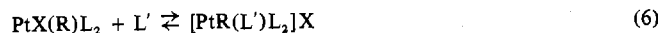


recent paper by Glyde and Mawby.<sup>28</sup> These workers obtained kinetic data for the reaction of  $\text{PtCl}(\text{C}_2\text{H}_5)(\text{CO})\cdot\{(\text{C}_6\text{H}_5)_3\text{As}\}$  with triphenylarsine, giving  $\text{PtCl}(\text{COC}_2\text{H}_5)\cdot\{(\text{C}_6\text{H}_5)_3\text{As}\}_2$ . From these data they argue for a three-coordinate intermediate,  $\text{PtCl}(\text{COC}_2\text{H}_5)\{(\text{C}_6\text{H}_5)_3\text{As}\}$ , in the reaction which then adds additional arsine to give the product. In addition, they observed that there is no evidence to support the formation of a 1:1 adduct of initial complex and added ligand. Such an adduct, if isolated, would have been identical to the intermediates proposed in the carbonylation and isocyanide insertion experiments; this would seem to be in contradiction to our conclusions. We are not dismayed by this difference, however, which in a sense may be accommodated by a consideration of the equilibrium reaction



We know<sup>2</sup> that for systems where  $\text{L}'$  is an isocyanide these equilibria appear strongly to favor the ionic product. However isocyanides appear to be quite unique; it seems reasonable that the complex  $[\text{PtCH}_3(\text{CO})\{(\text{C}_6\text{H}_5)_3\text{As}\}_2]\text{Cl}$  (the other alternative intermediate in the Glyde-Mawby reaction) would be unstable with respect to the reactants. Hence the equilibrium would lie far to the left, ruling out this species as a reasonable intermediate.

**Registry No.**  $\text{PtI}(\text{CH}_3)\{(\text{C}_6\text{H}_5)_3\text{P}\}_2$ , 28850-19-3; *trans*- $[\text{PtCH}_3(\text{CH}_3\text{NC})\{(\text{C}_6\text{H}_5)_3\text{P}\}_2]\text{I}$ , 27859-00-3;  $\text{PtCl}(\text{CH}_3)\{(\text{C}_6\text{H}_5)_3\text{P}\}_2$ , 28850-21-7;  $[\text{PtC}_6\text{H}_5(\text{CNCH}_3)\{(\text{C}_6\text{H}_5)_3\text{P}\}_2]\text{I}$ , 27710-54-9;  $[\text{PtC}_6\text{H}_5(\text{CNCH}_3)\{(\text{C}_6\text{H}_5)_3\text{P}\}_2]\text{Br}$ , 27710-51-6;

(28) R. W. Glyde and R. J. Mawby, *Inorg. Chem.*, **10**, 854 (1971).

$[\text{PtC}_6\text{H}_5(\text{CNCH}_3)\{(\text{C}_6\text{H}_5)_3\text{P}\}_2]\text{Cl}$ , 27710-53-8;  $[\text{PtC}_6\text{H}_5(\text{CNCH}_3)\{(\text{C}_6\text{H}_5)_3\text{P}\}_2]\text{PF}_6$ , 39531-94-7;  $[\text{PtCH}_3(\text{CNCH}_3)\{(\text{C}_6\text{H}_5)_2(\text{CH}_3\text{P})_2\}]\text{I}$ , 39612-69-6;  $[\text{PtCH}_3(\text{CNCH}_3)\{(\text{C}_6\text{H}_5)_2(\text{CH}_3\text{P})_2\}]\text{Br}$ , 39531-95-8;  $[\text{PtCH}_3(\text{CNCH}_3)\{(\text{C}_2\text{H}_5)_3\text{P}\}_2]\text{I}$ , 39531-96-9;  $[\text{PtCH}_3(\text{CNCH}_3)\{(\text{C}_2\text{H}_5)_3\text{P}\}_2]\text{Br}$ , 39531-97-0;  $[\text{PtCH}_3(\text{CNC}_6\text{H}_4\text{Cl})\{(\text{C}_6\text{H}_5)_2(\text{CH}_3\text{P})_2\}]\text{I}$ , 39531-98-1;  $[\text{PtCH}_3(\text{CNC}_6\text{H}_4\text{Cl})\{(\text{C}_6\text{H}_5)_2(\text{CH}_3\text{P})_2\}]\text{Br}$ , 39531-99-2;  $[\text{PtCH}_3(\text{CNC}_6\text{H}_4\text{Cl})\{(\text{C}_6\text{H}_5)_2(\text{CH}_3\text{P})_2\}]\text{PF}_6$ , 39532-00-8;  $[\text{PtCH}_3(\text{CNC}_6\text{H}_4\text{Cl})\{(\text{C}_2\text{H}_5)_3\text{P}\}_2]\text{I}$ , 39532-01-9;  $[\text{PtCH}_3(\text{CNC}_6\text{H}_4\text{Cl})\{(\text{C}_2\text{H}_5)_3\text{P}\}_2]\text{Br}$ , 39532-02-0;  $[\text{PtCH}_3(\text{CNC}_6\text{H}_4\text{Cl})\{(\text{C}_2\text{H}_5)_3\text{P}\}_2]\text{PF}_6$ , 39532-03-1;  $[\text{PtBr}(\text{C}_6\text{F}_5)\{(\text{C}_6\text{H}_5)_3\text{P}\}_2]$ , 33915-56-9;  $\text{PtCN}(\text{C}_6\text{F}_5)\{(\text{C}_6\text{H}_5)_3\text{P}\}_2$ , 27658-81-7;  $[\text{PtC}_6\text{F}_5(\text{CNCH}_3)\{(\text{C}_6\text{H}_5)_3\text{P}\}_2]\text{Br}$ , 27658-80-6;  $\text{PtI}\{(\text{C}(\text{CH}_3)=\text{NCH}_3)\{(\text{C}_6\text{H}_5)_3\text{P}\}_2$ , 27859-01-4;  $\text{PtI}\{(\text{C}(\text{C}_6\text{H}_5)=\text{NCH}_3)\{(\text{C}_6\text{H}_5)_3\text{P}\}_2$ , 27710-50-5;  $\text{PtBr}\{(\text{C}(\text{C}_6\text{H}_5)=\text{NCH}_3)\{(\text{C}_6\text{H}_5)_3\text{P}\}_2$ , 27710-52-7;  $\text{PtCl}\{(\text{C}(\text{C}_6\text{H}_5)=\text{NCH}_3)\{(\text{C}_6\text{H}_5)_3\text{P}\}_2$ , 27858-99-7;  $\text{PtI}\{(\text{C}(\text{CH}_3)=\text{NCH}_3)\{(\text{C}_6\text{H}_5)_2(\text{CH}_3\text{P})_2\}$ , 39532-10-0;  $\text{PtBr}\{(\text{C}(\text{CH}_3)=\text{NCH}_3)\{(\text{C}_6\text{H}_5)_2(\text{CH}_3\text{P})_2\}$ , 39531-83-4;  $\text{PtI}\{(\text{C}(\text{CH}_3)=\text{NC}_6\text{H}_4\text{Cl})\{(\text{C}_6\text{H}_5)_2(\text{CH}_3\text{P})_2\}$ , 39531-84-5;  $\text{PtBr}\{(\text{C}(\text{CH}_3)=\text{NC}_6\text{H}_4\text{Cl})\{(\text{C}_6\text{H}_5)_2(\text{CH}_3\text{P})_2\}$ , 39531-85-6;  $\text{PtI}\{(\text{C}(\text{CH}_3)=\text{NC}_6\text{H}_4\text{Cl})\{(\text{C}_2\text{H}_5)_3\text{P}\}_2$ , 39531-86-7;  $\text{PtBr}\{(\text{C}(\text{CH}_3)=\text{NC}_6\text{H}_4\text{Cl})\{(\text{C}_2\text{H}_5)_3\text{P}\}_2$ , 39531-87-8;  $\text{PtI}\{(\text{C}(\text{CH}_3)=\text{N}(\text{CH}_3)_2)\{(\text{C}_2\text{H}_5)_3\text{P}\}_2]\text{I}$ , 39532-12-2;  $\text{PtCN}(\text{CH}_3)\{(\text{C}_2\text{H}_5)_3\text{P}\}_2$ , 22289-45-8;  $\text{PtI}\{(\text{C}(\text{CH}_3)=\text{NCH}_3)\{(\text{C}_2\text{H}_5)_3\text{P}\}_2$ , 39531-89-0;  $\text{PtI}\{(\text{C}(\text{CH}_3)=\text{N}(\text{CH}_3)_2)\{(\text{C}_6\text{H}_5)_3\text{P}\}_2]\text{I}$ , 39532-13-3;  $[\text{PtI}\{(\text{C}(\text{C}_6\text{H}_5)=\text{NHCH}_3)\{(\text{C}_6\text{H}_5)_3\text{P}\}_2]\text{PF}_6$ , 39708-57-1;  $[\text{PtCNCH}_3\{(\text{C}_6\text{H}_5)=\text{NCH}_3\}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2]\text{I}\cdot\frac{1}{2}\text{CHCl}_3$ , 39531-90-3;  $[\text{Pt}(\text{CNCH}_3)\{(\text{C}(\text{C}_6\text{H}_5)=\text{NCH}_3)\{(\text{C}_6\text{H}_5)_3\text{P}\}_2]\text{Br}\cdot\text{CHCl}_3$ , 39531-91-4.

