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Macrocyclic Nickel(II) Complexes with New, Dimethyl-Substituted 13- and 14-Membered Tetraaza Ligands

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Catalytic reduction of the diimine linkages of 11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-11,13-dienenickel(II) hexafluorophosphate, $[\text{Ni}(\text{[13]dieneN}_4)](\text{PF}_6)_2$, and 12,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-12,14-dienenickel(II) hexafluorophosphate, $[\text{Ni}(\text{[14]dieneN}_4)](\text{PF}_6)_2$, in aqueous solution over Raney nickel yields Ni(II) complexes containing the fully reduced, dimethyl-substituted macrocyclic ligands. Conversion of the PF_6^- salts to NO_3^- derivatives has been accomplished by column chromatography. Compounds with a variety of other anions have been prepared by metathetical reactions on solutions of the NO_3^- complexes. Ten new complexes have been characterized on the basis of elemental analyses, conductivity and magnetic susceptibility measurements, and infrared and electronic spectral studies. $[\text{Ni}(\text{[13]aneN}_4)]\text{X}_2$ and $[\text{Ni}(\text{[14]aneN}_4)]\text{X}_2$ where $\text{X}^- = \text{PF}_6^-$ and I^- contain singlet ground-state Ni(II) and the planar forms of both macrocyclic ligands. Axial coordination occurs when $\text{X}^- = \text{Cl}^-$, Br^- , and NO_3^- and complexes of formulation $[\text{Ni}(\text{[14]aneN}_4)\text{X}_2]$ have been characterized as high spin tetragonal. Two complexes, $[\text{Ni}_2(\text{[13]aneN}_4)_2\text{ox}](\text{PF}_6)_2$ and $[\text{Ni}_2(\text{[14]aneN}_4)_2\text{ox}](\text{PF}_6)_2$, are dimers which contain oxalato bridging groups. These two compounds, along with monomeric $[\text{Ni}(\text{[14]aneN}_4)(\text{SCN})_2]$, exhibit pseudooctahedral Ni(II) spectral characteristics and must contain folded forms of the macrocyclic ligands. Analysis of electronic spectral data for the tetragonal complexes gives a Dq^{xy} of 1470 cm^{-1} for the dimethyl-substituted 14-membered ligand. This value is nearly the same as that reported for cyclam which leads us to conclude that substitution of two methyl groups on the cyclam ring has negligible steric and electronic effects.

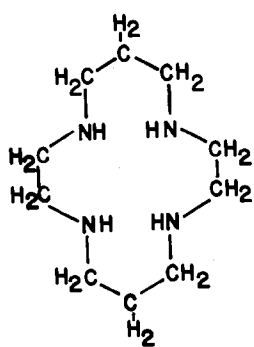
Introduction

Concentrated efforts in several research laboratories over the past 15 years have brought a new degree of sophistication to studies of macrocyclic metal complexes.¹⁻⁵ While the earlier work centered almost exclusively on development of new and sometimes novel methods for synthesis of a broad range of seemingly unrelated ligands and complexes, recent studies have involved application of synthetic expertise to the design of new series of compounds which possess specific structural characteristics.⁶⁻¹⁰ Structural parameters which can be varied almost at will include the nature and oxidation state of the metal ion, anion, ring size and charge, donor atoms, degree of unsaturation, and type of substituents on the rings. Further work has shown that cause and effect relationships exist between the chemical reactivity of the metal ion and the structural and electronic properties of the complex.^{5,11}

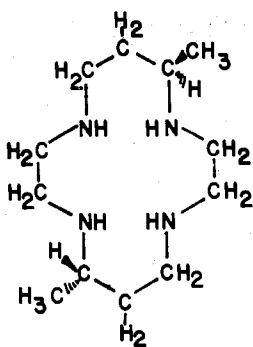
The synthetic studies derive added significance when the new compounds can be used as models for natural products; e.g., complexes with tetraaza macrocyclic ligands can be designed to have many characteristics in common with metalloporphyrins, vitamin B₁₂, and chlorophyll. Special types of chemical reactivity can sometimes be induced by elegant complex design; e.g., sterically hindered iron(II) porphyrins combine reversibly with molecular oxygen under relatively mild

conditions and thus serve as models for myoglobin.¹²⁻¹⁵

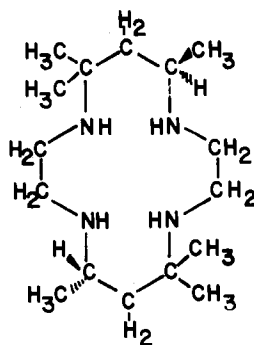
Recent physical studies on selected macrocyclic complexes have involved measurement of thermodynamic and kinetic stabilities and correlation of differences with specific structural features.¹⁶⁻¹⁹ Such studies when performed on model complexes are valuable in that they provide a means of evaluating the importance of specific factors which may affect biological activity. For example, it is well known that most macrocyclic ligands in aqueous solution form more stable complexes with metal ions than open-chain ligands with the same donor groups.^{3,17,18} Rather extensive investigation of the thermodynamics and kinetics of complexation of selected metal ions with tetraaza macrocyclic ligands has revealed that the differences are due not only to cyclization but also to (1) steric effects which arise from substitution on the alkyl backbone or nitrogen donor atoms of the ring, and (2) differences in reactivity of secondary vs. tertiary nitrogen donor atoms. The importance of steric effects has been demonstrated recently for Ni(II) and Cu(II) complexes with ligands I-IV.^{18,19} The ligands are identified as 1,4,8,11-tetraazacyclotetradecane (cyclam), I; *meso*-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane (5,12-Me₂cyclam), II; *meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (*tet-a*), III; and *rac*-5,7,7,12,14,14-hexamethyl-1,4,8,11-



