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Protonated Metal-Free Salt and Manganese Complex of a [14]TetraeneN_4 Macrocyclic Ligand

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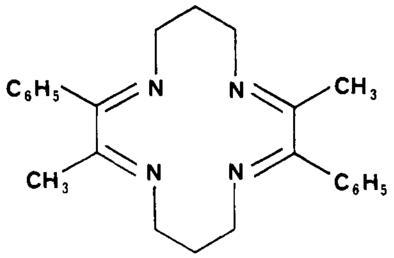
The protonated metal-free salt and the manganese(II) complex of 2,9-dimethyl-3,10-diphenyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene (hereafter denoted L) have been isolated and characterized. The tetrahydrobromide salt of L was prepared by treatment of $[CuL](PF_6)_2$ with LiBr and anhydrous HCl gas in CH_3CN. The Mn(II) complex of L was prepared by reacting L·4HBr with excess $Mn(OAc)_2$ in EtOH and was isolated as $[MnLBr](PF_6)$. Derivatives were generated by replacing Br^- with F^-, Cl^-, or I^-, but nitrogen heterocyclic derivatives were not isolated. The complexes were characterized by elemental analyses, conductivity and magnetic susceptibility measurements, infrared and electronic spectra, and cyclic voltammetry. All contain high-spin Mn(II) and are five-coordinate. The manganese ion in these complexes is surprisingly resistant to oxidation. No oxidation processes were observed in cyclic voltammograms in the range −2.4 to +1.0 V vs. ferrocene internal standard couple in Me_2SO. Two well-defined one-electron-reduction processes were observed at about −1.2 and −1.5 V.

Introduction

Template condensation of α-diketones with 1,3-diaminopropane in the presence of divalent metal ions provides the synthetic route to Fe, Co, Ni, and Cu complexes of [14]tetraeneN_4 macrocycles.[1-9] Manganese and zinc are not successfully employed in this method. The zinc complex of the ligand L was prepared by reductive transmetalation of $[CuL]^{2+}$ with Zn metal.[7,9,10] During the characterization of the zinc complexes we discovered that they react with Ni^{2+}, Cu^{2+}, or Co^{2+} in acidic (HCl) methanol solution to produce the corresponding metal complex of L.[7] These facile acid-catalyzed transmetalation reactions suggest that the protonated form of L has some stability in solution. Since neither reductive nor acid-catalyzed transmetalation reactions are successful for the preparation of $Mn^{II}L$ complexes, the protonated metal-free salt of L provides a necessary intermediate for the preparation of this complex. In this paper we report the isolation and partial characterization of the tetraprotonated form of the ligand L and its use in the preparation of the Mn(II) complex of L. Since this is the first report of a Mn complex of a 1,3,8,10-[14]tetraeneN_4 macrocycle, we have therefore investigated the chemistry of the complex by the preparation and characterization of axial ligand derivatives. This has resulted in a series of derivatives, $[MnLX]^+$, in which the axial ligand is F^-, Cl^-, Br^- or I^-. The complexes were characterized by elemental analyses, conductivity, magnetic susceptibility, spectroscopic measurements, and cyclic voltammetry.



L

Experimental Section

Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. A gravimetric analysis for bromide was performed on the ligand salt by precipitation of AgBr.[11] Infrared spectra obtained from mineral oil mulls and KBr pellets were recorded on a Perkin-Elmer Model 1330 spectrometer. Electronic spectra in the range 200–800 nm were obtained in CH_3CN on a Cary 219 spectrometer using 1-cm quartz cells. Solution conductivity measurements were made at room temperature by using an Industrial Instruments RCM-15B1 conductivity bridge and an immersion-type cell with a constant of 0.1047 cm^{-1}. The magnetic susceptibility measurements were made at room temperature with a Cahn 7600 Faraday, balance, employing $[Ni(en)_3]S_2O_3$ as a standard. Diamagnetic contributions from the ligand and anions were estimated with use of Pascal's constants.[12] The effective moment of manganese was evaluated with the equation $\mu_{eff} = 2.84(\chi_m T)^{1/2}$. Proton NMR spectra were recorded at 90 MHz on a Perkin-Elmer R-32 spectrometer at 35 °C. Electrochemistry was carried out in dry Me_2SO solution (10^{-3} M complex, 0.10 M Bu_4NPF_6 supporting electrolyte) under N_2 by using Princeton Applied Research equipment (Model 175 universal programmer, Model 173 potentiostat, and Houston Instruments RE0074 X-Y recorder) with a glassy-carbon disk as the working electrode and an Ag/0.1 M $AgNO_3$ in CH_3CN electrode as reference. Ferrocene was added as an internal standard for cyclic voltammograms. Solvents and supporting electrolytes for electrochemical measurements were obtained as ultrapure reagents from Burdick and Jackson Laboratories and Southwestern Analytical Chemicals.