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Contribution from the Department of Chemistry, Wright State University, Dayton, Ohio 45431

## Square-Planar Nickel(II) and Copper(II) Complexes Containing 14- and 15-Membered Tetraaza Macrocyclic Ligands

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The synthesis of nickel(II) and copper(II) complexes with uninegative and neutral macrocyclic ligands derived from acetylacetone and various linear tetramines has been studied in order to determine the scope of the cyclization reaction and to study the effect of ring size on the acidity of the coordinated neutral ligands. Both nickel(II) and copper(II) complexes containing 14-membered rings have been prepared in both forms I and II; whereas, complexes with a 15-membered ring have been isolated only for nickel(II) and only in form II. No copper(II) complexes with 15-membered rings nor nickel(II) or copper(II) complexes with 16-membered rings have been prepared by these techniques. The  $\text{p}K_a$  of  $\text{Ni}(\text{[14]dieneN}_4)\cdot(\text{PF}_6)_2$  is 6.45 while that of  $\text{Cu}(\text{[14]dieneN}_4)\text{I}_2$  is 9.3. These values are of the same order of magnitude as those obtained for the related  $\text{M}(\text{[13]dieneN}_4)\text{X}_2$  systems and it is concluded that the addition of an extra methylene group opposite the diimine ring does not change the steric environment of the proton which is ionized. No  $\text{p}K_a$  data could be obtained for  $\text{Ni}(\text{[15]dieneN}_4)(\text{PF}_6)_2$  in aqueous solution which indicates a marked decrease in ligand acidity in the 15-membered macrocycle. This has been explained in terms of steric crowding due to the positioning of three six-membered chelate rings adjacent to one another, which may prohibit formation of the basic uninegative form of the ligand.

### Introduction

Previously reported studies on the products formed *via* condensation of triethylenetetramine with acetylacetone in the presence of nickel(II)<sup>1-3</sup> and copper(II)<sup>4</sup> ions have

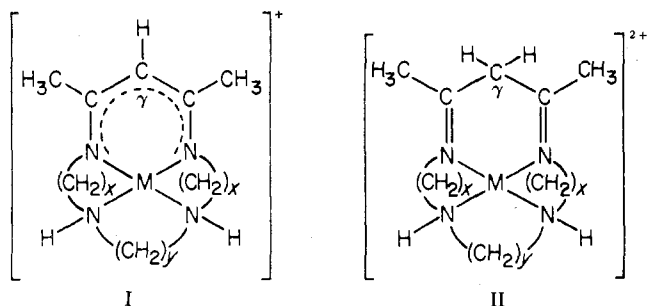
identified two types of macrocyclic metal complexes, I and II, where  $x = y = 2$ . The two forms can be interconverted in solution by adjustment of the pH. Thus, type I complexes which contain the uninegative form of the 13-membered

(1) S. C. Cummings and R. E. Sievers, *J. Amer. Chem. Soc.*, **92**, 215 (1970); *Inorg. Chem.*, **9**, 1131 (1970).

(2) W. H. Elfring, Jr., and N. J. Rose, Abstracts, 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970.

(3) M. F. Richardson and R. E. Sievers, *J. Amer. Chem. Soc.*, **94**, 4134 (1972).

(4) J. G. Martin, R. M. C. Wei, and S. C. Cummings, *Inorg. Chem.*, **11**, 475 (1972).



macrocyclic ligand predominate in basic solution, while type II complexes with the neutral form of the ligand exist in acid solution due to protonation at the  $\gamma$  carbon. The relative acidity of the coordinated neutral ligand depends markedly on the nature of the metal ion and is 1000-fold less for the copper(II) complexes<sup>4</sup> than the nickel(II) complexes.<sup>2</sup> This difference may be due to steric and/or electronic effects. In order to evaluate the importance of these two factors we have been studying the change in acidity of the coordinated ligands as a function of metal ion and macrocycle size. In this paper we wish to report on the extension of the cyclization reaction to 14-, 15-, and 16-membered ligands with copper(II) and nickel(II) ions and on the importance of ring size effects.<sup>5</sup> Studies related to the metal ion effects will be reported later.