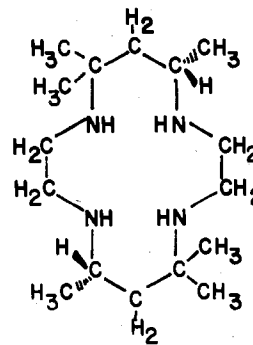
I



II



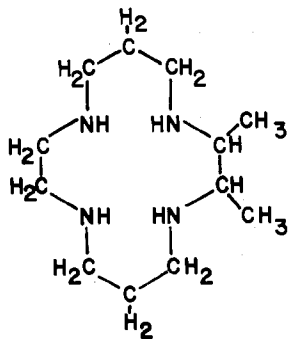
III



IV

tetraazacyclotetradecane (tet-*b*), IV. Log *K* values and complex formation rate constants obtained for these compounds show that destabilization generally results from methyl substitution on the alkyl backbone of the macrocyclic ligand. The effect is small for two methyl groups but quite significant with six. Differences in redox potentials of coordinated macrocyclic ligands and metal ions also seem to correlate with the extent of unsaturation and methyl substitution.⁵ Inductive as well as steric effects may be important here.

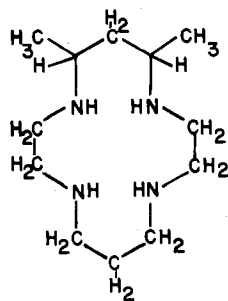
To date, the only dimethyl-substituted cyclam complexes which have been investigated thermodynamically and kinetically are the Ni(II) and Cu(II) complexes with the 5,12-dimethyl formulation.^{18,19} It should be noted that this structural variant places the methyl groups on carbon atoms of trimethylene bridges trans to one another. Dimethyl substitution at other positions on the cyclam backbone may have more consequential effects; however, this hypothesis has never been tested due in part to the lack of availability of a series of suitable compounds. Recently, complexes containing 2,3-Me₂cyclam, V, have been prepared.⁸ In this ligand, also



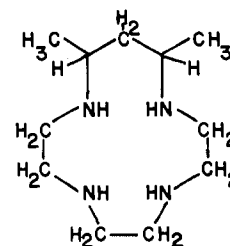
V

abbreviated DMC, the two methyl groups are located on adjacent carbon atoms which constitute one of the ethylene bridging units.

In this paper, we report the synthesis and characterization of new Ni(II) complexes which contain a third type of dimethylated cyclam ligand, 12,14-Me₂cyclam, VI, in which the



VI



VII

methyl substituents are bonded to carbon atoms of the same trimethylene bridge. Some Ni(II) complexes containing the corresponding 13-membered ligand, VII, have also been isolated and characterized.²⁰

Experimental Section

Materials. Activated Raney nickel catalyst, Grade 28, was obtained from W. R. Grace Chemicals, South Pittsburg, Tenn. Dowex 2X8 anion-exchange resin in the chloride form was obtained from J. T. Baker, Phillipsburg, N.J., and was converted to the nitrate form prior to use. This was accomplished by packing the resin into a 350 × 30 mm column and flushing it with concentrated nitric acid until no precipitate formed when the eluent was tested with silver nitrate solution. The resin was then thoroughly rinsed with distilled water. Solvents employed in physical measurements and reagents used as starting materials were purchased commercially and were spectro-quality and reagent grade. [Ni([14]dieneN₄)](PF₆)₂²¹ and [Ni([13]dieneN₄)](PF₆)₂,²¹ the β-diimine complexes which were used as starting materials, were prepared by published procedures.^{22,23}

Synthesis of 11,13-Dimethyl-1,4,7,10-tetraazacyclotridecane-nickel(II) Hexafluorophosphate, [Ni([13]aneN₄)](PF₆)₂. A 1-g sample of crude [Ni([13]dieneN₄)](PF₆)₂²³ (1.8 mmol) was dissolved in 100 ml of water which produced a yellow-brown solution. To this was added approximately 2 g of active Raney nickel catalyst. The mixture was placed in the pressure bomb of a Parr low-pressure hydrogenation apparatus which was then charged with 65 psi of hydrogen. The reaction mixture was allowed to shake for 24–30 h. At the end of this time, the catalyst was removed by gravity filtration. Concentration and refrigeration of the resulting clear yellow solution led to formation of bright yellow platelets of [Ni([13]aneN₄)](PF₆)₂. The product was separated by vacuum filtration and air-dried. Yields were essentially quantitative. Recrystallization of the product from hot water afforded a pure sample with elemental analyses reported in Table I.

Synthesis of Other Derivatives of Ni([13]aneN₄)²⁺. The NO₃⁻ derivative was prepared by anion-exchange chromatography of a 1% aqueous solution of the PF₆⁻ salt using a column of Dowex 2X8 anion-exchange resin in the nitrate form. A flow rate of about 1 drop/s off the column was used. The yellow solution which came off the column contained the nitrate derivative which could not be isolated except as a reddish brown oil. A solid I⁻ derivative was obtained via metathesis of an aqueous solution containing the NO₃⁻ salt by the addition of 0.54 g (3.6 mmol) of sodium iodide. An oxalato derivative was prepared by the addition of 0.48 g (3.6 mmol) of sodium oxalate to an aqueous solution containing 1 g of the PF₆⁻ salt. [Ni([13]aneN₄)]₂ crystallized as reddish brown needles while [Ni₂([13]aneN₄)₂](PF₆)₂ crystallized as lavender platelets. Results of elemental analyses on recrystallized samples of both compounds are given in Table I. Yields varied from 0.2 to 0.9 g. Attempts were made to synthesize Cl⁻, Br⁻, and SCN⁻ derivatives by methods similar to that used for the I⁻ complex, but these products could not be isolated in crystalline form.