All chemicals and solvents employed in the preparations below were reagent grade and used as obtained unless otherwise specified. Absolute EtOH for use in the preparation of manganese complexes was dried by distillation over CaH_2 in a N_2 atmosphere. Solvents were kept dry by storage over activated 4-Å molecular sieves. All of the manganese complexes were prepared in a nitrogen-filled glovebox (Vacuum Atmospheres) equipped with a HE-493 DriTrain.

2,9-Dimethyl-3,10-diphenyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene Tetrahydrobromide (L·4HBr). In an apparatus purged with dry N_2, anhydrous HCl gas (produced by dehydration of concentrated HCl (50 mL) by concentrated H_2SO_4[13]) carried in a stream of dry N_2 (flow rate 0.5–1.0 mL/min) was bubbled into a solution of LiBr (8.0 g) in dry CH_3CN (75 mL) held near 0 °C in an ice bath. After the HCl addition was complete, a solution of $[CuL](PF_6)_2$ (1.0 g, 1.38 mmol) in CH_3CN (75 mL) was added at a uniform rate of 1 drop/2 s with stirring and with the mixture kept near 0 °C. The mixture was stirred for an additional 10 min while a brown solution and a white precipitate formed. The ice bath was removed to allow the mixture to warm somewhat over 5–10 min. The precipitate was isolated by vacuum filtration in a sintered-glass filter with care taken to wash the precipitate with dry CH_3CN such that the solid material was always covered with liquid and the green color was removed. Before the precipitate was exposed, a stopper with a tube through it connected to a desiccant tower was placed on the filter. The dry air was sucked through the precipitate for approximately 2 min before it was quickly placed in a vacuum desiccator. The yield after

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drying in a vacuum at room temperature was 0.80–0.90 g (83–93%). Anal. Calcd for $C_{24}H_{32}N_4Br_4$: C, 41.41; H, 4.63; N, 8.05; Br, 45.9 Found: C, 38.15; H, 5.11; N, 8.32; Br, 46.0.

(2,9-Dimethyl-3,10-diphenyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene)bromomanganese(II) Hexafluorophosphate ([MnLBr]PF_6). In a nitrogen-filled glovebox, anhydrous $Mn(OAc)_2$ (0.48 g, 2.77 mmol, prepared from $Mn(OAc)_2{\cdot}4H_2O$ stirred in absolute EtOH, collected, and then dried in a vacuum) was added to dry EtOH and stirred for 10 min. L·4HBr (0.80–0.90 g, freshly prepared and dried) was added in bulk and the solution was stirred for 3 h while a red-brown solution developed. NH_4PF_6 (0.90 g, 5.52 mmol) in absolute EtOH (25 mL) was added dropwise to the stirred reaction mixture to yield a brown microcrystalline precipitate. The product was collected by vacuum filtration, washed with absolute EtOH, and dried in a vacuum (yield 0.45–0.51 g, 50–57%). Recrystallization in air from boiling CH_3CN/EtOH (1:2) gave a brown crystalline analytically pure product. Anal. Calcd for $C_{24}H_{28}N_4MnBrPF_6$: C, 44.19; H, 4.33; N, 8.59. Found: C, 44.17; H, 4.28; N, 8.70.

(2,9-Dimethyl-3,10-diphenyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene)chloromanganese(II) Hexafluorophosphate ([MnLCl]PF_6). In a nitrogen-filled glovebox, $AgBF_4$ (0.30 g, 1.54 mmol) was added to a solution of [MnLBr]PF_6 (1.00 g, 1.53 mmol) in CH_3CN (10 mL). After being stirred for 5 min, the solution was filtered through microcrystalline cellulose to remove AgBr. LiCl (0.20 g, 4.72 mmol) was added, and the solution was filtered again if necessary. NH_4PF_6 (1.25 g, 7.66 mmol) dissolved in EtOH (40 mL) was added dropwise, and the solution was allowed to stand for about 6 h; then it was filtered again if necessary. The solution was then rotoevaporated to yield a brown powder, which was collected by vacuum filtration, washed with EtOH, and dried in a vacuum (yield 0.76 g, 82%). Recrystallization in air from boiling CH_3CN/EtOH (1:2) gave a brown crystalline analytically pure product. Anal. Calcd for $C_{24}H_{28}N_4MnClPF_6$: C, 47.42; H, 4.64; N, 9.22. Found: C, 47.27; H, 4.74; N, 9.33.