### Experimental Section

**Materials.** Acetylacetone (acac) was obtained from Matheson Coleman and Bell, Inc., and *N,N'*-bis(2-aminoethyl)-1,3-propanediamine (2,3,2-tet) and *N,N'*-bis(3-aminopropyl)-1,3-propanediamine (3,3,3-tet) were purchased from Eastman Organic Chemicals, Rochester, N. Y. These materials were used as received. *N,N'*-Bis(3-aminopropyl)-1,2-ethanediamine (3,2,3-tet) was prepared by a modification of the method of Hamilton and Alexander.<sup>6</sup> Solvents employed in physical measurements were purchased commercially and were of spectroquality grade. All other solvents and metal salts were obtained commercially and were of reagent grade.

**Measurements.** Infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer using Nujol mulls or KBr disks. Visible and ultraviolet spectra were measured using a Cary 14 recording spectrophotometer. Magnetic susceptibility measurements were obtained utilizing the Faraday technique. Pmr spectra were obtained with a Varian HA-60 IL nmr spectrophotometer utilizing TMS as the internal standard. The mass spectra were obtained with a Consolidated Electrochemicals Corp. Model 104 mass spectrometer. Conductivities were calculated from electrical resistance measurements on  $10^{-3}$  M methanolic solutions using a Yellow Springs Instruments Model 31 conductivity bridge.  $pK_a$  values were determined from titrations of 0.005 M solutions of the metal complexes with either 0.1000 M HCl or 0.1000 M NaOH. Titrations were carried out under a  $N_2$  atmosphere at 0.1 M ionic strength (adjusted with  $NaClO_4$ ). The pH readings were taken using an Orion Model 801 digital pH meter. All titrations were completely reversible. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., and Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach, West Germany.

**Synthesis of 12,14-Dimethyl-1,4,8,11-tetraazacyclotetradeca-11,13-dienatonickel(II) Nitrate, Ni([14]diene $N_4$ )NO<sub>3</sub>.**<sup>7</sup> To a solution of 7.15 g (0.029 mol) of Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O in 250 ml of water was added 4.6 g (0.029 mol) of 2,3,2-tet. The solution was warmed and stirred for 15 minutes after which 5.8 g (0.058 mol) of acac was added. The solution was refluxed for 5 hr during which time the color of the solution changed from blue to red. The hot solution was then filtered into a concentrated aqueous solution of NaNO<sub>3</sub>. The pH of the solution was then adjusted to 10 with 6 N NaOH. Concentration and refrigeration of the solution yielded red platelets. The product was recrystallized from aqueous solution of pH 10. Results of elemental analyses are reported in Table I; yield ~2.5 g.

(5) Taken in part from the M.Sc. thesis of J. G. Martin, Wright State University, 1971 and presented at the 3rd Central Regional Meeting of the American Chemical Society, Cincinnati, Ohio, June 1971.

(6) H. G. Hamilton, Jr., and M. D. Alexander, *Inorg. Chem.*, **5**, 2060 (1966).

(7) For an explanation of the abbreviations see V. L. Goedken, P. H. Merrell, and D. H. Busch, *J. Amer. Chem. Soc.*, **94**, 3397 (1972).

**Synthesis of Other Derivatives of Ni([14]diene $N_4$ )<sup>+</sup>.** Method A. The Br<sup>-</sup>, I<sup>-</sup>, and PF<sub>6</sub><sup>-</sup> derivatives were prepared by substitution of the appropriate sodium or ammonium salt for NaNO<sub>3</sub> in the preceding synthesis; yield ~25%.

**Method B.** An alternate method for the preparation of the Br<sup>-</sup>, I<sup>-</sup>, and PF<sub>6</sub><sup>-</sup> derivatives was *via* metathetical reactions of Ni([14]diene $N_4$ )NO<sub>3</sub> in aqueous solutions containing an excess of the required sodium or ammonium salt. Isolation of the product in each case was accomplished by adjusting the pH of the solution to 10 with 6 N NaOH, concentrating and refrigerating the solution. The Br<sup>-</sup> derivative crystallized as fine orange needles. The I<sup>-</sup> and PF<sub>6</sub><sup>-</sup> derivatives crystallized as red platelets. Each product was recrystallized from aqueous solution of pH 10. Results of elemental analyses are reported in Table I; yield ~50-90%.

**Synthesis of 12,14-Dimethyl-1,4,8,11-tetraazacyclotetradeca-11,14-dienecopper(II) Salts, Cu([14]diene $N_4$ )X<sub>2</sub>.** The I<sup>-</sup> and PF<sub>6</sub><sup>-</sup> salts of Ni([14]diene $N_4$ )<sup>2+</sup> were prepared by dissolving the corresponding Ni([14]diene $N_4$ )X derivative in a strongly acidic aqueous solution containing an excess of the required sodium or ammonium salt and acetic acid. The Ni([14]diene $N_4$ )<sub>2</sub> crystallized as a brown granular solid whereas Ni([14]diene $N_4$ )(PF<sub>6</sub>)<sub>2</sub> crystallized as fine yellow needles. The results of elemental analyses are reported in Table I; yield ~50-80%.

**Synthesis of 13,15-Dimethyl-1,5,8,12-tetraazacyclopentadeca-12,15-dienecopper(II) Hexafluorophosphate, Ni([15]diene $N_4$ )(PF<sub>6</sub>)<sub>2</sub>.** To a solution of 7.15 g (0.029 mol) of Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O in 250 ml of water was added 5 g (0.029 mol) of 3,2,3-tet. The solution was warmed and stirred for 15 min after which 5.8 g (0.058 mol) of acac was added. The solution was refluxed for 5 hr during which time the color of the solution changed from blue to green. The hot reaction solution was then filtered into a concentrated aqueous solution of NH<sub>4</sub>PF<sub>6</sub>. Concentration of the solution yielded fine yellow crystals which were filtered and recrystallized from water; yield ~2.7 g. The results of elemental analyses are reported in Table I.

**Attempted Synthesis of 14,16-Dimethyl-1,5,9,13-tetraazacyclohexadeca-13,16-dienecopper(II) Hexafluorophosphate, Ni([16]diene $N_4$ )(PF<sub>6</sub>)<sub>2</sub>.** To a solution of 7.15 g (0.029 mol) of Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O in 250 ml of water was added 5.5 g (0.029 mol) of 3,3,3-tet. The solution was warmed and stirred for 15 min after which 5.8 g (0.058 mol) of acac was added. After refluxing for 5 hr, the hot solution was filtered into a concentrated aqueous solution of NH<sub>4</sub>PF<sub>6</sub>. Concentration and refrigeration of the solution yielded a pale yellow precipitate which became white after recrystallization; yield ~1.0 g. Results of elemental analyses are reported in Table I. A more efficient method of preparing this product which has been identified tentatively as the hexafluorophosphate salt of the macrocyclic ligand [16]diene $N_4$ ·2HPF<sub>6</sub> involved using half as much Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O.