Synthesis of 12,14-Dimethyl-1,4,8,11-tetraazacyclotetradecane-nickel(II) Hexafluorophosphate, [Ni([14]aneN₄)](PF₆)₂. [Ni([14]aneN₄)](PF₆)₂ was prepared in the same manner as [Ni([13]aneN₄)](PF₆)₂. The product crystallized as bright yellow platelets initially and as darker yellow platelets after recrystallization from

Table I. Analytical Data for Ni([14]aneN₄)X₂ and Ni([13]aneN₄)X₂ Complexes

Compd	% calcd						% found					
	C	H	N	Ni	X	Other	C	H	N	Ni	X	Other
[Ni([14]aneN ₄)](PF ₆) ₂	24.97	4.90	9.71	10.17	39.51 (F)	10.73 (O)	25.01	4.87	9.94	10.54	39.01 (F)	10.63 (P)
[Ni([14]aneN ₄)]I ₂	26.64	5.23	10.36	10.85	46.92 (I)		26.66	5.23	10.20	10.95	47.01 (I)	
[Ni([14]aneN ₄)Cl ₂]	40.25	7.90	15.65	16.40	19.80 (Cl)		40.34	7.68	15.46	16.52	20.12 (Cl)	
[Ni([14]aneN ₄)Br ₂]	32.24	6.33	12.54	13.14	35.76 (Br)		32.48	6.16	12.61	13.18	35.63 (Br)	
[Ni([14]aneN ₄) ₂ ox](PF ₆) ₂	35.05	6.88	20.44	14.28		23.35 (O)	34.95	6.77	20.48	14.23		23.57 (O)
[Ni([14]aneN ₄)](SCN) ₂	41.69	7.01	20.84	14.56		15.90 (S)	41.68	6.83	20.75	14.62		15.73 (S)
[Ni ₂ ([14]aneN ₄) ₂ ox](PF ₆) ₂	32.79	5.93	11.76	12.33	23.94 (F)	6.50 (P)	32.67	5.67	11.62	12.41	23.98 (F)	6.32 (P)
[Ni([13]aneN ₄)](PF ₆) ₂	23.46	4.66	9.95	10.43	40.49 (F)	11.00 (P)	23.41	4.75	9.92	10.62	40.61 (F)	11.13 (P)
[Ni([13]aneN ₄)]I ₂	25.07	4.98	10.64	11.14	48.17 (I)		24.87	5.12	10.48	11.26	47.87 (I)	
[Ni ₂ ([13]aneN ₄) ₂ ox](PF ₆) ₂	31.19	5.68	12.13	12.70	24.67 (F)	6.70 (P)	31.14	5.31	12.04	12.91	24.65 (F)	6.57 (P)

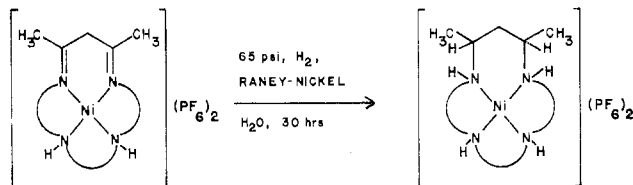


Figure 1. General synthetic route to the new fully reduced macrocyclic complexes.

hot deionized water; yield ~90%. Results of elemental analyses are given in Table I.

Synthesis of Other Derivatives of Ni([14]aneN₄)²⁺. The NO₃⁻, I⁻, Br⁻, Cl⁻, and SCN⁻ derivatives were prepared by metathesis using the appropriate sodium salts following chromatographic anion exchange as detailed above for the [13]aneN₄ complexes. [Ni([14]aneN₄)]I₂ crystallized as reddish brown platelets while [Ni([14]aneN₄)Br₂], [Ni([14]aneN₄)Cl₂], [Ni([14]aneN₄)](SCN)₂, [Ni([14]aneN₄)](NO₃)₂, and [Ni₂([14]aneN₄)₂ox](PF₆)₂ formed lavender platelets. All derivatives were purified by recrystallization from hot water. Yields ranged from 20 to 90%, with highest yields being obtained for the relatively insoluble iodide. Results of elemental analyses are given in Table I.