(2,9-Dimethyl-3,10-diphenyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene)iodomanganese(II) Hexafluorophosphate ([MnLI]PF_6). This compound was prepared analogously to [MnLCl]PF_6 with NaI used (0.69 g, 4.60 mmol) in place of LiCl. In this case rotoevaporation was not necessary for isolation of the brown product (yield 0.75 g, 70%). Recrystallization in air from boiling CH_3CN/EtOH (1:4) gave a brown crystalline analytically pure product. Anal. Calcd for $C_{24}H_{28}N_4MnIPF_6$: C, 41.22; H, 4.04; N, 8.01. Found: C, 40.66; H, 4.04; N, 8.01.

(2,9-Dimethyl-3,10-diphenyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene)fluoromanganese(II) Hexafluorophosphate ([MnLF]PF_6). In a nitrogen-filled glovebox, $AgBF_4$ (0.30 g, 1.54 mmol) was added to a suspension of [MnLBr]PF_6 (1.00 g, 1.53 mmol) in absolute EtOH (25 mL). After being stirred for 5 min, the solution was filtered through microcrystalline cellulose to remove AgBr. NaF (0.39 g, 9.29 mmol) was added, and the solution was stirred for 10 min. Then a solution of NH_4PF_6 (1.50 g, 9.20 mmol) in EtOH (20 mL) was added dropwise with stirring to produce an orange precipitate, which was collected, washed with EtOH, and dried in a vacuum (yield 0.76 g, 84%). Recrystallization in air from boiling CH_3CN/EtOH (1:4) gave an orange analytically pure product. Anal. Calcd for $C_{24}H_{28}N_4MnPF_7$: C, 48.74; H, 4.77; N, 9.47; F, 22.49. Found: C, 47.94; H, 4.70; N, 9.33; F, 21.99.

Results and Discussion

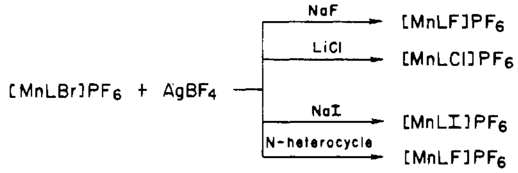
L·4HBr. Isolation of the ligand salt was accomplished by reacting [CuL]$(PF_6)_2$ with anhydrous HCl and excess LiBr in CH_3CN. The highest yields (about 90%) are consistently obtained if a solution of [CuL]$(PF_6)_2$ in CH_3CN is added to a solution of LiBr in CH_3CN that is saturated with anhydrous HCl gas. The success of this reaction is partially due to the fact that the bromide salt of the protonated ligand is insoluble in CH_3CN. Characterization is limited by the moisture sensitivity of the compound and its partial decomposition in any solvents in which it is soluble. The elemental analyses on the crude product, including gravimetric bromide analysis, are consistent with the formulation as a tetrahydrobromide salt. Attempts to determine the neutralization equivalent in aqueous solution with NaOH were inconclusive because the titration curve for the ligand salt resembles that of a very weak acid. Sadasivan and Endicott[14] report similar behavior for the titration of the diprotonated form of Me_6[14]dieneN_4. The proton NMR spectrum of L·4HBr in Me_2SO-d_6 contained resonances corresponding to the diaminopropane, methyl, and phenyl groups, which appeared at frequencies similar to those reported for macrocyclic complexes of L[6,7,10]; however, the calculated and expected integration ratios were in disagreement. This suggests that the ligand salt partially decomposes in solution.