**Synthesis of 12,14-Dimethyl-1,4,8,11-tetraazacyclotetradeca-11,13-dienatocopper(II) Nitrate, Cu([14]diene $N_4$ )NO<sub>3</sub>.** To a solution of 5.2 g (0.026 mol) of Cu(OAc)<sub>2</sub>·H<sub>2</sub>O in 500 ml of water was added 4.2 g (0.026 mol) of 2,3,2-tet. After warming and stirring the solution for 15 min, 5.2 g (0.052 mol) of acac was added. During the ensuing reflux a voluminous precipitate of Cu(acac)<sub>2</sub> appeared. After refluxing for 5 hr the solution was chilled and filtered to remove Cu(acac)<sub>2</sub>. The pH of the solution was then adjusted to 10 with 6 N NaOH and refiltered into a concentrated solution of NaNO<sub>3</sub>. Concentration and refrigeration of the solution yielded dark green crystals; yield ~1.8 g. The product was recrystallized from aqueous solution of pH 10. Results of elemental analyses are reported in Table I.

**Synthesis of Other Derivatives of Cu([14]diene $N_4$ )<sup>+</sup>.** Method A. The Br<sup>-</sup>, I<sup>-</sup>, and PF<sub>6</sub><sup>-</sup> derivatives were prepared by substitution of the appropriate sodium or ammonium salt for NaNO<sub>3</sub> in the above procedure; yield 18-20%. The various products were recrystallized from aqueous solution of pH 10.

**Method B.** An alternate method for preparing the derivatives of method A, above, was *via* metathetical reactions of aqueous solutions of Cu([14]diene $N_4$ )NO<sub>3</sub> with an excess of the required sodium or ammonium salt. Precipitation was effected by adjusting the pH of the solution to 10 with 6 N NaOH; yield ~50-80%. The Br<sup>-</sup> and I<sup>-</sup> derivatives were isolated as dark green platelets whereas the PF<sub>6</sub><sup>-</sup> derivative was isolated as dark green needles. Results of elemental analyses are reported in Table I.

**Synthesis of 12,14-Dimethyl-1,4,8,11-tetraazacyclotetradeca-11,14-dienecopper(II) Salts, Cu([14]diene $N_4$ )X<sub>2</sub>.** The I<sup>-</sup> and PF<sub>6</sub><sup>-</sup> derivatives were prepared by dissolving the required Cu([14]diene $N_4$ )X derivative in an acidic aqueous solution containing an excess of the appropriate sodium or ammonium salt and acetic acid. Cu([14]diene $N_4$ )<sub>2</sub> precipitated as maroon granules upon concentration and refrigeration whereas Cu([14]diene $N_4$ )(PF<sub>6</sub>)<sub>2</sub> precipitated as red needles which turned orange upon drying *in vacuo* at 100° for several

Table I. Results of Elemental Analyses on Metal Complexes

Compd	% calcd						% found					
	C	H	N	F	M	Other	C	H	N	F	M	Other
Ni([14] dienoN <sub>4</sub> )NO <sub>3</sub>	41.88	6.75	20.36		17.06		41.87	6.53	20.58		17.26	
Ni([14] dienoN <sub>4</sub> )Br	39.80	6.42	15.48		16.22	22.08, Br	39.71	6.48	15.51		16.38	22.06, Br
Ni([14] dienoN <sub>4</sub> )I	35.24	5.68	13.70		14.35	31.03, I	35.30	5.67	13.53		14.43	30.87, I
Ni([14] dienoN <sub>4</sub> )PF <sub>6</sub>	33.75	5.44	13.12	26.69	13.75	7.25, P	33.75	5.34	12.99	26.97	13.93	7.05, P
Ni([14] dieneN <sub>4</sub> )I <sub>2</sub>	26.84	4.51	10.44		10.93	47.27, I	26.79	4.72	10.24		10.97	47.40, I
Ni([14] dieneN <sub>4</sub> )(PF <sub>6</sub> ) <sub>2</sub>	25.14	4.23	9.78	39.78	10.24	10.87, P	25.11	4.36	9.80	39.95	10.31	10.55, P
Ni([15] dieneN <sub>4</sub> )(PF <sub>6</sub> ) <sub>2</sub>	26.57	4.59	9.61	38.70	9.97	10.52, P	26.57	4.00	9.71	39.13	9.91	10.48, P
Cu([14] dienoN <sub>4</sub> )NO <sub>3</sub>	41.30	6.66	20.08		18.21	13.76, O	41.35	6.20	20.09		18.33	14.09, O
Cu([14] dienoN <sub>4</sub> )Br·H <sub>2</sub> O	37.45	6.56	14.56		16.51	20.76, Br	37.41	6.20	14.79		16.29	21.13, Br
Cu([14] dienoN <sub>4</sub> )I	34.82	5.61	13.54		15.35	30.66, I	34.85	4.96	13.43		15.28	30.94, I
Cu([14] dienoN <sub>4</sub> )PF <sub>6</sub> ·H <sub>2</sub> O	32.03	5.61	12.46	25.34	14.12	6.88, P	34.76	5.73	12.64	25.22	14.04	6.97, P
Cu([14] dieneN <sub>4</sub> )(PF <sub>6</sub> ) <sub>2</sub>	24.93	4.19	9.70	39.45	10.99	10.72, P	24.89	4.49	9.81	39.71	10.72	10.56, P
Cu([14] dieneN <sub>4</sub> )I <sub>2</sub>	26.60	4.74	10.34		11.73	46.85, I	26.41	4.45	10.31		11.56	46.89, I
[16] dieneN <sub>4</sub> ·2HPPF <sub>6</sub>	30.88	5.56	10.29	41.88		11.38, P	30.83	5.02	10.51	41.76		11.52, P

hours. Results of elemental analyses are reported in Table I.

**Attempted Syntheses of Copper(II) Complexes with 15- and 16-Membered Ligands.** The same procedures as reported above were used except 3,2,3-tet and 3,3,3-tet were employed as the amines. The only products recovered from basic solution were the copper(II) amines. An unidentified beige powder was isolated from the acidic solutions.

## Results and Discussion

**Synthesis and Characterization of 14-Membered Macrocyclic Metal Complexes.** Two sets of macrocyclic complexes M([14] dienoN<sub>4</sub>)X and M([14] dieneN<sub>4</sub>)X<sub>2</sub>, where M = Ni(II) or Cu(II) and X<sup>-</sup> = NO<sub>3</sub><sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, or PF<sub>6</sub><sup>-</sup>, have been isolated from the reaction of the appropriate metal acetate with 2,3,2-tet and acac. The general method of synthesis is shown in Figure 1. The pH of the reaction solution at the time of isolation dictates which type of complex will be isolated since the coordinated ligand undergoes reversible protonation at the γ carbon. Four derivatives of M([14] dienoN<sub>4</sub>)X, *i.e.*, X<sup>-</sup> = NO<sub>3</sub><sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, and PF<sub>6</sub><sup>-</sup>, have been prepared while only two derivatives, *i.e.*, X<sup>-</sup> = PF<sub>6</sub><sup>-</sup> and I<sup>-</sup>, containing the neutral ligand have been isolated.