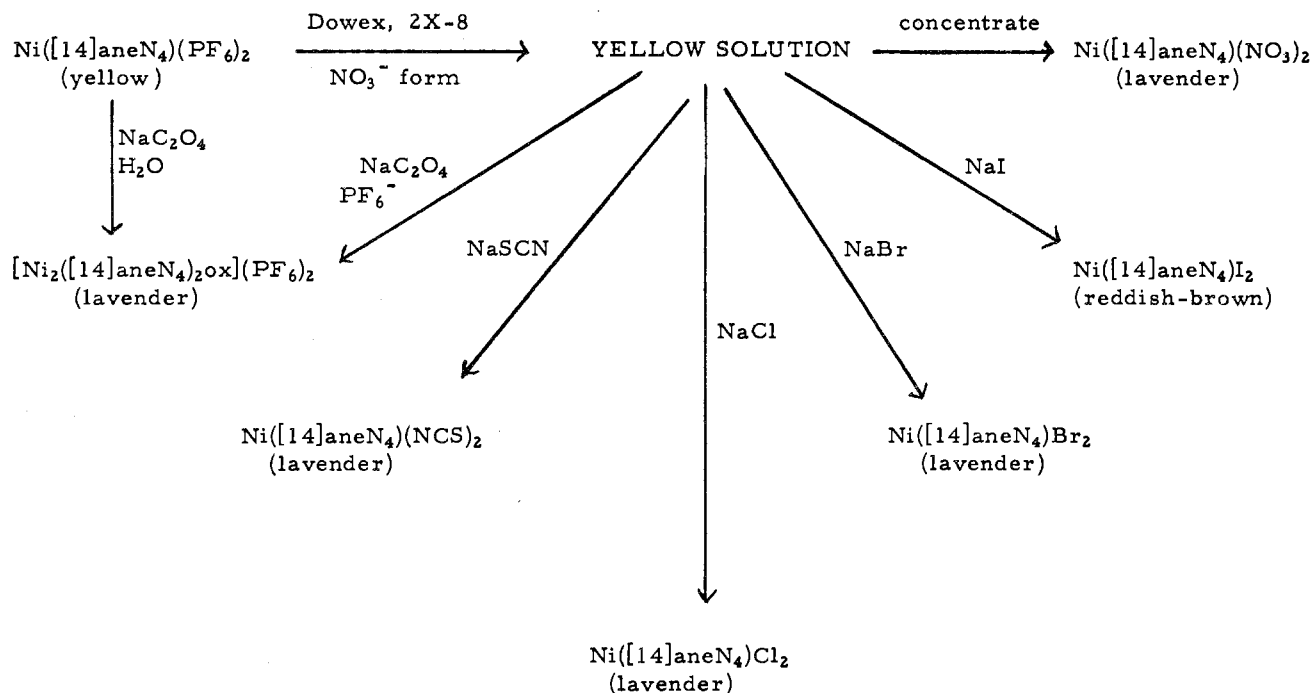
Measurements. Infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer using Nujol mulls and KBr disks. Visible and ultraviolet spectra were measured using a Cary 14 recording spectrophotometer. Both solution and diffuse transmittance techniques were used. Magnetic susceptibility measurements were obtained utilizing the Faraday technique. Diamagnetic corrections were based on Pascal's constants. ¹H NMR spectra were recorded

with a Varian HA-60-IL NMR spectrophotometer in deuterio-acetonitrile using TMS as the internal standard. Conductivities were calculated from electrical resistance measurements on 10⁻³ M chloroform, acetonitrile, and aqueous solutions using a Yellow Springs Instruments Model 31 conductivity bridge. Elemental analyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach, West Germany.

Results and Discussion

Synthesis and Characterization of 13- and 14-Membered Macrocyclic Metal Complexes. Ten new complexes containing fully saturated, dimethyl-substituted 13- and 14-membered macrocyclic tetraaza ligands have been prepared via catalytic hydrogenation of the corresponding coordinated β-diimine macrocycles. The general method of synthesis of both [Ni([13]aneN₄)](PF₆)₂ and [Ni([14]aneN₄)](PF₆)₂ is shown in Figure 1. Anion-exchange chromatography of the relatively insoluble PF₆⁻ derivatives has been used to prepare solutions of the corresponding NO₃⁻ complexes. Metathetical reactions, as outlined in Figure 2 for the Ni([14]aneN₄)²⁺ complexes, were then employed to prepare a wide range of derivatives. Complexes which have been prepared include Ni([14]aneN₄)X₂, where X⁻ = PF₆⁻, I⁻, Br⁻, Cl⁻, NO₃⁻, and SCN⁻; [Ni([13]aneN₄)]X₂, where X⁻ = PF₆⁻ and I⁻; and [Ni₂([13]aneN₄)₂ox](PF₆)₂ and [Ni₂([14]aneN₄)₂ox](PF₆)₂. Fewer derivatives of the 13-membered macrocycle have been isolated due to their tendency to oil rather than crystallize from solution.

All of the new complexes have been characterized based on

Figure 2. Method of synthesis of other Ni([14]aneN₄)²⁺ complexes via column chromatography and metathetical reactions in aqueous solution.

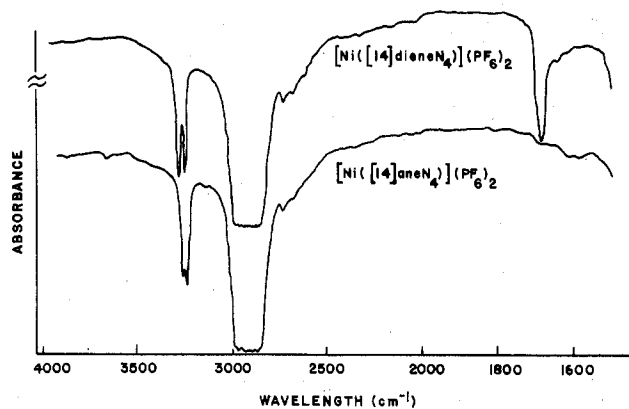


Figure 3. Infrared spectra in Nujol of $[\text{Ni}([14]\text{dieneN}_4)](\text{PF}_6)_2$ and $[\text{Ni}([14]\text{aneN}_4)](\text{PF}_6)_2$ in selected regions.

results of elemental analyses, conductivity and magnetic susceptibility measurements, and visible, ultraviolet and infrared spectral studies. The results of elemental analyses, reported in Table I, indicate stoichiometries which are in agreement with those formulations given.

