14]aneN_4)^{2+}}$, $\mathrm{Hg([14]aneN_4)^{2+}}$, and $\mathrm{H_2[14]aneN_4{}^{2+}}$. These waves are assigned to oxidation of the coordinated $\mathrm{[14]aneN_4}$. Since cyclam is insoluble in nitrile solvents at the temperatures used, no direct comparison of oxidation potentials for complex and free ligands can be made.

For $\mathrm{Hg([14]aneN_4)^{2+}}$, the oxidation wave in the +1.6 to 1.8 V region described above can be assigned to the process:

$$\mathrm{Hg^{II}([14]aneN_4)^{2+} \rightarrow Hg^{III}([14]aneN_4)^{3+} + e}$$

Another tetranitrogen macrocyclic complex, $\mathrm{Hg(Me_6[14]aneN_4)^{2+}}$, exhibits a comparable cyclic voltammogram with the waves at 1.83 and 2.29 V being assigned to metal and ligand oxidations, respectively.

The redox and ionization potentials in Table III and the third ionization potential, 3300 kJ, of mercury are consistent with oxidation of mercury although a slightly less positive potential was anticipated. In a few cyclic voltammograms of $\mathrm{[Cd^{II}([14]aneN_4)][BF_4]_2}$, shoulders appeared on the ligand oxidation waves but no features could be assigned reliably to metal oxidation of this compound or of $\mathrm{[Zn^{II}([14]\cdot ane\,N_4)][BF_4]_2}$.

Coulometry of $\mathrm{[Hg^{II}([14]aneN_4)][BF_4]_2}$ and Decomposition of the Product. During the electrolysis of a stirred solution of 1 × 10^{-4} mol of $\mathrm{[Hg([14]aneN_4)][BF_4]_2}$ in acetonitrile at +1.7 V and −40°, the magnitude of i_{ox}, reflecting the concentration of $\mathrm{[Hg([14]aneN_4)][BF_4]_2}$, decreased steadily and was nil after the passage of 1.94 × 10^{-4} faradays indicating an overall two-electron process with decomposition of starting

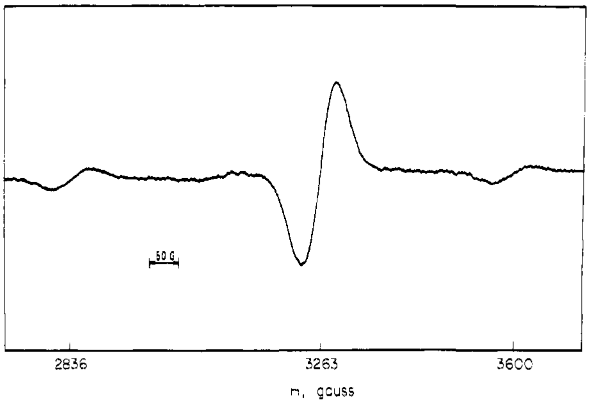


Figure 3. ESR spectrum of $[Hg([14]aneN_4)]^{3+}$ in propionitrile at −78°.

material. Electrolysis at +1.7 V of a second sample of 1×10^{-4} mol of $[Hg([14]aneN_4)][BF_4]_2$ was stopped after passage of 0.6×10^{-4} faradays, the solvent was evaporated, and the product was found to contain protonated $[14]aneN_4$ ($\nu_{N-H} = 1610\ cm^{-1}$) but no oxidized $[14]aneN_4$ ($\nu_{C=N} = 1660\ cm^{-1}$ absent). Separate experiments show stoichiometric displacement of mercury(II)

$$2H^+ + Hg([14]aneN_4)^{2+} \rightarrow H_2[14]aneN_4^{2+} + Hg^{2+}$$

by protonic acids in various solvents.

The Hg(III) complex may decompose by reaction with the solvent (or its impurities including water) and/or by an internal redox process resulting in the formation of an intermediate nitrogen radical and a proton, as proposed[24,28] for analogous Ni(III) and Ag(III) complexes. $[Ag^{III}([14]aneN_4)]^{3+}$ is reduced instantly to $[Ag^{II}([14]aneN_4)]^{2+}$ by water without the occurrence of detectable oxidation of cyclam ligands.[24] Both $[Cu^{III}(Me_6[14]aneN_4)]^{3+}$ and $[Cu^{III}([14]aneN_4)]^{3+}$ are unstable above −15° and the former has been shown[7] to release protons during decomposition. By analogy, two oxidation-reduction cycles for $[Hg^{II}([14]aneN_4)]^{2+}$ would produce stoichiometrically electroinactive, solvated Hg(II) ions and diprotonated $[14]aneN_4$.