Characterization of these complexes is based on the results of elemental analyses, conductivity and magnetic susceptibility measurements, visible, ultraviolet, infrared, pmr, and mass spectra, and acid-base titrations. The results of elemental analyses, reported in Table I, indicate stoichiometries which are in agreement with those calculated for structures I and II where *x* = 2, *y* = 3. Although no attempt was made to determine the exact degree of hydration, several of the copper(II) complexes required the inclusion of water in the formulation to give the best fit to the analytical data. These samples always exhibited bands attributable to water in their infrared spectra.

Molar conductances (Λ<sub>M</sub>) for the M([14] dienoN<sub>4</sub>)X and M([14] dieneN<sub>4</sub>)X<sub>2</sub> complexes in methanol have average values of 94 and 144 mhos which indicate that the complexes are 1:1 and 2:1 electrolytes, respectively.<sup>8</sup> Magnetic susceptibility measurements show all of the nickel(II) derivatives to be diamagnetic (μ<sub>eff</sub> < 0.5 BM) and all of the copper(II) compounds to have one unpaired electron (μ<sub>eff</sub> ≈ 1.80 BM).

The visible and ultraviolet spectra of the metal complexes containing 14-membered ligands are very similar to those of the corresponding 13-membered macrocycles.<sup>1,4</sup> Spectra of both Ni([14] dienoN<sub>4</sub>)X and Ni([14] dieneN<sub>4</sub>)X<sub>2</sub> obtained in methanol and Nujol mulls exhibit an absorption at ~18,300 cm<sup>-1</sup> (ε ~90 and ~35, respectively) which is assigned as the <sup>1</sup>B<sub>1g</sub> ← <sup>1</sup>A<sub>1g</sub> transition. The two types of compounds can be

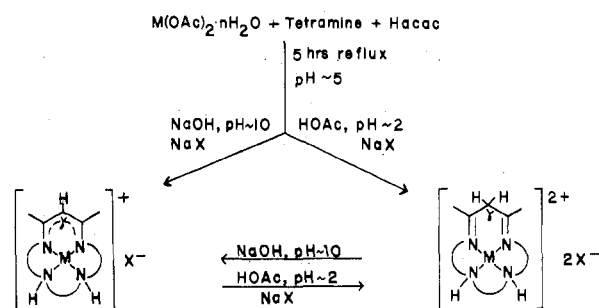


Figure 1. General synthetic routes to macrocyclic metal complexes.

differentiated by the difference in molar absorptivities of this d-d band. Absorptions with higher intensities at 22,000–24,000, ~27,800, ~29,000, ~35,500, ~38,800, and ~45,000 cm<sup>-1</sup> are assigned as charge-transfer and intraligand transitions.

The Cu([14] dienoN<sub>4</sub>)X complexes exhibit four bands, two of which fall in the visible region and are assigned as d-d transitions and two of which fall in the ultraviolet region. The d-d transitions occur at 16,000 (ε ~100) and 23,500 cm<sup>-1</sup> (ε ~200) and are tentatively assigned to the <sup>2</sup>A<sub>1g</sub> ← <sup>2</sup>B<sub>1g</sub> and <sup>2</sup>E<sub>1g</sub> ← <sup>2</sup>B<sub>1g</sub> transitions, respectively, of square-planar copper(II). The bands in the ultraviolet region fall at ~29,200 (ε ~20,000) and ~43,400 cm<sup>-1</sup> (ε ~25,000) and are assigned as either charge-transfer and/or intraligand electron transitions. The Cu([14] dieneN<sub>4</sub>)X<sub>2</sub> complexes exhibit one broad band in the visible region, ~20,000 cm<sup>-1</sup> (ε ~150), which probably contains both d-d transitions, and two bands in the ultraviolet region at ~29,000 (ε ~2500) and ~43,400 cm<sup>-1</sup> (ε ~12,000) which are assigned to charge-transfer and/or intraligand electron excitations.

Similarities between the 13- and 14-membered macrocyclic systems are also observed in the infrared spectra of the nickel(II) and copper(II) complexes. Absorptions of primary importance in the spectra of Ni([14] dienoN<sub>4</sub>)PF<sub>6</sub> and Cu([14] dienoN<sub>4</sub>)PF<sub>6</sub> are a sharp NH stretching vibration which occurs at 3245 and 3270 cm<sup>-1</sup>, respectively, and two relatively strong bands at ~1555 and 1530 cm<sup>-1</sup> which are attributed to the C=C and C=N stretching modes of the conjugated six-membered chelate ring. The spectra of Ni([14] dieneN<sub>4</sub>)(PF<sub>6</sub>)<sub>2</sub> and Cu([14] dieneN<sub>4</sub>)(PF<sub>6</sub>)<sub>2</sub> also exhibit a sharp NH stretching vibration at 3240 and 3280 cm<sup>-1</sup>, respectively, but only a single strong absorption at ~1690 cm<sup>-1</sup> assigned as the C=N stretching mode. The absence of a band attributable to the C=C stretching mode in these latter complexes is evidence for the localized β-diimine structure(II) and is in agreement with data presented in earlier

studies.<sup>1,2,4</sup> Infrared spectra of the other derivatives indicate that none of the anions are coordinated.<sup>9-12</sup>

Additional structural evidence for the nickel(II) derivatives has been obtained from the pmr spectra of these complexes which are listed in Table II. The pmr spectra of complexes containing the uninegative ligand can be resolved into four distinct regions corresponding to resonances resulting from the -NH, =CH-, -CH<sub>2</sub>-, and -CH<sub>3</sub> protons. Integrations of the pmr signals yield proton ratios of 2:1:14:6, respectively. Within the Ni([14]dieno)<sup>+</sup> series the pmr spectra are virtually identical with the exception of the position of the -NH resonance which varies with the nature of the anion. The more electronegative anions, e.g., Br<sup>-</sup>, hydrogen bond to the amine proton thus deshielding it and shifting the resonance downfield. The position of the -NH resonance is also solvent dependent as can be seen from the large upfield shift of this signal in acetone-*d*<sub>6</sub>. The overall appearance of the spectra and the positions of the methyl and methine proton resonances are in close agreement with those reported for the similar Ni([13]dienoN<sub>4</sub>)X complexes, which are found at 1.90 and 4.73 ppm.<sup>1</sup>

The pmr spectra of the Ni([14]dieneN<sub>4</sub>)X<sub>2</sub> complexes differ in several respects from those of the Ni([14]dienoN<sub>4</sub>)X system. The pmr spectra can be resolved into two regions which correspond to the presence of -CH<sub>3</sub> protons and -CH<sub>2</sub>- and -NH protons. Integrations of the signals yield proton ratios of 6:17 as opposed to the calculated ratios of 6:18 for (CH<sub>3</sub>):(CH<sub>2</sub> + NH). As anticipated, the =CH- resonance has disappeared since protonation takes place at this carbon atom. The resultant bridge methylene resonance is obscured by the multiplet resulting from methylene protons in the amine backbone. A further consequence of protonation is the downfield shift of the methyl resonance since the methyl groups are now adjacent to localized imine bonds and are thus deshielded to a greater extent. The deshielding effect is also apparent in the methylene region which is now spread further downfield, thus obscuring the NH resonance. A more detailed analysis of the nmr spectral data has been made and will be reported elsewhere.<sup>13</sup>