Evidence for complete hydrogenation of the diimine linkages of the 13- and 14-membered macrocyclic starting materials has been obtained from infrared spectral measurements. Portions of the ir spectrum of $[\text{Ni}([14]\text{dieneN}_4)](\text{PF}_6)_2$ and that of the product isolated after reduction with H_2 -Raney nickel are shown in Figure 3. It can be seen that both the starting material and product exhibit strong absorptions at 3265 and 3240 (sh) cm^{-1} , in the $-\text{NH}$ stretching region. The presence of two bands may be due to the presence of different stereoisomers since only a single vibration is expected for a coordinated secondary amine. The starting material also exhibits a strong band at 1680 cm^{-1} which is characteristic of the $-\text{C}=\text{N}$ stretching mode of coordinated imines. Absence of this band in the spectrum of the reduced complex confirms that complete hydrogenation has occurred. Reaction for shorter periods of time or in the presence of other catalysts resulted in incomplete or no hydrogenation. Comparable behavior is observed upon hydrogenation of $[\text{Ni}([13]\text{-dieneN}_4)](\text{PF}_6)_2$. In addition to ir-active vibrations from the coordinated macrocyclic ligand, spectra of the PF_6^- , SCN^- , NO_3^- and ox^{2-} derivatives exhibit absorption bands due to the anions. Spectra of the monomeric PF_6^- derivatives exhibit intense bands at ~ 830 and 565 cm^{-1} which are typical of ionic hexafluorophosphate. Spectra of the dimeric complexes $[\text{Ni}_2([13]\text{aneN}_4)_2\text{ox}](\text{PF}_6)_2$ and $[\text{Ni}_2([14]\text{aneN}_4)_2\text{ox}](\text{PF}_6)_2$ show very similar absorption bands in the PF_6^- regions along with a new band at $\sim 1645 \text{ cm}^{-1}$ which is attributed to the $-\text{C}=\text{O}$ stretching vibration of coordinated oxalate.²⁴ The spectra of $[\text{Ni}([14]\text{aneN}_4)(\text{SCN})_2]$ and $[\text{Ni}([14]\text{aneN}_4)(\text{NO}_3)_2]$ also show bands due to the anions; however, these bands are poorly resolved making it impossible to deduce the mode of anion coordination from the ir data alone. Results of magnetic susceptibility and conductivity measurements and electronic spectral studies have made such assignments possible (vide infra).

Magnetic susceptibility measurements on the complexes indicate that the coordination geometry of Ni(II) depends on the anion. Thus, the PF_6^- and I^- salts exhibit diamagnetic behavior, with $\mu_{\text{eff}} = 0.5\text{--}0.6 \text{ BM}$; while the Cl^- , Br^- , SCN^- , NO_3^- , and ox^{2-} derivatives are paramagnetic, with $\mu_{\text{eff}} = 2.86\text{--}3.07 \text{ BM}$. Conductivities were measured in each of four solvents (nitromethane, chloroform, acetonitrile, and water) whenever solubility permitted. The Br^- , Cl^- , NO_3^- , and SCN^- derivatives of $[\text{Ni}([14]\text{aneN}_4)\text{X}_2]$ are nonelectrolytes in nitromethane and chloroform which indicates that both anions are coordinated. Molar conductances for the I^- , PF_6^- , and

Table II. Electronic Spectra of Reduced Nickel(II) Complexes

Compd	Absorption bands ^a	
	Soln λ_{max} (ϵ)	Solid-state λ_{max} ^b
$[\text{Ni}([13]\text{aneN}_4)](\text{PF}_6)_2^c$	23 364 (145)	23 256
	45 662 (12 300)	41 667
$[\text{Ni}([14]\text{aneN}_4)](\text{PF}_6)_2^c$	22 124 (65)	21 834
	44 543 (14 600)	42,553
$[\text{Ni}([13]\text{aneN}_4)]\text{I}_2^c$	23 256 (138)	22 988 ^d
		35 087
$[\text{Ni}([14]\text{aneN}_4)]\text{I}_2^c$	44 444 (42 700)	45 454
	22 026 (62)	21 413
$[\text{Ni}([14]\text{aneN}_4)]\text{Br}_2^e$	44 248 (40 300)	35 088
	7 874 (3)	46 512
$[\text{Ni}([14]\text{aneN}_4)\text{Cl}_2]^e$	14 545 (3)	7 576
	18 939 (7)	13 423
$[\text{Ni}([14]\text{aneN}_4)(\text{NO}_3)_2]^e$	28 369 (7)	18 957
	37 383 (4870)	27 778 ^d
$[\text{Ni}([14]\text{aneN}_4)(\text{SCN})_2]^e$	40 816 (6700)	35 088
	8 439 (3)	8 403
$[\text{Ni}_2([13]\text{aneN}_4)_2\text{ox}](\text{PF}_6)_2^f$	14 599 (4)	14 925
	19 011 (7)	19 048
$[\text{Ni}_2([14]\text{aneN}_4)_2\text{ox}](\text{PF}_6)_2^f$	29 197 (30)	28 902
	8 850 (3)	
$[\text{Ni}([14]\text{aneN}_4)(\text{NO}_3)_2]^e$	14 925 (4)	14 492
	19 417 (7)	19 802
$[\text{Ni}([14]\text{aneN}_4)(\text{SCN})_2]^e$	31 746 (47)	31 250
	10 929 (10)	10 869
$[\text{Ni}_2([13]\text{aneN}_4)_2\text{ox}](\text{PF}_6)_2^f$	12 461 (7)	
	19 608 (10)	19 881
$[\text{Ni}_2([14]\text{aneN}_4)_2\text{ox}](\text{PF}_6)_2^f$	30 769 (16)	31 250
	11 049 (57)	10 989
$[\text{Ni}([14]\text{aneN}_4)(\text{NO}_3)_2]^e$	12 376 (46) ^d	
	18 182 (64)	18 018
$[\text{Ni}([14]\text{aneN}_4)(\text{SCN})_2]^e$	28 985 (138)	27 972
	10 989 (20)	11 111
$[\text{Ni}([14]\text{aneN}_4)(\text{NO}_3)_2]^e$	12 422 (13)	
	18 433 (28)	18 182
$[\text{Ni}([14]\text{aneN}_4)(\text{SCN})_2]^e$	28 776 (61)	29 411