Table I. Selected Infrared Data[a]

compd	$\nu_{C=N}$	$\nu_{C=C}$	α-diimine
H_4LBr_4	1670 (w), 1635 (s)	1585 (s, sp)	1295 (m)
[MnLF]PF_6	1657 (w), 1610 (s)	1595 (s, sp)	1220 (sp)
[MnLCl]PF_6	1650 (w), 1605 (s)	1590 (s, sp)	1222 (sp)
[MnLBr]PF_6	1645 (w), 1602 (s)	1588 (s, sp)	1220 (sp)
[MnLI]PF_6	1640 (w), 1599 (s)	1588 (s, sp)	1220 (sp)

[a] Units: cm^{-1}. Abbreviations: s = strong, sp = sharp, m = medium, w = weak.

Scheme I



The infrared spectrum of L·4HBr is most revealing. Bands attributed to functional groups in the macrocycle are observed in the following regions (cm^{-1}): 3000–3100, aromatic ν_{C-H}; 2900–3000, aliphatic ν_{C-H}; 1300–1450, δ_{CH_3} and δ_{CH_2}; 690–780, phenyl out of plane bending modes. A broad intense band due to $C{=}NRH^+$ occurs at 2300–2500 cm^{-1}. Also, several combination bands in the 1900–2000-cm^{-1} region are characteristic of the salts of open and cyclic imines.[15,16] The absence of an amine N—H or ketone C=O stretching band is indicative of the existence of an intact macrocyclic structure. Other diagnostic bands characteristic of the macrocycle are presented in Table I. The C=N stretching frequencies are higher for the ligand salt than for the coordinated macrocycle.[6,7,10] Also in the ligand salt, $\nu_{C=C}$ of phenyl remains unchanged and the strong band characteristic of the α-diimine[1,2] is less intense and is shifted to higher frequency.

Ni(II) and Cu(II) complexes of L are readily prepared from the ligand salt:

$$\mathrm{L{\cdot}4HBr + 2M(OAc)_2{\cdot}}x\mathrm{H_2O \xrightarrow[\text{ROH, N}_2]{\text{NH}_4\text{PF}_6} [ML](PF_6)_2}$$

These results further indicate the intact nature of the macrocyclic ligand.

Manganese Complexes. Attempts to prepare the manganese complex of L by previously established methods were unsuccessful. Mn(II) appears to catalyze polymerization of the reagents when used in the template synthesis. Zinc(II) behaves similarly.[7] Although traces of $Mn^{II}L$ complex could be isolated from the reductive transmetalation reaction

$$\mathrm{[CuL](PF_6)_2 \xrightarrow[\text{ROH, N}_2]{\text{Mn, LiBr}} [MnLBr]PF_6 + Cu^0}$$

the yields were too small and inconsistent to make this method synthetically useful. However, reasonable yields of the Mn complex could be obtained from the reaction of L·4HBr and anhydrous Mn(II)acetate in absolute EtOH:

$$\mathrm{L{\cdot}4HBr + 2Mn(OAc)_2 \xrightarrow[\text{EtOH, N}_2]{\text{NH}_4\text{PF}_6} [MnLBr]PF_6 + 4HOAc}$$

Anhydrous conditions increase the yield of complex by preventing hydrolysis of the ligand during the time required for complexation.

In our attempts to prepare axial ligand derivatives of $[MnLBr]^+$, we found that direct displacement of the Br^- axial ligand by nucleophiles such as other halides or nitrogen heterocycles was not possible without prior removal of coordinated Br^- by use of $AgBF_4$. The results of derivative preparations are summarized

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Table II. Conductivities, Magnetic Moments, and Spectral Data for Manganese Complexes

compd	Λ_m[a]	μ_{eff}[b]	$\lambda_{max}(\epsilon)$[c]
[MnLF]PF$_6$	148	5.90	228, 272 (12600, 5100)
[MnLCl]PF$_6$	127	5.84	228, 274 (13300, 7100)
[MnLBr]PF$_6$	146	5.99	228, 274 (12070, 6760)
[MnLI]PF$_6$	150	5.93	236, 272 (13500, 8100)

[a] 10^{-3} M solutions in CH$_3$CN. Units: Ω^{-1} cm^2 mol^{-1}. [b] Solid state, room temperature. Units: μ_B. [c] 10^{-4} M solutions in CH$_3$CN. Units λ_{max}, nm; ϵ, L mol^{-1} cm^{-1}.

in Scheme I. Anhydrous conditions under a N$_2$ atmosphere are necessary for optimum yields. In the absence of a suitable axial ligand, the Mn^{II}L complex is unstable. The decomposition in the atmosphere could be due possibly to dissociation and hydrolysis of the ligand or to oxidation of the metal ion and subsequent decomposition. In the solid state the halide derivatives are stable for months in the atmosphere. In solution at 10^{-3} M or higher concentration, they are stable for at least a day.