Mass spectra of the nickel(II) complexes have also been useful in completing the characterization. Ni([14]dienoN<sub>4</sub>)Br shows a mass spectrum similar to that of Ni([13]dienoN<sub>4</sub>)Br<sup>1</sup> except that the highest mass peak in the latter was found to be due to (P - HBr)<sup>+</sup>, while the highest mass peak found in the spectrum of the former occurs at *m/e* 281 which corresponds to (P - Br)<sup>+</sup>. The fragmentation pattern observed corresponds to the unwinding and sequential loss of elements of the amine backbone. This proceeds until *m/e* 152 which coincides with a fragment consisting of nickel and the imino chelate ring minus a proton. Thus the fragmentation pattern seems to reflect the additional stability afforded the imino ring by partial electron delocalization. In addition to those peaks resulting from hydrogen transfer, there are peaks in the Ni([14]dienoN<sub>4</sub>)Br spectrum corresponding to the appropriate isotope patterns for nickel and bromine.

The mass spectrum of Ni([14]dieneN<sub>4</sub>)(PF<sub>6</sub>)<sub>2</sub> shows the same general pattern as that of Ni([14]dienoN<sub>4</sub>)Br except

Table II. Pmr Spectra of Ni([14]dienoN<sub>4</sub>)X and Ni([14]dieneN<sub>4</sub>)X<sub>2</sub> Complexes

Compd	Solvent	Assignment <sup>a</sup>			
		-CH <sub>3</sub>	-CH <sub>2</sub> - <sup>b</sup>	=CH-	-NH
Ni([14]dienoN <sub>4</sub> )NO <sub>3</sub>	CDCl <sub>3</sub>	1.90	2.00-3.50	4.68	5.07
Ni([14]dienoN <sub>4</sub> )Br	CDCl <sub>3</sub>	1.90	2.00-3.50	4.68	5.25
Ni([14]dienoN <sub>4</sub> )PF <sub>6</sub>	CD <sub>3</sub> COCD <sub>3</sub>	1.93	2.16-3.33	4.75	3.75
Ni([14]dieneN <sub>4</sub> )(PF <sub>6</sub> ) <sub>2</sub>	CD <sub>3</sub> COCD <sub>3</sub>	2.22	2.33-4.33		<sup>c</sup>
Ni([14]dieneN <sub>4</sub> )I <sub>2</sub>	D <sub>2</sub> O	2.03	2.33-4.33		<sup>c</sup>

<sup>a</sup> Values are expressed in ppm downfield from TMS. <sup>b</sup> Boundaries of multiplet region. <sup>c</sup> NH resonance is obscured by -CH<sub>2</sub>- multiplet region.

that the most intense peak is no longer the parent ion minus an anion but is due to the PF<sub>4</sub><sup>+</sup> fragment. The second most intense peak, at *m/e* 280, is assigned as (P - 2HPF<sub>6</sub>)<sup>+</sup>. In addition to the pattern resulting from the breakdown of the macrocycle, there is an interesting pattern resulting from the breakdown of the anion starting with the PF<sub>4</sub><sup>+</sup> moiety and continuing through PF<sub>3</sub><sup>+</sup>, PF<sub>2</sub><sup>+</sup>, and PF<sup>+</sup>. As with Ni([14]dienoN<sub>4</sub>)Br, peaks resulting from hydrogen transfer and appropriate isotope patterns of nickel were observed throughout the spectrum.

On the basis of the physical evidence cited, the Ni([14]dienoN<sub>4</sub>)X and Cu([14]dienoN<sub>4</sub>)X derivatives have been identified as the 14-membered macrocyclic complexes shown in structure I while the Ni([14]dieneN<sub>4</sub>)X<sub>2</sub> and Cu([14]dieneN<sub>4</sub>)X<sub>2</sub> complexes exist in the related macrocyclic form shown in II.

**Synthesis and Characterization of 15-Membered Macrocyclic Metal Complexes.** One macrocyclic nickel(II) complex, Ni([15]dieneN<sub>4</sub>)(PF<sub>6</sub>)<sub>2</sub>, has been isolated from the reaction of nickel(II) ions with 3,2,3-tet and acetylacetonone. Results of the elemental analyses have been reported in Table I. These data, coupled with a molar conductance of 167 mhos, indicate the presence of two PF<sub>6</sub><sup>-</sup> ions per nickel(II). A residual magnetic moment of 0.67 BM and an electronic spectrum consisting of absorptions at 18,400 (10), 23,200 (68), 27,900 (135), 32,700 (570), 36,400 (880), and 46,100 (13,000) cm<sup>-1</sup> substantiate the presence of square-planar nickel(II). The mass spectrum of this compound exhibits a peak at 294 mass units attributable to (P - 2HPF<sub>6</sub>)<sup>+</sup> and a fragmentation pattern which is quite similar to that of the 14-membered analog. The pmr spectrum of Ni([15]dieneN<sub>4</sub>)(PF<sub>6</sub>)<sub>2</sub> consists of two major regions including a sharp singlet at 2.31 ppm (6 protons) attributed to the methyl groups and a broad multiplet region extending from 2.33 to 4.00 ppm due to the methylene and secondary amine groups (20 protons). The overall appearance of the pmr spectrum is like that of Ni([14]dieneN<sub>4</sub>)(PF<sub>6</sub>)<sub>2</sub> except all of the resonances are shifted downfield slightly.

The infrared spectrum of Ni([15]dieneN<sub>4</sub>)(PF<sub>6</sub>)<sub>2</sub> is somewhat different from the spectra of the 13- and 14-membered macrocycles and provides the only bit of data which cannot be completely reconciled with the macrocyclic structure II where *x* = 3, *y* = 2. The absorptions of primary concern are two medium-intensity bands at 3400 and 3280 cm<sup>-1</sup> (the latter band exhibits a medium-intensity shoulder at 3250 cm<sup>-1</sup>), a strong band at 1630 cm<sup>-1</sup>, and medium-intensity absorptions at 1670 and 1585 cm<sup>-1</sup>. On deuteration, the high-energy bands shift to lower energies by a factor of 1.35, the band at 1585 cm<sup>-1</sup> shifts only 55 cm<sup>-1</sup>, and those at 1670 and 1630 cm<sup>-1</sup> do not shift at all. The shoulder at 3250 and the band at 1670 cm<sup>-1</sup> correlate nicely with -NH and >C=N vibrational modes. The extra bands at 3400, 3280, 1630, and 1585 cm<sup>-1</sup> suggest the presence of -NH<sub>2</sub> and >C=O groups which would indicate that condensation

(9) M. M. Chamberlain and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **81**, 6412 (1959).