^a Reported in cm^{-1} . ^b Diffuse transmittance. ^c $10^{-3}\text{--}10^{-5} \text{ M}$ aqueous solutions. ^d Shoulder. ^e $10^{-2}\text{--}10^{-4} \text{ M}$ chloroform solutions. ^f $10^{-2}\text{--}10^{-4} \text{ M}$ acetonitrile solutions.

ox^{2-} complexes, which are insoluble in nitromethane and chloroform, were measured in acetonitrile. The molar conductances obtained, $\Lambda_{\text{M}} = 280\text{--}310 \text{ mhos}/(\text{cm mol})$, are consistent with formulation of these complexes as 2:1 electrolytes.²⁵ All of the derivatives are 2:1 electrolytes in water,²⁶ with $\Lambda_{\text{M}} = 185\text{--}230 \text{ mhos}/(\text{cm mol})$.

Electronic spectral measurements have been most useful in distinguishing between the possible geometries of the new complexes. The visible and ultraviolet spectra which are observed can be divided into three distinct types: type A is exhibited by the simple PF_6^- and I^- derivatives; type B is produced by the oxalato and SCN^- derivatives; and type C is observed for the Cl^- , Br^- , and NO_3^- complexes. The spectra of the 14-membered ox^{2-} , Cl^- , and PF_6^- complexes are reproduced in Figure 4 and are representative of the three different types. A complete list of electronic absorption bands for all of the new compounds is given in Table II.

In general, the type A spectrum consists of one low-energy band. In both the aqueous solution and solid-state spectra of $[\text{Ni}([13]\text{aneN}_4)](\text{PF}_6)_2$, $[\text{Ni}([13]\text{aneN}_4)]\text{I}_2$, $[\text{Ni}([14]\text{-aneN}_4)](\text{PF}_6)_2$, and $[\text{Ni}([14]\text{aneN}_4)]\text{I}_2$, the low-energy band occurs at $\sim 22700 \text{ cm}^{-1}$. This band is assigned to the ${}^1\text{B}_{1g} \leftarrow {}^1\text{A}_{1g}$ transition of square-planar Ni(II).²⁷ The molar absorptivity of the absorption band is ~ 140 for the 13-membered ring system and ~ 62 for the larger 14-membered system. The larger value observed for the smaller macrocycle may indicate the presence of some ring strain in the 13-membered ring. Spectra of these four derivatives also exhibit higher energy bands at $\sim 35000\text{--}45000 \text{ cm}^{-1}$ which are assigned to

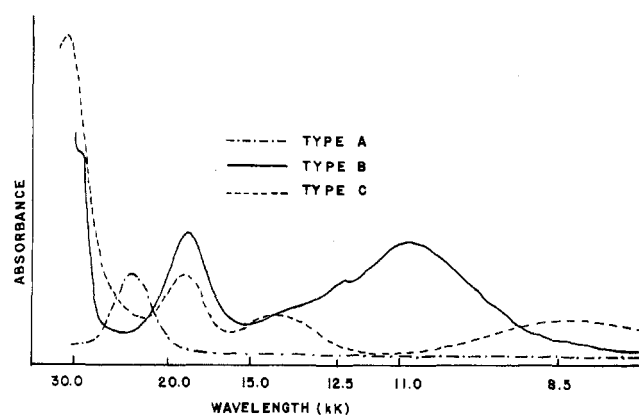
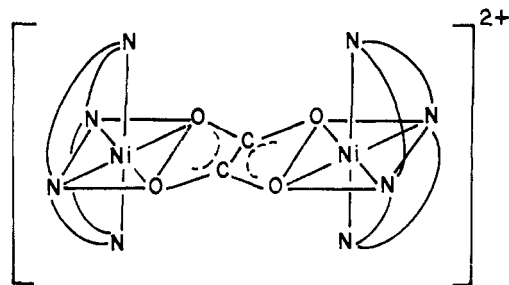


Figure 4. Electronic spectra of 14-membered reduced macrocyclic complexes: type A, $[\text{Ni}(\text{[14]aneN}_4)](\text{PF}_6)_2$ in H_2O ; type B, $[\text{Ni}_2(\text{[14]aneN}_4)_2\text{ox}](\text{PF}_6)_2$ in CH_3CN ; type C, $[\text{Ni}(\text{[14]aneN}_4)\text{Cl}_2]$ in CHCl_3 .

charge-transfer or parity-allowed transitions of the ligand.

The oxalato and thiocyanato complexes exhibit type B spectral behavior. As can be seen from Figure 4, this type of spectrum consists of four bands due to d-d transitions. The SCN^- and ox^{2-} derivatives of $\text{Ni}(\text{[14]aneN}_4)^{2+}$ show absorptions at ~ 11000 ($\epsilon \approx 15$), ~ 12400 ($\epsilon \approx 10$), ~ 18500 ($\epsilon \approx 18$), and ~ 29000 cm^{-1} ($\epsilon \approx 40$). The 13-membered oxalato complex exhibits similar bands with somewhat higher extinction coefficients (Table II). The bands are attributed to the ${}^3\text{T}_{2g} \leftarrow {}^3\text{A}_{2g}$, ${}^1\text{E}_g \leftarrow {}^3\text{A}_{2g}$, ${}^3\text{T}_{1g}(\text{F}) \leftarrow {}^3\text{A}_{2g}$, and ${}^3\text{T}_{1g}(\text{P}) \leftarrow {}^3\text{A}_{2g}$ transitions of pseudooctahedral $\text{Ni}(\text{II})$.²⁸