Attempts were made to synthesize derivatives containing pyridine, *N*-methylimidazole, or benzimidazole as axial ligands. In each case the only product isolated was [MnLF]PF$_6$. These results are in contrast to those for the Zn(II) complexes of L where under similar conditions the heterocyclic derivatives were isolated and no fluoride derivative could be prepared.[10] It is apparent that either BF$_4^-$ or PF$_6^-$ is the source of F$^-$ in [MnLF]$^+$ isolated from the preparations containing heterocyclic ligands. The presence of the heterocycle is necessary, too, since no fluoride derivative was isolated in the absence of heterocycle or in the preparation of the Cl$^-$ or I$^-$ derivatives. Reedijk[17] has recently reviewed the preparation of metal fluoride derivatives in which the source of F$^-$ is BF$_4^-$. The presence of heterocyclic ligands such as pyrazoles, pyridines, imidazoles, or pyridine *N*-oxides facilitates the liberation of F$^-$ from BF$_4^-$ through formation of the BF$_3$–heterocycle adduct, thus making F$^-$ available for coordination to metal ions. It is likely that a similar effect is operating in the case of Mn^{II}L complexes and that Mn^{II}L binds preferentially to F$^-$ over heterocyclic ligands in EtOH.

All of the [MnLX]PF$_6$ derivatives are brown or orange crystalline solids and have elemental analyses consistent with their formulation as listed in the Experimental Section. Molar conductivities of 10^{-3} M solutions in CH$_3$CN (Table II) are all in the range expected for 1:1 electrolytes.[18,19] The derivatives are thus formulated as five-coordinate with the halide ion occupying an axial site. Additionally, limiting conductance values and slopes of Onsager plots over the range 10^{-3}–10^{-4} M are in the range expected for 1:1 electrolytes[19] for the Cl$^-$, Br$^-$, and I$^-$ derivatives (Λ_0 = 150, 154, and 159 Ω^{-1} cm^2 equiv^{-1} and slope = 338, 344, and 328, respectively). Below 10^{-4} M the slopes of the Onsager plots increase, indicating dissociation of the axial ligand. However, [MnLF]PF$_6$ has values of 170 Ω^{-1} cm^2 equiv^{-1} and 685 for the limiting conductance and slope. These values are within the range expected for a 2:1 electrolyte and indicate that the complex exists as a dimer in solution, since the molar conductivity at 10^{-3} M was in the 1:1 electrolyte range. The solid-state magnetic moments of the derivatives (Table II) are all very close to the spin-only value of 5.92 μ_B as is expected for high-spin d^5 complexes. There is no indication of metal–metal interaction in the solid state from the magnetic data for the fluoride derivative.

The infrared spectra in mineral oil mulls and KBr pellets are very similar to those of the [ZnLX]$^+$ or [CuLX]$^+$ complexes.[7,10] Thus, no gross differences in conformation of the macrocyclic ligand are expected in comparison to the approximately planar conformation determined by X-ray crystallographic studies of Co and Cu complexes of this class of ligand.[20,21] The C=N stretching bands (Table I) occur at frequencies comparable to those of the Zn complexes (1600–1615 cm^{-1}) and slightly higher than those of the Cu complexes (1585–1595 cm^{-1}), indicating a relative unimportance of metal to ligand π-back-bonding. The slight trend toward lower frequency in the C=N stretching bands as one progresses down the series of derivatives in Tables I may be due either to differences in coordination geometry, e.g., displacement of the metal ion from the N$_4$ plane or to slight differences in bonding. Similar to those in all other complexes of L, a sharp band near 1220 cm^{-1} observed in all the spectra is associated with the coordinated α-diimine moiety.

Table III. Half-Wave Potentials and Peak Separation for Manganese Complexes[a]

compd	$E_{1/2}(1)$	$\Delta E_p(1)$	$E_{1/2}(2)$	$\Delta E_p(2)$
[MnLF]PF$_6$	-1.29	100	-1.51	85
[MnLCl]PF$_6$	-1.19	90	-1.55	85
[MnLBr]PF$_6$	-1.17	84	-1.52	80
[MnLI]PF$_6$	-1.18	97	-1.51	75

[a] Vs. ferrocene/ferrocenium couple in Me$_2$SO, 0.10 M Bu$_4$NPF$_6$ supporting electrolyte. Units: $E_{1/2}$, V; ΔE_p, mV.