Plans to attempt the synthesis of a tripositive mercury complex of $[14]ane(NMe)_4$, which would be unlikely to form the above intermediate nitrogen radical, were abandoned when E_{ox} for $[Ni^{II}([14]ane(NMe)_4)]^{2+}$ was observed to be at least 0.57 V more positive than for $[Ni^{II}([14]aneN_4)]^{2+}$ and when E_{ox} for $[Ag^{II}([14]ane(NMe)_4)]^{2+}$ was reported[24] to be 0.25 V more positive than for $[Ag^{II}([14]aneN_4)]^{2+}$.

Electron Spin Resonance. The ESR spectrum in Figure 3 was scanned during electrolysis of 0.05 M $[Hg([14]aneN_4)][BF_4]_2$ in propionitrile at −78° under flow conditions. This ESR spectrum of the product of electrolysis at 1.3 V (0.07 mA) differed only in having greater intensity than spectra obtained at 0.6 V (0.003 mA), at 1.0 V (0.03 mA), or at higher temperatures. When electrolysis and flow were stopped, the ESR spectrum decayed with a half-life of ca. 5 s at −78°.

The g factor of the central line (^{200}Hg, $I = 0$, 69.9%) is 2.014. From an exact calculation,[29] the hyperfine coupling constant, A_{iso} (^{199}Hg, $I = \frac{1}{2}$, 16.86%), is 2124 MHz and the above value of g_{av} is confirmed. Hyperfine splitting due to ^{201}Hg ($I = \frac{3}{2}$, $Q = 0.45$, 13.25%) is calculated[30] from ^{199}Hg splitting to occur at ~2824 G, ~3666 G, and at two intermediate positions determinable by higher-order treatment.[31] Thus, as observed, the ^{201}Hg splittings should increase slightly the intensity of the observed low-field hyperfine line and decrease the intensity of the high-field half of the other observed hyperfine line. Central lines due to ^{201}Hg were not resolved, perhaps a consequence of the large nuclear quadrupole moment.[31] Observed line-widths are 63 G.

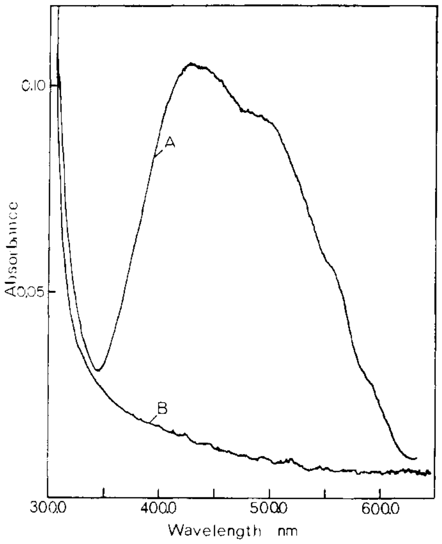


Figure 4. (A) Visible absorption spectrum recorded during electrolysis, at +1.4 V vs. SCE, of 0.05 M $[Hg([14]aneN_4)][BF_4]_2$ at −80° in propionitrile under flow conditions. The reference sample contained 0.05 M $[Hg([14]aneN_4)][BF_4]_2$ and was at 25°. (B) Baseline before electrolysis and after decay of signal.

In the absence of the principal values of the g and A tensors (rapid decay precluded obtaining the ESR spectrum of a radical in a rigid matrix by quenching freshly electrolyzed drops in liquid nitrogen) and of a knowledge of the symmetry of the oxidized complex, a detailed treatment of g and A values must be deferred. For steric reasons, $[Hg([14]aneN_4)]^{2+}$ cannot have a planar structure and perhaps the initially formed $[Hg([14]aneN_4)]^{3+}$ with a folded structure decomposes before rearrangement occurs. The formation of the analogous complex, $[Cu([14]aneN_4)]^{2+}$, involves (1) an intermediate having a pentacoordinated metal and a folded ligand and (2) subsequent deprotonation of the ligand followed by a conformational change to give a square planar structure.[32] The observed magnitude of g_{av} and the tendency of higher-row ions to complex with $[14]aneN_4$ in a folded configuration[33] are consistent with a d^9, low-symmetry,[34] tripositive mercury complex. For $^{199}Hg^+$, with the spin in the 6s orbital, the hyperfine splitting is ca. 12 500 G[30] and far larger than the splitting of 746 G for $[Hg([14]aneN_4)]^{3+}$. Therefore, the s character of the orbital containing the spin is <6%. The absence of splitting by ^{14}N is consistent with metal oxidation rather than ligand oxidation.