On the basis of the visible spectral measurements as well as conductivity and infrared spectral data, the oxalato complexes are formulated as dimers with tetradentate oxalate bridging the $\text{Ni}(\text{II})$ ions. The cis coordination of the oxalate requires that the macrocyclic ligand adopt a folded configuration around the metal ion. A schematic drawing of the bridged complexes is shown in VIII. Similar types of bridged



VIII

complexes have been reported in other macrocyclic systems.¹⁻³ Because the visible and ir spectra of the ox^{2-} and SCN^- complexes are so similar, we conclude that $[\text{Ni}(\text{[14]aneN}_4)(\text{SCN})_2]$ may also contain the folded form of the ligand although it is possible that $Dq^{\text{NCS}} \approx Dq^{\text{ring}}$, in which case electronic spectra will not distinguish between cis and trans structures. The large ligand field strength of thiocyanate in this complex suggests that it is N rather than S bonded to the $\text{Ni}(\text{II})$ ion. Although no Cl^- , Br^- , NO_3^- , or SCN^- derivatives of $\text{Ni}(\text{[13]aneN}_4)^{2+}$ were isolated in this study, they would be expected to contain the folded ligand configuration as has been reported for other 13-membered macrocyclic systems.²⁹

The third type of visible spectral behavior is exhibited by the Cl^- , Br^- , and NO_3^- derivatives of $\text{Ni}(\text{[14]aneN}_4)^{2+}$. The type C spectrum, Figure 4, is characterized by four absorption bands in a pattern which is typical of tetragonally distorted $\text{Ni}(\text{II})$. Bands at $8400\text{--}8900$ ($\epsilon \approx 3$), $14500\text{--}14900$ ($\epsilon \approx 4$), ~ 19000 ($\epsilon \approx 7$), and ~ 29500 cm^{-1} ($\epsilon \approx 30$) are assigned to

the ${}^3\text{E}_g \leftarrow {}^3\text{B}_{1g}$, ${}^3\text{B}_{2g} \leftarrow {}^3\text{B}_{1g}$, $({}^3\text{E}_g, {}^3\text{A}_{2g}) \leftarrow {}^3\text{B}_{1g}$, and ${}^3\text{T}_{1g}(\text{P}) \leftarrow {}^3\text{B}_{1g}$ transitions of tetragonal $\text{Ni}(\text{II})$. Calculation of the spectral parameter Dq^{xy} based on an extension of the method of Wentworth and Piper³⁰ gives an average Dq^{xy} of 1469 cm^{-1} for the coordinated 12,14-Me₂cyclam ligand. This value is nearly identical with that reported³¹ for the $\text{Ni}(\text{II})$ complex of cyclam, I (1480 cm^{-1}), but substantially higher than that calculated for tet-a or tet-b, III or IV (~ 1160 cm^{-1}).²⁹ No value of Dq^{xy} for $\text{Ni}(\text{DMC})^{2+}$ has been reported; however, by analogy with data given for the corresponding $\text{Co}(\text{III})$ systems, $Dq^{xy}(\text{DMC}(\text{V}))$ is expected to be nearly the same as that for cyclam, i.e., $1470\text{--}1480$ cm^{-1} . Apparently, the introduction of two methyl groups on the cyclam backbone has minimal effect on ligand field strength whereas inclusion of six methyl substituents has a significant effect. Small differences still may be detectable thermodynamically or kinetically; hence, conclusions as to the role of pairs of methyl substituents must await such stability studies. Analysis of the spectrum of $[\text{Ni}(\text{[14]aneN}_4)(\text{NCS})_2]$ by this same technique yields a Dq^{xy} which is inconsistent with the average value reported above. This lends further support to the conclusion that the folded ring occurs in the thiocyanato complex.

Several diastereoisomers of both $\text{Ni}(\text{[13]aneN}_4)^{2+}$ and $\text{Ni}(\text{[14]aneN}_4)^{2+}$ are possible. These forms arise due to combinations of the configurations of the four asymmetric coordinated secondary amine nitrogens present in these systems. No attempt has been made in the present study to separate these isomers and results of limited ${}^1\text{H}$ NMR studies on the diamagnetic complexes have been inconclusive. A crystal of $[\text{Co}(\text{[14]dieneN}_4)\text{H}_2\text{O}](\text{PF}_6)_2$ has recently been investigated by x-ray structure analysis³² and has been shown to exist in the cis-meso configuration in which the two amine hydrogens lie on the same side of the ring. The six-membered ring which contains the two imine bonds is nearly planar while the saturated ring trans to it is in the chair form. Both five-membered chelate rings have the δ configuration. These results, coupled with the results of stereochemical studies on related structures,^{31,33-36} and examination of framework molecular models lead us to conclude that the cis-meso- $\delta\gamma\lambda\gamma$ isomer may be preferred. More extensive ${}^1\text{H}$ NMR studies and a structure determination on $[\text{Ni}(\text{[14]aneN}_4)](\text{PF}_6)_2$ are in progress.