The electronic spectra of the derivatives in CH$_3$CN are nearly identical. All feature two shoulders at about 230 and 270 nm (Table II) on the side of the intense intraligand transitions that start at about 220 nm. From the molar absorptivities of these bands and from their insensitivity to the variation of the axial ligand, it can be concluded that they most likely arise from metal–macrocycle charge-transfer transitions. No bands attributable to d–d transitions were observed at longer wavelengths. This is consistent with high-spin d^5 metal ions.

The electrochemical behavior of the complexes was studied by cyclic voltammetry in Me$_2$SO. All of the redox processes observed were diffusion-controlled as indicated by linear plots of peak current vs. the square root of the scan rate. The difference between the anodic and cathodic peak potentials, ΔE_p, for a given wave provides a measure of the thermodynamic reversibility of the couple. Comparison of the ΔE_p values in Table III with that for ferrocene (about 70 mV) in the same medium indicates that the reductions are quasi-reversible. This finding is supported further by the fact that ΔE_p for these couples is scan-rate dependent and approaches a value of 75 mV as the scan rate is reduced. The magnitudes of the peak currents in comparison with the one-electron process of ferrocene along with the ΔE_p values both indicate that, with the exception of [MnLF]PF$_6$, the processes in Table III are all one-electron reductions. The peak current of the second wave of [MnLF]PF$_6$ is approximately half the value of the first wave. Thus, for this complex there may be several electroactive species in solution. Recall that the complex conductivity behavior of [MnLF]PF$_6$ was indicative of dimers in CH$_3$CN: thus there may exist equilibria between several species also in Me$_2$SO. The potentials of the reductions for all the derivatives are nearly equal and occur at values very similar to those for macrocyclic ligand reductions observed for [CuLX]$^+$ and [ZnLX]$^+$ complexes in aprotic solvents.[22] Therefore, it is likely that the reductions in Table III correspond to ligand reductions. This hypothesis is supported by the finding that the half-wave potentials are largely insensitive to added excess axial ligand.

Of the derivatives, only [MnLBr]PF$_6$ and [MnLI]PF$_6$ showed any oxidation waves in the range +1.0 to −1.0 V vs. Ag/AgNO$_3$. Irreversible oxidations with peak currents indicative of approximately one-electron transfer were observed in the cyclic voltammograms of the bromide and iodide derivatives at 0.60 and 0.00 V (50 mV/s scan rate). Addition of excess axial ligand halide caused the peak current for these processes to greatly increase. Also, the observed potentials closely correspond to those for the oxidation waves in solutions containing tetrabutylammonium halide and no [MnLX]$^+$. Thus, these two oxidation processes are thought to correspond to the generation of Br$_2$ or I$_2$. No electrode activity was observed for the chloride or fluoride derivatives in

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this range. Thus, the complexes appear to be relatively stable toward oxidation to Mn(III). Treatment of $[MnLBr]PF_6$ with Ce^{4+} in CH_3CN did cause a color change indicative of possible oxidation. In comparison, Bryan and Dabrowiak[23] reported the irreversible oxidation of $[MnMe_6[14]aneN_4]^{2+}$ in CH_3CN at -0.1 V vs. Ag/AgCl (saturated NaCl). The manganese complexes of two unsaturated macrocyclic ligands having two imine and two amide donors, $[Mn[14]12eneN_4Cl]$ and $[Mn(TPP)ClH_2O]$, exhibit Mn(III)/Mn(II) couples at approximately -0.7 V vs. Ag/AgCl (saturated NaCl) and at -0.6 V vs. $Ag/AgNO_3$, respectively.[24,25] Also, the manganese complexes of the lacunar macrocyclic ligands of Herron and Busch[26] have Mn(III)/Mn(II) half-wave potentials near -0.5 V vs. $Ag/AgNO_3$. Thus, the resistance of MnL complexes to oxidation and, indeed, the isolation of the Mn(II) complexes at all must be viewed as unusual. Of course the possibility exists that the lack of electroactivity of $[MnLX]^+$ complexes is due to large shifts because of extreme irreversibility. However, similar behavior was observed at the Pt electrode; also, the complexes are stable in air both in solution and in the solid state. Thus, it is likely that they do exhibit unusual stability. This behavior is consistent with the fact that the $[14]tetraeneN_4$ ligand is known to stabilize low oxidation states with other metals, e.g., Co(I), Cu(I), and Fe(II).