Visible Spectrum. Upon electrochemical oxidation of $[Hg([14]aneN_4)][BF_4]_2$ at low temperatures, a red color appeared near the anode but faded rapidly. The color was not due to a platinum complex since the platinum anode did not lose weight during extensive electrolysis. The visible spectrum, Figure 4, which was recorded under flow and electrolysis conditions exhibits broad overlapping absorptions with maxima at 428 and 506 nm and a (estimated) > 1000. Absorbance decay after current and flow interruption revealed two decay processes, one with half-lives from ca. 1.5 s at −40° to 4 s at −80° and the second with half-lives from ca. 12 s at −40° to 60 s at −80°. The more slowly decaying species absorbed less strongly (ca. one-sixth) than the rapidly decaying species. Similar spectra were recorded for the perchlorate salt.

The visible bands presumably arise from either nitrogen to mercury(III) or mercury(II) to intermediate nitrogen-radical charge-transfer processes, as in spectra of analogous Cu(III) and Ni(III) complexes.[7,35] The initial rapid decay appears to be due to the decomposition of the tripositive mercury complexes since this decay rate is comparable to that of the ESR signal. The long wavelength absorption is consistent with strong oxidizing power of Hg(III) relative to other M(III) complexes.[36] The weak d-d transition is obscured either by these charge-transfer bands or, more likely, by the intense charge-transfer bands of $[Hg([14]aneN_4)]^{2+}$ in the uv region.

Conclusions

Visible spectroscopy, cyclic voltammetry, and ESR each lead to the same value of the half-life of the initial product of electrochemical oxidation of $[Hg^{II}([14]aneN_4)]^{2+}$. The spectral properties of this product are consistent with the formation of mercury(III). This is the first example of the removal of a d electron from a group 2b element in a condensed phase. While a tetranitrogen macrocyclic complex of mercury(III) is unstable under the conditions employed in this investigation, attempts to stabilize mercury(III) in complexes such as $KHgF_4$ or K_3HgF_6 appear feasible.

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(36) $Cu([14]aneN_4)^{3+}$ and $Cu(Me_6[14]aneN_4)^{3+}$ exhibit intense absorptions at 385 nm (ref 12) and 425 nm (ref 7).

Synthesis and Structure of the Hydroxyl Derivative of "Titanocene"

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Abstract: The crystal and molecular structures of μ-(η^5:η^5-fulvalene)-di-μ-hydroxyl-bis(cyclopentadienyltitanium), the hydroxyl derivative of "titanocene", were determined from x-ray counter data. The molecular structure is a $(C_5H_5)Ti(OH)(C_5H_4-)$ dimer; the titanium atoms are bridged by two OH ligands and the fulvalene ligand, which is η^5-bonded to both titanium atoms. Each dimeric molecule crystallizes with one molecule of tetrahydrofuran which hydrogen bonds to one of the bridging OH's. Two types of Ti–OH–Ti geometries result with Ti–O of 2.10 (2) Å and Ti–O–Ti of 98.8 (5)° for the oxygen involved in hydrogen bonding and Ti–O of 2.05 (1) Å and Ti–O–Ti of 102.7 (6)° for the other OH bridge. The Ti···Ti separation is 3.195 Å. The fulvalene ligand is folded with 15.1° between C_5 rings which are separated by 1.43 (3) Å. The angle subtended at Ti by the centroids of the two η^5-C_5 rings is 133.5 (1)°. Crystals are orthorhombic, space group $Pna2_1$, with $a = 10.143$ (6), $b = 23.571$ (14), and $c = 9.009$ (8) Å with four dimers and four solvent molecules per cell (ρ(calcd) = 1.42 g cm^{-3}). The refinement gave a conventional R value of 0.110 for 1122 reflections with $F_o > 2\sigma(F_o)$.

We report here the isolation and crystal structure of the hydroxyl derivative of "titanocene", μ-(η^5:η^5-fulvalene)-di-μ-hydroxyl-bis(cyclopentadienyltitanium), $[(C_5H_5)(C_5H_4)TiOH]_2$. The crystal structure of this compound allows us to define in detail the geometry of a structure believed to be closely related to titanocene. In addition, study of this molecule provides information on a product of partial hydrolysis of a titanium(III) compound. Direct structural information on the course of hydrolysis of low-valent titanium compounds is extremely rare.

Much of the recent interest in the nature of titanocene was stimulated by the work of Brintzinger and Bercaw[1] who for-