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Registry No. $[\text{Ni}(\text{[14]aneN}_4)](\text{PF}_6)_2$, 57808-50-1; $[\text{Ni}(\text{[14]aneN}_4)]\text{I}_2$, 57808-51-2; $[\text{Ni}(\text{[14]aneN}_4)\text{Cl}_2]$, 57808-52-3; $[\text{Ni}(\text{[14]aneN}_4)\text{Br}_2]$, 57808-53-4; $[\text{Ni}(\text{[14]aneN}_4)(\text{NO}_3)_2]$, 57808-54-5; $[\text{Ni}(\text{[14]aneN}_4)(\text{SCN})_2]$, 57808-55-6; $[\text{Ni}_2(\text{[14]aneN}_4)_2\text{ox}](\text{PF}_6)_2$, 57821-10-0; $[\text{Ni}(\text{[13]aneN}_4)](\text{PF}_6)_2$, 57884-51-2; $[\text{Ni}(\text{[13]aneN}_4)]\text{I}_2$, 57884-52-3; $[\text{Ni}_2(\text{[13]aneN}_4)_2\text{ox}](\text{PF}_6)_2$, 57842-78-1; $[\text{Ni}(\text{[14]dieneN}_4)](\text{PF}_6)_2$, 39561-16-5; $[\text{Ni}(\text{[13]dieneN}_4)](\text{PF}_6)_2$, 57808-57-8.

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- (20) Taken in part from the M.S. thesis of M. S. Holtman, Wright State University, Aug 1973; a preliminary account of this work was presented at the 5th Central Regional Meeting of the American Chemical Society, Cleveland, Ohio, May 13-15, 1973.
- (21) Full names of these complexes are 12,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-11,13-dienickel(II) hexafluorophosphate, which is abbreviated as Ni(12,14-Me₂-[14]-11,13-dieneN₄)(PF₆)₂ or more simply Ni([14]dieneN₄)(PF₆)₂, and 11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-10,12-dienickel(II) hexafluorophosphate, which is abbreviated Ni(11,13-Me₂-[13]-10,12-dieneN₄)(PF₆)₂ or more simply Ni([13]dieneN₄)(PF₆)₂. These abbreviations and those used for the fully reduced complexes are based on the method of V. L. Goedken, P. H. Merrell, and D. H. Busch, *J. Am. Chem. Soc.*, **94**, 3397 (1972).
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Ion Chemistry and Gas-Phase Basicity of Nickelocene by Ion Cyclotron Resonance Spectroscopy

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The gas-phase ion chemistry of bis(η^5 -cyclopentadienyl)nickel (nickelocene) is studied using the techniques of ion cyclotron resonance spectroscopy. Total rate constants for the reactions of the primary fragment ions at 70 eV are determined using trapped-ion methods. The long-lived nickelocene anion, Ni(C₅H₅)₂⁻, is formed directly by electron attachment and is unreactive with a variety of simple molecules. Nickelocene is observed to be an exceptionally strong base in the gas phase. Equilibrium proton-transfer reactions are observed in mixtures of nickelocene with (CH₃)₃N and (C₂H₅)₂NH, from which the gas-phase basicity or proton affinity (PA) is determined to be 218.9 ± 1.0 kcal/mol relative to PA(NH₃) = 201 ± 1 kcal/mol. Attempts to determine the site of protonation were inconclusive. The ion chemistry and base strength of nickelocene and ferrocene are compared.

Introduction

While the ion-molecule reactions of organic and simple inorganic molecules have been extensively studied and characterized,² the ion-molecule reactions of organometallic complexes have, in comparison, received relatively little attention. Schumacher and Taubenest first observed the ions Fe₂(C₅H₅)₃⁺ and Ni₂(C₅H₅)₃⁺ in the mass spectrum of ferrocene and nickelocene, respectively, at a source pressure of 10⁻⁵ Torr.³ It was later suggested that these ions may result from the fragmentation of a small amount of neutral metallocene dimer, rather than as the product of an ion-molecule reaction.⁴ More recent investigations of the gas-phase ion chemistry of ferrocene, using both high-pressure mass spectrometry⁵ and ion cyclotron resonance spectroscopy,⁶ prove this supposition to be incorrect, however. Müller has studied ligand displacement processes such as illustrated in eq 1 for

$$L_nM^+ + L' \rightarrow L_{n-m}L'M^+ + mL \quad (1)$$

various organometallic species L_nM⁺.⁷ The ion-molecule reactions of ions derived from Fe(CO)₅ with a variety of σ - and π -electron-donating ligands have been recently investigated.^{8,9}

The present work describes an ion cyclotron resonance (ICR) study of the ion chemistry of nickelocene, both alone and in mixtures with other molecules. Because of its thermal stability and moderate vapor pressure,¹⁰ nickelocene was chosen to compare with the results of our earlier study of the

ion chemistry of ferrocene.⁶ An attempt to study the ion chemistry of bis(η^5 -cyclopentadienyl)chromium was unsuccessful, primarily because of the low vapor pressure of this substance at ambient temperatures. Of particular interest in our previous investigation of metallocene ion chemistry was the unexpectedly high base strength observed for ferrocene in the gas phase.⁶ For comparison, the gas-phase basicity of nickelocene is determined in the present study. Previous investigations of the mass spectrometry^{3,4,11-13} and photoelectron spectrum¹⁴ of nickelocene provide information useful in interpreting our results.

Experimental Section

The theory and instrumentation of ICR mass spectrometry have been previously described.^{2,15,16} This work employed an instrument built at Caltech equipped with a 15-in. electromagnet capable of a maximum field strength of 23.5 kG.

Nickelocene was prepared as described in the literature¹⁷ and determined to be pure by melting point, ir, and conventional mass spectrometric techniques.¹⁸ The sample was pulverized in a nitrogen drybox, sublimed before use, and degassed by several freeze-pump-thaw cycles; no impurities were evident in the ICR mass spectrum. The vapor pressure of nickelocene at room temperature (20-25 °C) is ~10⁻² Torr,¹⁰ which was adequate for all of the present experiments. The vapor from a sublimed crystalline sample was introduced into the spectrometer by means of the normal inlet system through a variable-leak valve. All other chemicals used in this study were obtained from commercial sources and used as supplied except for degassing with several freeze-pump-thaw cycles.