In conclusion, the chemistry of $[14]tetraeneN_4$ macrocycles has been extended to include the protonated form of the metal-free ligand and this has made possible the synthesis of Mn(II) complexes. These complexes are stable in the presence of a single halide axial ligand and are surprisingly resistant to oxidation.

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Registry No. H_4LBr_4, 100927-35-3; $[MnLF]PF_6$, 100909-21-5; $[MnLCl]PF_6$, 100909-23-7; $[MnLBr]PF_6$, 100909-25-9; $[MnLI]PF_6$, 100909-27-1; $[CuL](PF_6)_2$, 77154-14-4.

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Photosubstitution Reactions of the Ruthenium(II) Arene Complexes $Ru(\eta^6\text{-arene})L_3^{2+}$ (L = NH_3 or H_2O) in Aqueous Solution

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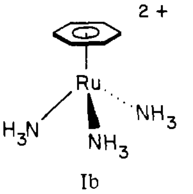
Irradiation of the ruthenium(II) complexes $Ru(\eta^6\text{-arene})L_3^{2+}$ (arene = benzene, toluene, or isopropyltoluene; L = NH_3 or H_2O) in aqueous solution leads in each case to aquation of arene as the only observable photoreaction ($Ru(\eta^6\text{-arene})L_3^{2+} + 3H_2O \rightarrow Ru(H_2O)_3L_3^{2+}$ + arene). Quantum yields ϕ_L for this process were a function of λ_{irr}, relatively low for the irradiation into the lowest energy absorption band but progressively higher at shorter wavelengths. The triammine ion $Ru(\eta^6\text{-}C_6H_6)(NH_3)_3^{2+}$ showed no evidence for ammine aquation or for photooxidation to Ru(III). The ϕ_L values were found to be nearly independent of whether L = NH_3 or H_2O although there are significant spectral differences between these complexes. In contrast, ϕ_L was found to be quite responsive to the nature of substituents on the arene ring. The spectral properties and potential mechanisms for arene photosubstitution are discussed.

Introduction

The work described here is concerned with the characterization of the quantitative photochemistry of a series of mono(η^6-arene) complexes of ruthenium(II), e.g.



Ib

Complexes such as Ib, which is stable toward oxidation in aqueous solution and is relatively substitution inert,[2] fall into an interface between classical "Werner type" complexes and organometallic compounds. Hexaammineruthenium(II),[3] $Ru(NH_3)_6^{2+}$ (and related Ru(II) ammine complexes),[4] as well as (benzene)(cyclopentadienyl)ruthenium(II),[5] $Ru(\eta^6\text{-}C_6H_6)(\eta^5\text{-}C_5H_5)^+$, have been investigated photochemically. In both cases, photosubstitution is a dominant reaction pathway, NH_3 being liberated from $Ru(NH_3)_6^{2+}$ and benzene from $Ru(\eta^6\text{-}C_6H_6)(\eta^5\text{-}C_5H_5)^+$. In this context, it was of interest to delineate the photoreaction properties of Ib and the similar η^6-arene ruthenium(II) complexes $Ru(\eta^6\text{-arene})L_3^{n+}$ (L = H_2O or NH_3, arene = benzene, toluene, or *p*-cymene). Of particular interest is whether the arene, which nominally occupies three coordination sites on the Ru(II) and is more robust toward thermal aquation than are the monodentate ligands, would be photolabilized preferentially to the monodentate ligands.

Some qualitative observations have been described for the photochemistry of such compounds. Bennett and Smith[6] have reported that $Ru(\eta^6\text{-arene})Cl_2P(n\text{-}Bu)_3$ dissolved in another arene undergoes exchange of coordinated and solvent arenes when irradiated with UV light. Also, Taube and co-workers[7] have noted that an osmium(II) complex $Os(\eta^6\text{-}C_6H_6)Cl_2$ dissolved in water (to give, probably, $Os(\eta^6\text{-}C_6H_6)(H_2O)_3^{2+}$) decomposes upon UV irradiation to give free benzene as one reaction product. However, to our knowledge, no quantitative investigation of such systems has been undertaken.

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