(10) B. M. Gatehouse, S. E. Livingstone, and R. S. Nyholm, *J. Chem. Soc. A*, 4222 (1957).

(11) L. E. Moore, R. B. Gayhart, and W. E. Bull, *J. Inorg. Nucl. Chem.*, **26**, 896 (1964).

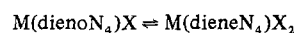
(12) K. Nakamoto in "Spectroscopy and Structure of Metal Chelate Compounds," K. Nakamoto and P. J. McCarthy, Ed., Wiley, New York, N. Y., 1968, Chapter 4.

(13) N. J. Rose, private communication, June 1972.

had occurred at only one end of the tetramine with formation of a linear pentadentate ligand. Results from elemental analyses do not agree with such a formulation. To be consistent with the magnetic and electronic spectral data, the resulting pentadentate ligand would have to function as a tetradentate and coordinate either through the four nitrogen atoms or through three of the nitrogen atoms and the carbonyl oxygen. Regardless of which donor atoms had coordinated, the nmr spectrum of such a complex should exhibit two methyl resonances (barring any accidental degeneracies). Since only one signal is observed in the methyl region, even when the spectrum is expanded, presence of any singly condensed ketoimine is considered unlikely and the complex is assigned the macrocyclic structure.<sup>14</sup>

The nickel(II) complex containing the 15-membered uninegative ligand, the nickel(II) complexes of both 16-membered ligands, and the corresponding copper(II) complexes could not be prepared, although what appears to be the hexafluorophosphate salt of the 16-membered ligand [16]dieneN<sub>4</sub>·2HPF<sub>6</sub> has been isolated from the nickel(II) reaction which suggests that the metal ion may be acting as a template for ring formation. The failure to isolate some of the complexes containing the 15- and 16-membered ligands may reflect low stabilities due to steric crowding effects (see discussion in next section) or may be related to the mechanism of ligand formation. It is known that *N,N'*-ethylenebis(acetylacetonimine) undergoes an intramolecular reaction under acidic conditions to form the seven-membered cyclic diazapine.<sup>15</sup> Under similar conditions, ethylenediamine reacts with  $\alpha,\beta$ -unsaturated ketones to form 14-membered macrocycles as well as the seven-membered rings.<sup>16</sup> While the 14-membered ring formed very easily, formation of large rings in diazapine systems normally requires special techniques. Since the macrocyclic complexes discussed in this paper are formed by the condensation of tetramines in the presence of excess  $\beta$ -diketone and acid, it is reasonable to assume that the cyclization proceeds *via* a diazapine intermediate which may limit ring size.

**Relative Acidity of the Coordinated Ligands.** In order to determine what effect overall ring size might have on the relative acidity of the coordinated macrocyclic ligands, the  $pK_a$  for the reaction



has been measured for complexes with the 14- and 15-membered ligands. Acid-base titrations were performed by titrating aqueous solutions of the metal complexes with standard NaOH or HCl and then back-titrating. The calculated  $pK_a$  values are listed in Table III along with those values previously reported for the 13-membered macrocycles. It is seen that replacement of nickel(II) by copper(II) in both the 14- and 13-membered systems results in a 1000-fold decrease in acidity.<sup>4</sup> However, there is no significant difference in the acidities of the 13- and 14-membered systems for a given metal ion; therefore, the introduction of one "extra" methylene group in the chelate ring opposite the imine ring appears to have no effect on acidity. A marked decrease in ligand acidity is seen on going from the 13- or 14-membered ring to

Table III. Results of Acid-Base Titrations of Macrocyclic Complexes

Compd	$pK_a^a$	Compd	$pK_a^a$
Ni([13] dieneN <sub>4</sub> )(PF <sub>6</sub> ) <sub>2</sub>	6.55 <sup>b</sup>	Cu([13] dienoN <sub>4</sub> )I	9.45
Ni([14] dieneN <sub>4</sub> )(PF <sub>6</sub> ) <sub>2</sub>	6.45	Cu([14] dienoN <sub>4</sub> )I	9.30
Ni([15] dieneN <sub>4</sub> )(PF <sub>6</sub> ) <sub>2</sub>	<sup>c</sup>		

<sup>a</sup> All values reported are  $\pm 0.05$ . <sup>b</sup> Rose and Elfring<sup>2</sup> have reported  $K_a = 10^{-6}$ . <sup>c</sup> No detectable end point.

that with 15 ring members. In fact, no  $pK_a$  value could be measured for Ni([15] dieneN<sub>4</sub>)(PF<sub>6</sub>)<sub>2</sub> in aqueous solution. We feel that these data, coupled with our inability even to isolate a complex with the 15-membered uninegative ligand or any 16-membered ligands, can be explained in terms of steric crowding arising from the introduction of "extra" methylene groups in the chelate rings adjacent to the imine ring, although solvent effects may also be important.

While it is well known that the thermodynamic chelate effect favors complexes containing saturated five-membered rings, this is not necessarily the case for systems containing fused chelate rings. For example, recent studies by Margerum<sup>17,18</sup> and Powell<sup>19</sup> and coworkers have shown that formation constants for square-planar nickel(II)- and copper(II)-tetramine complexes decrease in the order 2,3,2-tet > 3,2,3-tet > 2,2,2-tet (trien) > 3,3,3-tet with an overall change in  $K_1$  of  $10^6$ . A similar order is reflected in a study of ligand field strengths of various square-planar macrocyclic Schiff base complexes of copper(II),<sup>19</sup> in which bridge combinations in order of decreasing stability were found to be 3,2,3,2 > 3,2,2,2 > 3,3,3,2 > 3,3,3,3 regardless of donor atom hybridization. Recent calculations<sup>20</sup> of strain energies in macrocyclic systems have also shown that the relative order based on ring size is 14 < 13 < 15 < 16. These examples show that systems which contain alternating five- and six-membered fused chelate rings are the most stable presumably because the presence of six-membered rings relieves ring strain inherent in the 2,2,2-tet arrangements and allows the five-membered rings to adopt the favored gauche configuration. Positioning six-membered rings adjacent to one another introduces steric crowding and reduces overall stabilities.

Cumulative ring strain and steric crowding effects should be even more important in macrocyclic systems which contain electron delocalization, *e.g.*, complexes of  $M(\text{dienoN}_4)X$  which contain uninegative ligands, since the six-membered imino ring is essentially planar. Indeed the strain inherent in the imino chelate ring of Ni([13] dienoN<sub>4</sub>)ClO<sub>4</sub> is indicated by a 128° bond angle at the  $\gamma$  carbon instead of the theoretical  $sp^2$  bond angle of 120°. The presence of saturated six-membered rings adjacent to the imino ring should introduce considerably more steric crowding and lead to reduced stability in the 15- and 16-membered uninegative systems. Steric strain is expected to be lessened in those complexes which contain the neutral macrocyclic ligands because protonation at the  $\gamma$  carbon will change the hybridization to  $sp^3$  and allow the carbon atom to drop out of the plane containing the metal ion and nitrogen atoms and approach an angle of 109°. This in turn is expected favorably to alter the "bite" size of the imine ring. Similar "ruffling

(14) Preliminary X-ray data give monoclinic cell dimensions of  $a = 8.48 \text{ \AA}$ ,  $b = 14.70 \text{ \AA}$ , and  $c \sin \beta = 25.9 \text{ \AA}$ , with space group  $P2_1/c$  and  $Z = 6$  for  $d_{\text{obsd}} = 1.8 \text{ g/cm}^3$ . The presence of very few spots at Bragg angles greater than 15° indicates disorder and precludes an accurate structural determination: M. F. Richardson, private communication, May 1972.

(15) C. N. O'Callaghan and D. Twomey, *J. Chem. Soc. C*, 2400 (1967).

(16) K. Hideg and D. Lloyd, *Chem. Commun.*, 929 (1970).

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(18) F. P. Hinz and D. W. Margerum, Abstracts, 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971.

(19) G. R. Hedwig, J. L. Love, and H. K. J. Powell, *Aust. J. Chem.*, 23, 981 (1970), and references therein.

(20) L. DeHayes, Ph.D. Dissertation, The Ohio State University, 1972.

effects" have been noted in various metalloporphyrin systems.<sup>21</sup> The experimental data presented here support these ideas since both nickel(II) and copper(II) complexes containing the 14-membered rings ( $x = 2, y = 3$ ) have been prepared in both forms I and II, while complexes with the 15-membered ring ( $x = 3, y = 2$ ) have been isolated only for nickel(II) and only in form II. No copper(II) complexes with 15-membered rings have been isolated which may reflect increased steric crowding due to the slightly larger size of the copper(II) ion. In addition, neither nickel(II) nor copper(II) seemed to form a complex with the 16-membered ligands. We therefore conclude that the  $M(\text{dienoN}_4)X$  and  $M(\text{dieneN}_4)X_2$  complexes become less stable as steric crowding increases in the larger macrocyclic rings and that sterically strained configurations containing adjacent six-membered rings are most stable in form II which contains the neutral ligands while

(21) J. L. Hoard in "Structural Chemistry and Molecular Biology," W. H. Freeman, San Francisco, Calif., 1968, pp 573-594, and references therein.

those less strained can exist in both forms I and II. Measurements of stability constants for these complexes should provide more definitive evidence for the explanations given here.

**Registry No.** Ni([14] dienoN<sub>4</sub>)NO<sub>3</sub>, 39556-33-7; Ni([14] dienoN<sub>4</sub>)Br, 39556-34-8; Ni([14] dienoN<sub>4</sub>)I, 39556-35-9; Ni([14] dienoN<sub>4</sub>)PF<sub>6</sub>, 39042-83-6; Ni([14] dieneN<sub>4</sub>)I<sub>2</sub>, 39561-15-4; Ni([14] dieneN<sub>4</sub>)(PF<sub>6</sub>)<sub>2</sub>, 39561-16-5; Ni([15] dieneN<sub>4</sub>)(PF<sub>6</sub>)<sub>2</sub>, 39561-23-4; Cu([14] dienoN<sub>4</sub>)NO<sub>3</sub>, 39561-17-6; Cu([14] dienoN<sub>4</sub>)Br, 39561-18-7; Cu([14] dienoN<sub>4</sub>)I, 39561-19-8; Cu([14] dienoN<sub>4</sub>)PF<sub>6</sub>, 39561-20-1; Cu([14] dieneN<sub>4</sub>)(PF<sub>6</sub>)<sub>2</sub>, 39561-21-2; Cu([14] dieneN<sub>4</sub>)I<sub>2</sub>, 39561-22-3; [16] dieneN<sub>4</sub>·2HPF<sub>6</sub>, 39526-74-4; acac, 123-54-6; 2,3,2-tet, 4741-99-5; 3,2,3-tet, 10563-26-5; 3,3,3-tet, 4605-14-5.

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## Circular Dichroism of Amino Acid Complexes of Nickel(II)

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Quantitative circular dichroism (CD) data are presented for a series of bis(amino acid) complexes of nickel(II). The complexes prepared were those of alanine, valine, isoleucine, proline, histidine, serine, asparagine, ornithine, glutamic acid, and aspartic acid. Certain differences from previous qualitative spectra have been found in some instances and the spectra have been found to fit into certain categories related to the overall structure of the complexes. The CD pattern of the d-d transitions together with the CD sign of the ultraviolet tail offers a potentially useful tool in assigning structure in this type of complex.

### Introduction

It is well known that the coordination of an optically active ligand to a metal ion induces optical activity into the d-d electronic transitions of the metal ion and circular dichroism (CD) is observed. Coordination of a chelating ligand can contribute to the observed optical activity in two ways: (i) through the conformational effect whereby dissymmetry is conferred about the metal due to puckering of the chelate rings and (ii) through the vicinal effect whereby the dissymmetry of the ligand itself is presented to the metal chromophore and gives rise to optical activity. For square-planar complexes or octahedral molecules with  $D_{4h}$  symmetry, only these contributions are possible since there is no net chirality for the complex.

In recent years a number of studies have been carried out on the optical activity of amino acid complexes of copper(II) and nickel(II)<sup>1-3</sup> and a hexadecant rule has been proposed<sup>4,5</sup> as an aid for interpreting the observed CD spectra. For copper(II) the component bands are often masked due to severe overlap of the component d-d transi-

tions but for nickel(II) these transitions are significantly different in energy and a number of CD bands are observed. In order to apply general rules for the CD of these complexes, one must be certain to compare complexes with similar structures and refer to the CD of corresponding absorption bands. Much of the previous work reported for nickel(II) has involved solution CD spectra obtained by mixing simple nickel(II) salts and various amino acids in appropriate ratios. We have carried out studies using freshly prepared solutions of the actual complexes and in some instances have found certain differences in spectra from those reported previously. In this paper we wish to report the results of our studies and a potential means for predicting stereochemistry in these complexes.

### Experimental Section

All amino acids were obtained from Nutritional Biochemicals Corp., Cleveland, Ohio, with the exceptions of L-alanine (British Drug Houses) and L-histidine and L-isoleucine (Eastman Organic Chemicals). All were used directly with no further purification.

Three methods were employed in the preparation of the NiL<sub>2</sub> complexes.

**Method I (D- and L-Alanine, D-Aspartic Acid, L-Proline, and L-Histidine).** This method was adapted from that used by Nakamoto.<sup>6</sup> An aqueous solution of 0.01 mol of amino acid was heated with excess nickel carbonate. (For the aspartic acid complex the pH was adjusted to 8.5 using NaOH.) After sufficient stirring, the mixture was filtered and taken to dryness on a rotatory evaporator. (For alanine, evaporation of the sample was carried

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